Intramolecular Charge-Transfer Polymers between Dithiafulvene and Pyridinium Units: Conjugative Effect through Saturated Polymethylene Chains

Kensuke Naka,* Takashi Uemura, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501

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New polymers containing an intramolecular charge-transfer (ICT) structure (pyridinium–dithiafulvene–pyridinium) in the main chain were prepared. UV–vis measurements of the polymers suggested that conjugative effects occur through saturated polymethylene chains, and that such effects are enhanced as the length of the spacer polymethylene chain decreases. Polyviologens showed small but similar conjugations in their UV–vis measurements. A PM3 calculation of 1,1′-(1,2-ethanediyl)bis(pyridinium) suggested that low-lying LUMO resulting from an interaction between the σ^* of the ethylene unit and π^* of the pyridinium moiety affords the conjugative effect. The PM3 calculations and the UV–vis results show that the incorporation of the ICT moiety in the polymeric framework increases the conjugative effect through the polymethylene chains. The redox and conducting properties of the ICT polymers were also investigated. Both studies gave some implications of the conjugative effects of the polymers.

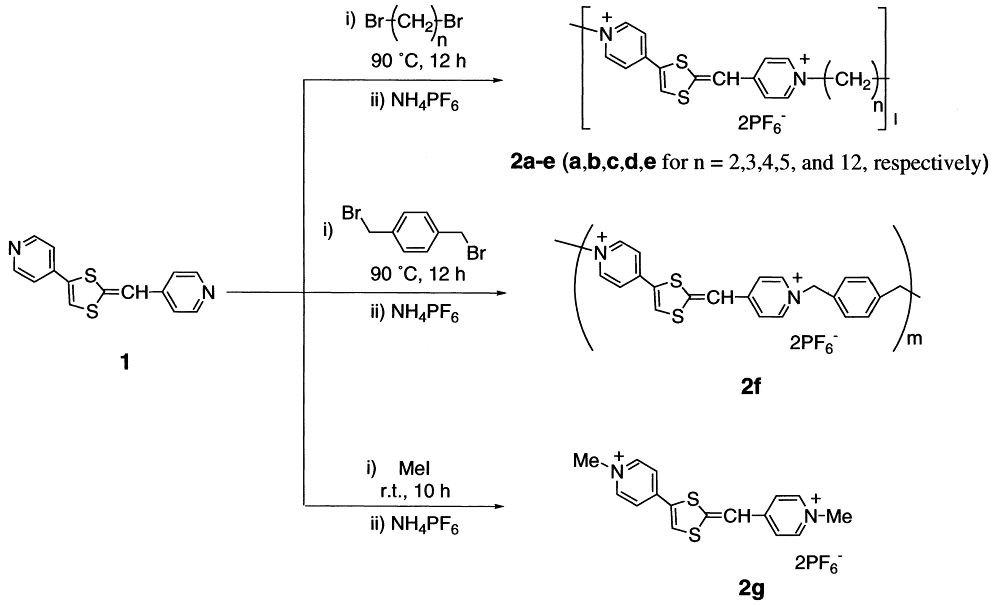
Intramolecular charge transfer (ICT) systems based on electron-donating dithiafulvenyl compounds linking to a π-acceptor through a σ- or π-bond covalently[1–3] have found several applications, including nonlinear optics,[4–7] long time charge separations,[8,9] single-component conductors,[10] and supramolecular switches.[11,12] Therefore, incorporation of such ICT units into polymers, especially into conjugated polymers, is important, since they are expected to show high intrinsic conductivities[13–16] and good nonlinear optical properties.[17–21]

We have recently reported studies of π-conjugated polymers with electron-donating dithiafulvene unit in the main chain.[22–27] In the series of the poly(dithiafulvene)s, alternating copolymers of the dithiafulvene with electron-poor pyridine moieties resulted in ICT states, leading to changes of redox properties and increased intrinsic conductivities.[24,26] Here we describe the syntheses of ICT polymers composed of pyridinium–dithiafulvene–pyridinium units as an acceptor–donor–acceptor structure in the main chain. An effective ICT interaction resulting from the electron-sufficient dithiafulvene tethering covalently to the electron-deficient pyridinium moieties is well known.[11,12,28–31] In addition, UV measurements of the ICT polymers in this work implied unexpected electron delocalized σ–π systems between the π-units and the saturated polymethylene chains. Electron delocalization between σ bonds and π systems (σ–π conjugation) has been developed in various disilyl compounds containing unsaturated or aromatic groups;[32–37] however, it has never been established in combinations of π-units and polymethylene chains. Exceptionally, substitution of an alkyl group on an aromatic compound leads to delocalization of σ-electrons into an adjacent π-bond, known as hyperconjugation.[38–41]

