Macromolecules **2000,** *33,* 4733−4737

Synthesis and Properties of π-Conjugated Poly(dithiafulvene)s by Cycloaddition Polymerization of Heteroaromatic Bisthioketenes

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Received December 30, 1999; Revised Manuscript Received April 17, 2000

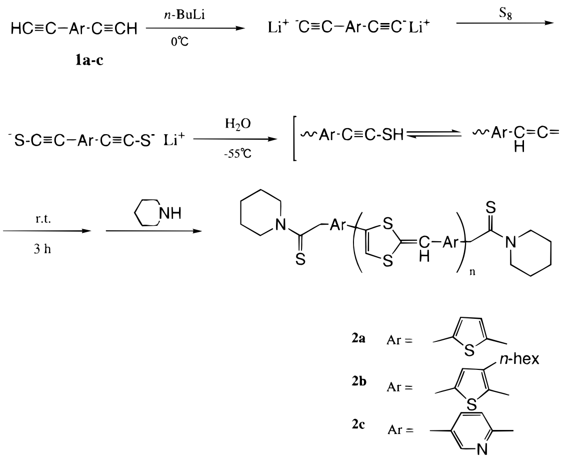
ABSTRACT: π-Conjugated polymers (**2**) having electron-donating dithiafulvene units and typical heteroaromatic (thiophene or pyridine) units in the main chain were prepared by the cycloaddition polymerization of aldothioketenes derived from heteroaromatic diynes (2,5-diethynylthiophene, 2,5-diethynyl-3-hexylthiophene, and 2,5-diethynylpyridine) with their alkynethiol tautomers. The obtained polymers were soluble in DMSO and DMF. The structures of the polymers were confirmed by ^{1}H NMR and IR spectra. The UV−vis absorption spectra of **2** suggested that the π-conjugation systems in the polymers expanded more effectively than the polymer obtained from 1,4-diethynylbenzene reported previously. The cyclic voltammetry analysis of **2a** (prepared from 2,5-diethynylthiophene) showed an anodic shift and a broadening of the oxidation peak for the dithiafulvene unit compared with that of 2,6-bis(2-thienyl)-1,4-dithiafulvene (**3**), due to the effective expansion of the π-conjugation in **2a**. All polymers **2** formed soluble charge-transfer complexes with TCNQ in DMSO. The UV−vis absorption and IR spectra of the resulting CT complexes indicated that two different types of TCNQ, anion radical of TCNQ and partially charge transferred TCNQ, interacted with the dithiafulvene unit in **2**. Undoped polymer **2c** (prepared from 2,5-diethynylpyridine) showed an unusual high electrical conductivity of 1.6×10^{-4} S/cm due to incorporation of the π-deficient pyridine unit in the dithiafulvene polymer. The CT complex of **2a** with TCNQ has a conductivity of 1.0×10^{-4} S/cm, 2 orders of magnitude greater than that of the uncomplexed polymer **2a**.

Introduction

The chemistry of dithiafulvenes and their analogues, including tetrathiafulvalenes (TTF), has been the focus of a considerable interest because of their ability to form stable and highly conducting charge-transfer (CT) salts with a number of electron acceptors.[1] Fascinated by their unique electronic properties, scientists have made several attempts to incorporate such donor molecules into polymeric matrices in order to improve the processability of charge-transfer salts.[2] The design of dithiafulvene-based donors with linearly extended π-conjugation has progressively emerged as one of the main synthetic strategies toward higher dimensionality of the conduction process in the doped state.[3] However, examples of polymers containing dithiafulvene derivatives in the π-conjugate main chain have been limited.[4] Recently, we reported the synthesis of new π-conjugated polymers having dithiafulvene unit in the main chain by the cycloaddition polymerization of aldothioketenes derived from aromatic diynes with their alkynethiol tautomers.[5] Although thioketenes are regarded as highly reactive and very useful species in organic reactions, similar to their ketene analogues,[6] the direct use of thioketenes in polymer synthesis has been very limited until now. The UV−vis absorption spectra and cyclic voltammetry measurements showed an effective expansion of the π-conjugation system in the polymers. These polymers formed soluble CT complexes with tetracyanoquinodimethane (TCNQ).[5a,c]

Dithiafulvene analogues including five-membered heterocyclic compounds such as furan, thiophene, and pyrrole have been reported.[7] As the aromatic resonance energy of these five-membered heterocycles is lower than that of benzene, a better π-electron delocalization over the whole donor molecule can be anticipated because of the fact the such heterocyclic compounds form quinonoid conformations easily in their π-conjugated system.