Results and Discussion

Polymerization. Scheme 1 provides the syntheses of a series of new ICT polymers. Treatments of a slightly excess of 2,6-bis(4-pyridyl)-1,4-dithiafulvene (**1**) and dibromoalkanes in DMF produced polymeric precipitates. Counter ion exchanges from Br^- to PF_6^- in water gave polymers (**2a–f**) with an acceptor–donor–acceptor (pyridinium–dithiafulvene–pyridinium) moiety in the π-unit (Table 1). After this exchange, the polymers became soluble in DMSO and DMF, and partially soluble in CH_3CN. A low molecular weight compound **2g** as a model compound was also prepared by use of the **1** and iodomethane (Scheme 1). The structures of **2a–f** were confirmed spectroscopically in comparison with that of **2g** (Fig. 1). In the ^{1}H NMR spectra of polymers **2a–f**, incidental small peaks to the main peaks for the dithiafulvene and pyridinium units were observed. No signals corresponding to bromomethyl or hydroxymethyl moieties were found in the spectra. These results indicated that the incidental peaks were due to the π-unit of the polymer end groups and that both ends of the polymers were composed of the pyridyl moieties.[42] For example, the ^{1}H NMR spectrum of **2d** (Fig. 1, bottom) showed small peaks due to the terminal protons at 7.2, 7.6, 8.1 and 8.6 ppm, these appeared at slightly upfield compared with the main peaks of the corresponding repeating units. Judging from the peak intensities, one can determine the number-average molecular weights (M_n) of **2a–f**; these ranged from several thousands to twelve thousand (aberrations are ±5%). Due to polycationic natures of **2a–f**, GPC measurement of the polymers was ineffective; adhesions of the polymers to the GPC column prevented success.

UV–Vis Absorption Study. UV–vis absorption spectra of



Scheme 1.

Table 1. Synthesis of ICT Polymers

Polymer	Yield/%[a)]	M_n[b)]	Degree of polymerization (D. P.)[b)]
2a	61	3350	5.2
2b	74	5450	8.6
2c	77	7610	11.9
2d	79	9160	14.1
2e	58	12150	16.3
2f	82	4520	6.4

a) Isolated yields after washing with water.

b) Determined from ^{1}H NMR. Aberrations are ±5%.

2 were obtained in DMSO (Fig. 2 and Table 2). Although the adjacent π-units were tethered by the non-conjugated polymethylene chains, the absorption peaks due to π–π* transition of the π-units in polymers **2a**–**f** showed relatively large bathochromic shifts from that of the model compound **2g**. In addition, the peaks of **2a**–**e** were found to show gradual red-shifts as the methylene intervals became shorter; the peak intensities of the absorptions of **2** were proportional to the concentrations of the sample solutions. These facts suggest some conjugative effects (C–C hyperconjugations) through saturated polymethylene chains in the polymer systems; such effects were enhanced with a decrease of the methylene length. The series of compounds **2** had significantly red-shifted absorption maxima compared with that of the monomer **1** (λ_{max} = 371 nm) because of effective ICT interactions between the dithiafulvene and the the pyridinium moieties of **2**.[28–31]

To understand the unexpected optical properties of **2**, we prepared viologen (bipyridinium) monomers, dimer, and polymers (**3**, **4**) (Scheme 2).[42,43] UV–vis absorptions of the polymers (**3a**, **b**) and methylviologen (**3c**) were measured in CH_3CN. The absorptions of **3a,b** were located at 269 and 264 nm, respectively, showing small bathochromic shifts from that of **3c** (λ_{max} = 259 nm) and these values shifted to longer wavelengths with decrease of the methylene spacer (Fig. 3). Ethylviologen (**3d**) shows an absorption peak at similar position (λ_{max} = 258 nm) to **3c**, indicating no effect of an alkyl substitution on the UV absorption. A bisviologen compound (**4**)[43] having ethylene spacer unit showed an absorption (λ_{max} = 260 nm) between those of **3a** and **3c**. Furue and Nozakura have also observed such red-shifts of absorptions for bisviologens with various polymethylene spacers, as their spacer lengths decreased.[43] These results suggested conjugation-like interactions between the pyridinium units and the methylene chains in polymers **3a,b** and supported the above UV–vis results of **2**. Interpolymer effects on the absorptions of **3a**,**b** were excluded, since those spectra were in accordance with the Lambert–Beer law. Benzene analogues connected by ethylene units do not show such effects, indicating interruptions of π-conjugations by the saturated units in the benzene analogues.[40,44]

Solvent effect on the UV–vis absorption of **2** was investigated by use of THF/DMSO mixed solvent. It was observed that the peaks of **2c**–**f** in THF/DMSO (98:2) became close to that of **2g**, in contrast, the absorption of **2a** in the mixed solvent was the same as that in DMSO (Fig. 4 and Table 2). Since both λmax positions of **2g** in DMSO and in THF/DMSO are almost the same, the peak shifts of **2c**–**f** in THF/DMSO should result from conformational changes of the polymers, leading to interruption of the interaction between the π-units and the polymethylene units. The small peak difference in **2a** system indicates that the short ethylene chain between the units retains and restricts the polymer conformation of **2a**. The resultant rigid conformation of **2a** might also cause the conjugation effect through the ethylene chain.

Calculations for Molecular Orbitals. PM3 calculations of a series of pyridinium compounds (Scheme 3) were carried out. The calculation of HOMO and LUMO energies of 1,1′-(1,2-ethanediyl)bis(pyridinium) (**5a**) will predict the conjugative effect for polyviologen **3a**. Although a through-space in-

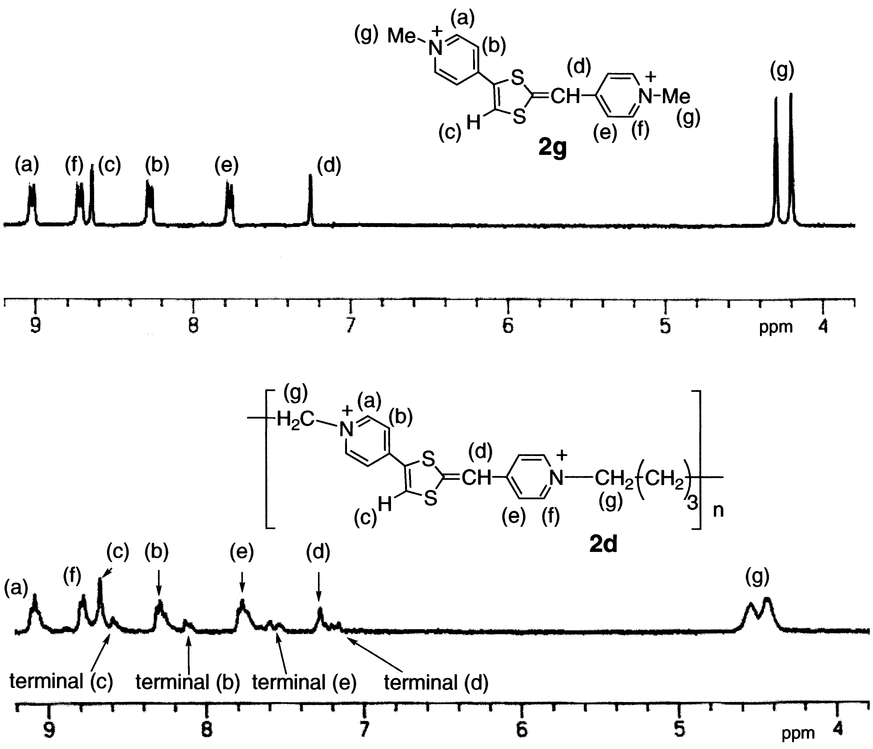


Fig. 1. ^{1}H NMR spectra of **2g** (upper) and **2d** (bottom) in DMSO-d_6.

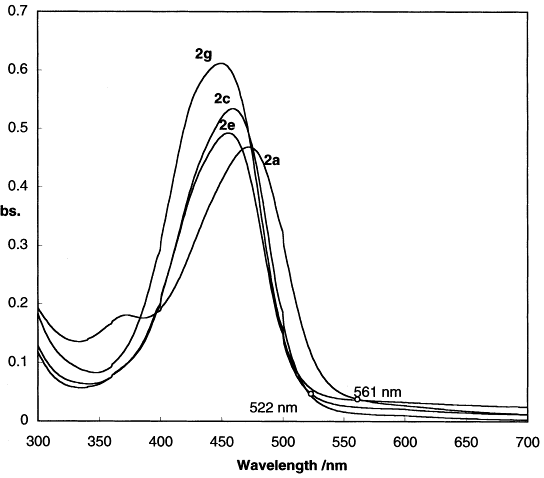
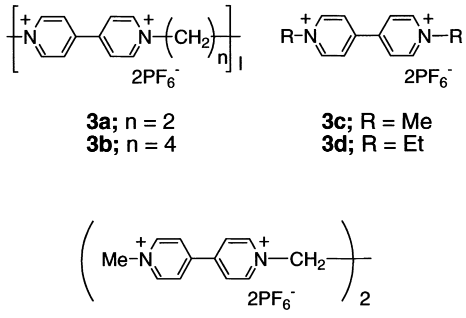


Fig. 2. UV-vis absorptions of **2a**, **2c**, **2e**, and **2g** in DMSO. Circular markings indicate absorption edges of **2a** and **2g**.