Scheme 1



π-Conjugated polymers having donor−acceptor pairs in their backbone are fascinating materials in view of their achieving a small band gap due to their intramolecular CT structures.[8] Small band gaps for π-conjugated polymers are pursued because of their higher intrinsic (undoped) conductivity and they might give a clue for real intrinsically metallic organic polymer. Poly(pyridine)s are known as electron-accepting polymers and show n-doping properties.[9] Therefore, it is of interest to synthesize π-conjugated polymers comprising alternately linked electron-donating dithiafulvene and pyridine moieties.

In this paper, we describe the synthesis and properties of new π-conjugated polymers having dithiafulvene

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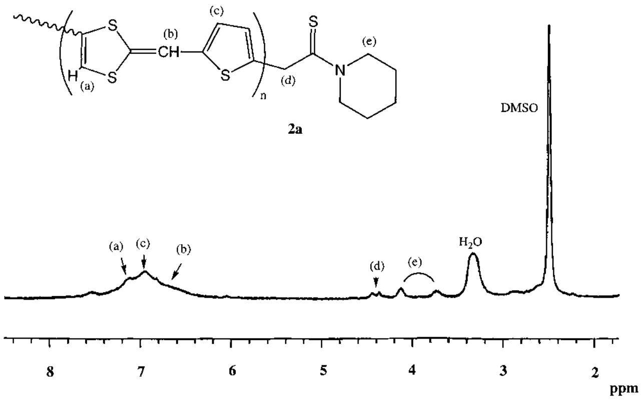
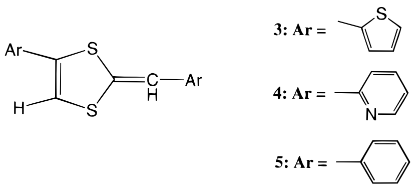


Figure 1. ^{1}H NMR spectrum of **2a** in DMSO-d_6.

and heteroaromatic units such as thiophene and pyridine in the main chain. CT complexes of those polymers with TCNQ were also studied.

Results and Discussion

The polymerization reactions were carried out by the method of cycloaddition of aldothioketenes derived from heteroaromatic diynes **1** (Scheme 1). All polymers **2** were soluble in DMSO and DMF. Although one *n*-hexyl chain was attached on the thiophene unit, the solubility of **2b** was not improved. The molecular weight measurements were performed by GPC in eluent DMSO with poly(ethylene oxide) standard. The number-average molecular weights (M_n) of **2a** and **2c** were 3230 and 4170, respectively.



The IR and ^{1}H NMR spectra of **2a**−**c** were reasonable for their structures compared with those of model compounds **3** and **4**[6b,d] which were prepared from 2-ethynylthiophene and 2-ethynylpyridine, respectively. The IR spectra of **2a** and **2c** exhibited respective peaks at 1576 and 1584 cm^{-1}, corresponding to a C=C vibration of the dithiafulvene units. Those spectra also showed peaks at around 1500 and 1285 cm^{-1} which were assigned to the terminal thioamide moieties[5a,b,6e,f] of the polymers. The ^{1}H NMR spectrum of **3** showed peaks corresponding to dithiafulvene protons at 6.44 and 6.74 ppm in $CDCl_3$. The peaks of the dithiafulvene protons shifted downmagneticfield to be detected at 6.97 and 7.16 ppm in DMSO-d_6. In the ^{1}H NMR spectrum of **2a** (Figure 1), a broad peak for the benzylidene proton of dithiafulvene appeared from 6.5 to 6.8 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.2 ppm in DMSO-d_6. This broadening was due to the relatively low solubility of **2a** in DMSO. The peaks for the terminal thioamide group were observed at 3.7, 4.1, and 4.4 ppm.[5a,b,6e,f] The ^{1}H NMR spectrum of **2c** showed a broad peak from 6.5 to 7.0 ppm, assigned to the dithiafulvene protons and also showed peaks of the pyridyl protons at 7.4, 7.7−7.9, and 8.7 ppm. Comparison of the intensities of the absorptions of the dithiafulvene and the aromatic protons in the repeating unit with those of the absorptions of the terminal thioamide protons resulted in estimation of number-average degree of polymerization (DP) as 28 (M_n = 5810) in **2a**, 19 (M_n = 5660) in **2b** and 20 (M_n = 4210) in **2c**. These values are almost same as those from GPC data.