Table 2. UV–Vis Results of **2**

Compound	λ_{max} in DMSO/nm	λ_{max} in THF/DMSO (98:2)/nm	$\Delta\lambda$/nm[a)]
2a	473	471	24
2b	463	456	14
2c	461	449	12
2d	457	443	8
2e	455	446	6
2f	465	451	16
2g	449	448	–

a) $\Delta\lambda = \lambda_{max}$ (polymers) in DMSO $-\lambda_{max}$ (**2g**) in DMSO.



3a; n = 2
3b; n = 4

3c; R = Me
3d; R = Et

4

Scheme 2.

teraction of the π system is possible in the syn conformation, the C_{2h} anti conformation was the plausible geometry for **5a**. In the anti conformation, the π systems are distant from one another and unlikely to couple through-space. Interaction of the π* orbitals of the two pyridinium rings through C_{sp3}–C_{sp3} σ* bond gives rise to an effective σ*–π* conjugation, leading to a reduction of the orbital energy of the LUMO (Fig. 5). No σ orbitals of the ethylene moiety appear in the HOMO level of **5a**. These results suggest that the bathochromic shift for **3a** is caused by its low-lying LUMO level that is due to the σ*–π* conjugation. Additionally, the same calculation for 1,1′-(1,4-butanediyl)bis(pyridinium) (**5b**) also showed some formation of the σ*–π* conjugation. The C–C hyperconjugation is developed by combination with electron-deficient π units due to a usual electron releasing property of the C–C bond.[45–47]

The PM3 calculation of dithiafulvene-pyridinium compounds **6** showed that HOMO–LUMO band gaps of **6a** and **6b**

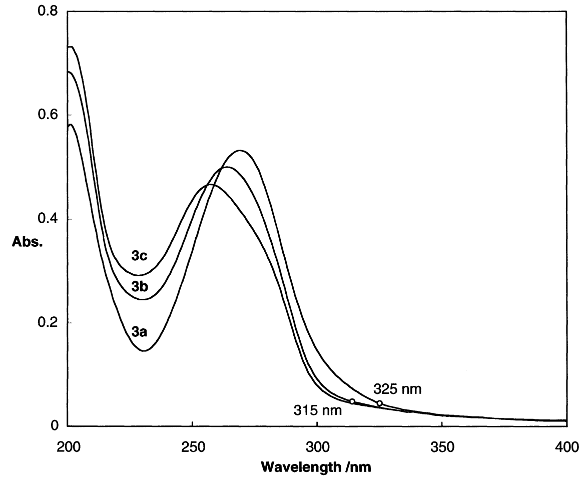


Fig. 3. UV-vis absorptions of **3a–c** in CH_3CN. Circular markings indicate absorption edges of **3a** and **3c**.

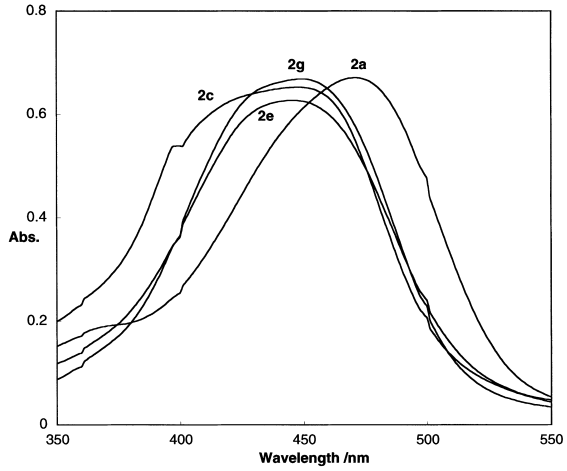
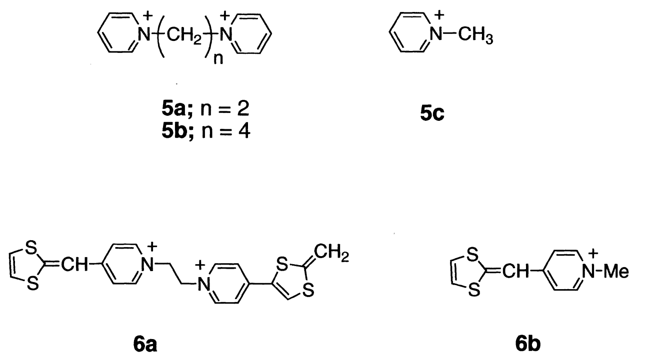


Fig. 4. UV-vis absorptions of **2a**, **2c**, **2e**, and **2g** in THF/DMSO (98/2) mixed solvent.



Scheme 3.

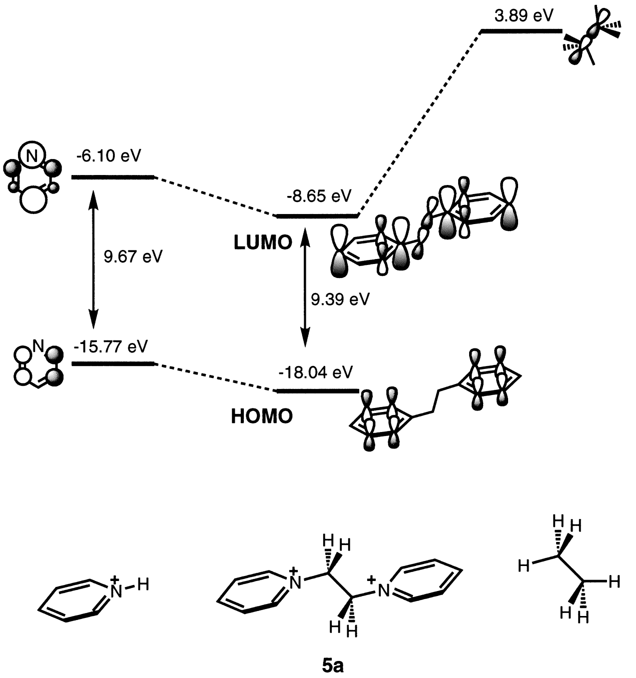


Fig. 5. Orbital correlation diagram for **5a**, based on the PM3 Hamiltonian.

were 5.15 and 5.95 eV, respectively. The gap difference between **6a** and **6b** is found to be 0.80 eV, which is larger than that between **5a** and **5c** (HOMO–LUMO gap difference = 0.25 eV) calculated by the same method. This result also supports the observed effective σ–π conjugation system of **2a** in the UV spectrum. The positions of the absorption edges of **2a** and **2g** (**2a**; 561 nm, **2g**; 522 nm: Fig. 2) gave respective band gaps of 2.21 and 2.38 eV. In the same way, the band gaps of **3a** and **3c** (band edge of **3a**; 325 nm, **3c**; 315 nm: Fig. 3) are obtained as 3.82 and 3.94 eV, respectively. Comparison of the gap difference between **3a** and **3c** (= 0.12 eV) to that between **2a** and **2g** (= 0.17 eV) suggests that the electronic delocalization in **2a** is very efficient. The significant electronic delocalizations in **2a–f** may be owing to the ICT structure. The electron-donating dithiafulvene units increase electron densities of the adjacent pyridinium moieties by the CT interaction, which may effectively enhance the electronic flows along the polymer chains. To the best of the author's knowledge, these polymers, particularly **2a**, showed the first effective conjugation throughout saturated methylene chains in polymeric systems.

Electrochemical Property. In order to elucidate the redox properties of the dithiafulvene moieties in **2**, cyclic voltammetry measurements were carried out. A cast film sample of model compound (**2g**) showed an irreversible oxidation peak for the dithiafulvene moiety at 0.80 V vs Ag/Ag^+ in CH_2Cl_2 (Fig. 6a), which appeared at more positive potential than those of 2,6-diphenyl-1,4-dithiafulvene (**7**, E_{pa} = 0.40 V)[23] and 2,6-bis(2-pyridyl)-1,4-dithiafulvene (**8**, E_{pa} = 0.45 V)[24] reported previously (Scheme 4), owing to the enhanced ICT of **2g**. Figure 6b showed a voltammogram of a cast film of **2f** as a representative polymer. The ICT polymers **2a–f** gave an irreversible oxidation peaks between 1.5 and 1.6 V vs Ag/Ag^+ in CH_2Cl_2, which were located at higher positions than those of previous poly(dithiafulvene)s[23,24] such as **9** (E_{pa} = 0.61 V) and **10** (E_{pa} = 1.38 V) (Scheme 4). Apparent positive shifts of the oxidation potentials for the dithiafulvene unit in **2a–f** compared with that of **2g** indicated that incorporations of the dithiafulvene units in the polymeric systems led to stabilization of the dithiafulvene moiety against oxidation. Several electrochemically

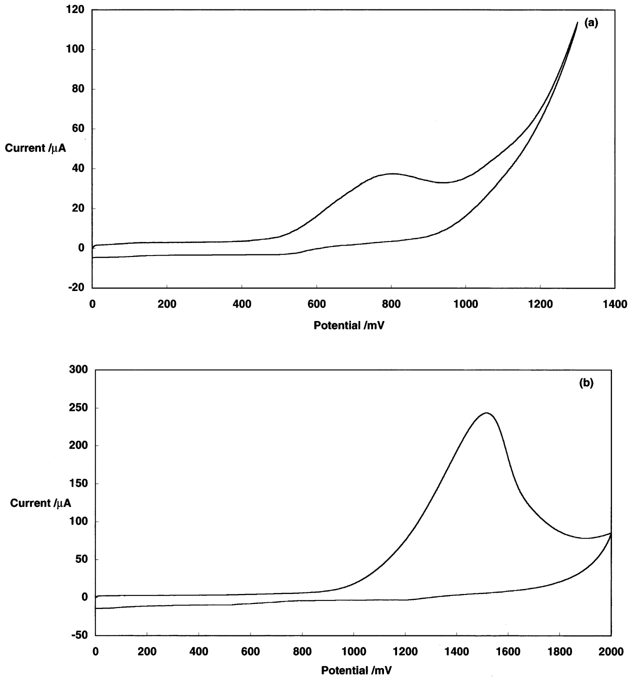
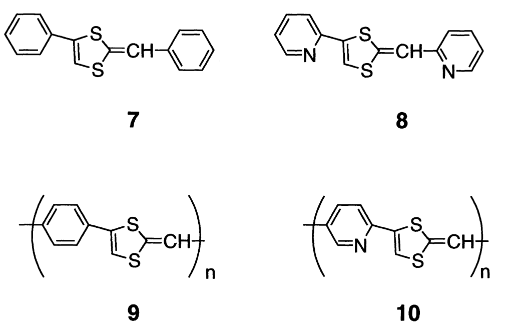


Fig. 6. Cyclic voltammograms of (a) **2g** and (b) **2f** in CH_2Cl_2.



Scheme 4.

Table 3. Conductivities of **2a**, **2c**, **2e**, **2f**, and **2g**

Polymer	conductivity/S cm^{-1}
2a	1.5×10^{-4}
2c	5.4×10^{-5}
2e	4.7×10^{-6}
2f	2.9×10^{-4}
2g	1.8×10^{-4}

active π-conjugated polymers as well as the previous poly(dithiafulvene)s that contain the dithiafulvene units in the π-conjugated main chains showed similar positive shifts in their CV measurements,[22–27,48,49] suggesting that the observed peak shifts in this work are arisen from the σ–π conjugative effects of the polymers **2a–f**.

Conductivity. The intrinsic electrical conductivities (unoxidized conductivities) of **2a**, **2c**, **2e**, **2f** and **2g** were measured by a conventional two-probe technique and the results are summarized in Table 3. Even though they were not doped with any oxidant, the conductivities of them were relatively high.

Conclusion

We prepared some new polymers (**2a–f**) containing the ICT structure composed of the electron-donating dithiafulvene and the electron-accepting pyridinium units in the main chain. The UV–vis results suggested that extensions of the hyperconjugations were achieved through saturated chains and were enhanced by the incorporation of the ICT structure into the π-unit; this conclusion was also supported by molecular orbital calculations. This effect was controllable by systematic changes of the polymethylene spacer length. The redox properties of **2** also suggested the conjugative effects. The examples presented here will have implications for other cases where observations of unusual electronic interactions have been made.

Experimental

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2. Viologen compounds **3a**,**b** and **4** were prepared by reported methods.[42,43]

Measurements. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. UV–vis spectra were obtained on a JASCO V-530 spectrophotometer. Calculations for molecular orbitals were carried out by use of the Spartan Package; Wavefunction, Inc., Irvin, CA, USA. The orbital energies for **5** and **6** were evaluated after calculation of geometry optimization by PM3 semi-empirical molecular orbital method. For cyclic voltammetry studies, cast film samples were deposited on an indium-tin-oxide (ITO) coated glass electrode as working electrode. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer in CH_2Cl_2 containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The scan rate was 300 mV/s. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit. The polymer film was prepared by dropping of a DMF solution onto glass plates equipped with platinum electrodes, followed by drying at room temperature in vacuo.

2,6-Bis(4-pyridyl)-1,4-dithiafulvene (1). 4-(4-Pyridyl)-1,2,3-thiadiazole (2.44 g, 15 mmol) dissolved in dry CH_3CN (45 mL) was mixed with NaH (60 mg, 60% mineral oil dispersion, 15 mmol) and the mixture was left overnight. Then it was filtered to give 2,6-bis(4-pyridyl)-1,4-dithiafulvene **1** as a yellow solid (1.61 g, 79%). ^1H NMR (270 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.92 (s, 1H), 7.17 (d, 2H), 7.33 (d, 2H), 8.58 (d, 2H), 8.65 (d, 2H); Elemental analysis. Calcd for $C_{14}H_{10}N_2S_2$: C, 62.19; H, 3.73; N, 10.36; S, 23.72%. Found: C, 61.66; H, 3.87; N, 10.51; S, 23.38%.

Polymerization. The general procedure for the polymerization of **2a–f** is as follows. Dibromoalkanes (0.50 mmol) and 2,6-bis(4-pyridyl)-1,4-dithiafulvene (138 mg, 0.51 mmol) were dissolved in DMF (4 mL). The mixture was agitated with heating at 90 °C for 12 h. The resultant precipitate was collected and suspended in water. A saturated aqueous solution of NH_4PF_6 was added to the suspension until no further precipitation was observed. After filtration, the precipitate was washed with water and dried.

2a: 61% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 5.0, 5.1, 7.3, 7.7, 8.3, 8.6, 8.7, 9.0.

2b: 74% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 2.6, 4.6, 4.7, 7.3, 7.8, 8.3, 8.6, 8.8, 9.1.

2c: 77% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 2.0, 4.5, 4.6, 7.3, 7.8, 8.3, 8.7, 8.8, 9.1.

2d: 79% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 1.4, 1.9, 4.4, 4.5, 7.3, 7.8, 8.3, 8.7, 8.8, 9.1.

2e: 58% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 1.3, 1.9, 4.4, 4.5, 7.3, 7.7, 8.3, 8.7, 8.8, 9.1.

2f: 82% yield; ^{1}H NMR (270 MHz, DMSO-d_6) δ 5.7, 5.8, 7.3, 7.6, 7.8, 8.3, 8.7, 8.9, 9.2.

Model Compound (2g). Methyl iodide (1.71 g, 12 mmol) and 2,6-bis(4-pyridyl)-1,4-dithiafulvene (135 mg, 0.50 mmol) were dissolved in DMF (4 mL). The mixture was stirred at room temperature for 10 h. The resultant precipitate was collected and suspended in water. A saturated aqueous solution of NH_4PF_6 was added to the suspension until no precipitation was observed. The precipitate was washed with water (202 mg, 68%). ^{1}H NMR (270 MHz, DMSO-d_6) δ 4.20 (s, 3H), 4.30 (s, 3H), 7.26 (s, 1H), 7.77 (d, 2H), 8.28 (d, 2H), 8.65 (s, 1H), 8.72 (d, 2H), 9.02 (d, 2H); Elemental analysis. Calcd for $C_{16}H_{16}F_{12}N_2P_2S_2$: C, 32.55; H, 2.73; N, 4.75%. Found: C, 32.78; H, 2.70; N, 4.79%.

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References

1 M. R. Bryce, *Adv. Mater.*, **11**, 11 (1999).

2 M. R. Bryce, *J. Mater. Chem.*, **10**, 589 (2000).

3 M. B. Nielsen, C. Lomholt, and J. Becher, *Chem. Soc. Rev.*, **29**, 153 (2000).

4 R. Andreu, A. I. de Lucas, J. Garín, N. Martín, L. Sánchez, and C. Seoane, *Synth. Met.*, **86**, 1817 (1997).

5 A. I. de Lucas, N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, R. Alcalá, and B. Villacampa, *Tetrahedron*, **54**, 4655 (1998).

6 M. R. Bryce, A. Green, A. J. Moore, D. F. Perepichka, A. S. Batsanov, J. A. K. Howard, I. Ledoux-Rak, M. González, N. Martín, J. L. Segura, J. Garín, J. Orduna, R. Alcalá, and B. Villacampa, *Eur. J. Org. Chem.*, **2001**, 1927.

7 M. González, J. L. Segura, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, V. Hernández, and J. T. López Navarrete, *J. Org. Chem.*, **66**, 8872 (2001).

8 J. L. Segura, E. M. Priego, N. Martín, C. Luo, and D. M. Guldi, *Org. Lett.*, **25**, 4021 (2000).

9 D. M. Guldi, S. González, N. Martín, A. Antón, J. Garín, and J. Orduna, *J. Org. Chem.*, **65**, 1978 (2000).

10 J. Khodorkovsky and J. Y. Becker, "Organic Conductors: Fundamentals and Applications," Macel Dekker, New York (1994).

11 M. B. Nielsen, S. B. Nielsen, and J. Becher, *Chem. Commun.*, **1998**, 475.

12 M. B. Nielsen, J. G. Hansen, and J. Becher, *Eur. J. Org. Chem.*, **1999**, 2807.

13 E. E. Havinga, W. Ten Hoeve, and H. Wynberg, *Polym. Bull.*, **29**, 119 (1992).

14 J. P. Ferraris, A. Bravo, W. Kim, and D. C. Hrncir, *J. Chem. Soc., Chem. Commun.*, 991 (1994).

15 M. Karikomi, C. Kitamura, S. Tanaka, and Y. Yamashita, *J. Am. Chem. Soc.*, **117**, 6791 (1995).

16 T. Yamamoto, Z-h. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B-L. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, and S. Sasaki, *J. Am. Chem. Soc.*, **118**, 10389 (1996).

17 M. Moroni, J. de Moigne, T. A. Pham, and J.-Y. Bigot, *Macromolecules*, **30**, 1964 (1997).

18 K. Koishi, T. Ikeda, K. Kondo, T. Sakaguchi, K. Kamada, K. Tawa, and K. Ohta, *Macromol. Chem. Phys.*, **201**, 525 (2000).

19 W. Leng, Y. Zhou, Q. Xu, and J. Liu, *Macromolecules*, **34**, 4774 (2001).

20 X. Zhan, Y. Liu, D. Zhu, and W. Huang, Q. Gong, *Chem. Mater.*, **13**, 1540 (2001).

21 Z. An and K. Y. Wong, *J. Chem. Phys.*, **114**, 1010 (2001).

22 K. Naka, T. Uemura, and Y. Chujo, *Macromolecules*, **31**, 7570 (1998).

23 K. Naka, T. Uemura, and Y. Chujo, *Macromolecules*, **32**, 4641 (1999).

24 K. Naka, T. Uemura, and Y. Chujo, *Macromolecules*, **33**, 4733 (2000).

25 K. Naka, T. Uemura, and Y. Chujo, *Macromolecules*, **33**, 6965 (2000).

26 K. Naka, T. Uemura, and Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 4083 (2001).

27 K. Naka, T. Uemura, and Y. Chujo, *Macromolecules*, **35**, 3539 (2002).

28 L. M. Goldenberg, J. Y. Becker, O. Paz-Tal Levi, V. Y. Khodorkovski, and M. R. Bryce, *J. Chem. Soc., Chem. Commun.* **1995**, 475.

29 L. M. Goldenberg, J. Y. Becker, O. Paz-Tal Levi, V. Y. Khodorkovski, L. M. Shapio, M. R. Bryce, J. P. Cresswell, and M. C. Petty, *J. Mater. Chem.*, **7**, 901 (1997).

30 K. B. Simonsen, N. Thorup, M. P. Cava, and J. Becher, *Chem. Commun.*, **1998**, 901.

31 R. Andreu, I. Malfant, P. G. Lacroix, and P. Cassoux, *Eur. J. Org. Chem.*, **2000**, 737.

32 M. Ishikawa, *Pure Appl. Chem.*, **50**, 11 (1978).

33 M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, **19**, 51 (1981).

34 H. Sakurai, *J. Organomet. Chem.*, **200**, 261 (1980).

35 T. Iwahara, S. Hayase, and R. West, *Macromolecules*, **23**, 1298 (1990).

36 J. Ohshita, T. Watanabe, D. Kanaya, H. Ohsaki, M. Ishikawa, H. Ago, K. Tanaka, and T. Yamabe, *Organometallics*, **13**, 5002 (1994).

37 A. Kunai, T. Ueda, E. Horata, E. Toyoda, J. Ohshita, M. Ishikawa, and K. Tanaka, *Organometallics*, **15**, 2000 (1996).

38 R. S. Mulliken, *J. Chem. Phys.*, **7**, 399 (1939).

39 N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954).

40 L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966).

41 P. von R. Schleyer, J. W. de M. Carnerio, W. Koch, and D. A. Forsyth, *J. Am. Chem. Soc.*, **113**, 3990 (1991).

42 A. D. Wilson and H. J. Prosser, "Developments in Ionic

Polymers 2," Elsevier, London (1983).

43 M. Furue and S. Nozakura, *Bull. Chem. Soc. Jpn.*, **55**, 513 (1982).

44 M. Remmers, M. Schulze, and G. Wegner, *Macromol. Rapid Commun.*, **17**, 239 (1996).

45 W. J. Archer, M. A. Hossaini, and R. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 181.

46 H. C. Brown, M. Periasamy, and P. T. Perumal, *J. Org. Chem.*, **49**, 2754 (1984).

47 B. W. Gung and M. M. Yanik, *J. Org. Chem.*, **61**, 947 (1996).

48 T. Yamamoto, T. Morikita, T. Maruyama, K. Kubota, and M. Katada, *Macromolecules*, **30**, 5390 (1997).

49 T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994).