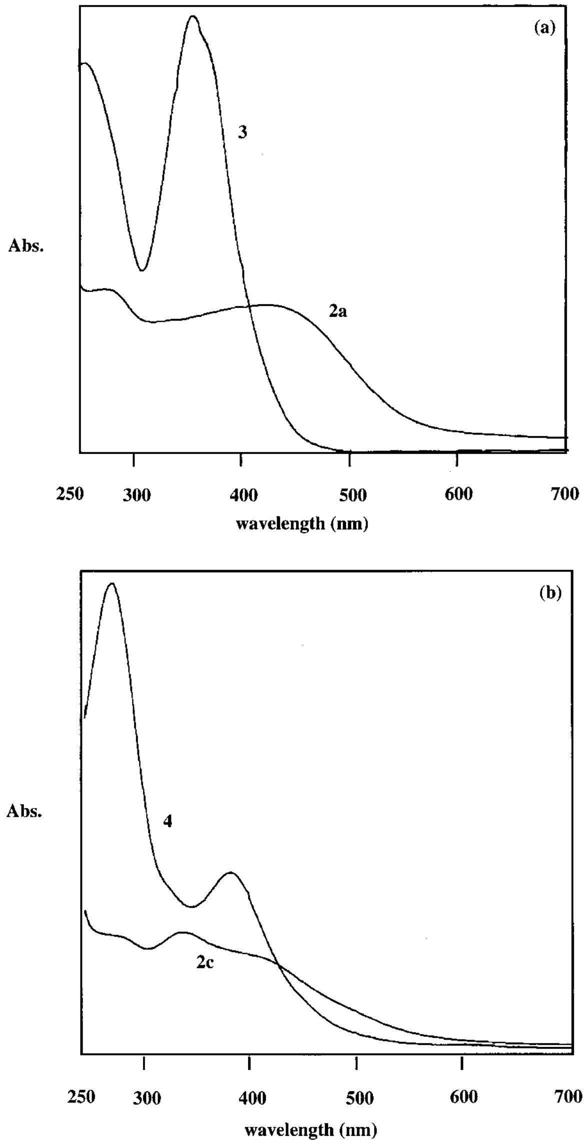
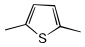
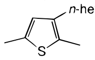
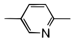
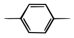


Figure 2. UV−vis absorption spectra of (a) **2a** and **3** and (b) **2c** and **4** in CH_3CN.

UV−vis absorption spectra of polymers and their model compounds were obtained for CH_3CN solutions. As shown in Figure 2, the UV−vis absorption spectra of the polymers **2a** and **2c** show largely bathochromic shift from those of their model compounds. The polymer **2a** showed an absorption in the visible range with a peak at 421 nm, due to the $\pi-\pi^*$ transition of the polymer. The peak position was largely shifted to longer wavelength by 66 nm from the absorption band of **3** (Figure 2a). Moreover, the UV−vis absorption of **2a**−**c** is located at a longer wavelength than that of the benzene analogue (**2d**) (Table 1, run 4), indicating that the π-conjugations through the heteroaromatic moieties are more effectively expanded than that through the benzene moiety. This fact, in thiophene polymers **2a** and **2b**, was caused by the lower aromatic resonance energy of the thiophene unit compared with that of the benzene ring. The lower energy absorption edge of **2c** was largely bathochromic shifted in comparison with that of the model compound **4**. The bathochromic shift of **4** from λ_{max} of **3** and that of 2-benzylidene-4-phenyl-1,3-dithiole

Table 1. Synthesis of Dithiafulvene Polymers by Using Various Monomers

run	Ar		yield(%)	M_n [a)]	UV absorption λ_{max} (nm) [b)]	ε (M^{-1} cm^{-1})	oxidation potential E_{pa}(V) [c)]
1		**2a**	65	5810	421	7790	0.78
2		**2b**	25	5660	406 (sh) [d)]	7090	0.55
3		**2c**	72	4210	416 (sh) [d)]	4220	1.38
4[e]		**2d**	76	5440	398	12300	0.61
5	**model compound 3**		-	-	355	19200	0.36
6	**model compound 4**		-	-	384	8400	0.45

[a] Determined from ^{1}H NMR. [b] Measured in a diluted CH_3CN solutions at room temperature. [c] Measured in a CH_3CN solution of 0.1 M $[NEt_4]BF_4$ at 300 mV/s. [d] Shoulder peak of the spectra. [e] Prepared from 1,4-diethynylbenzene.

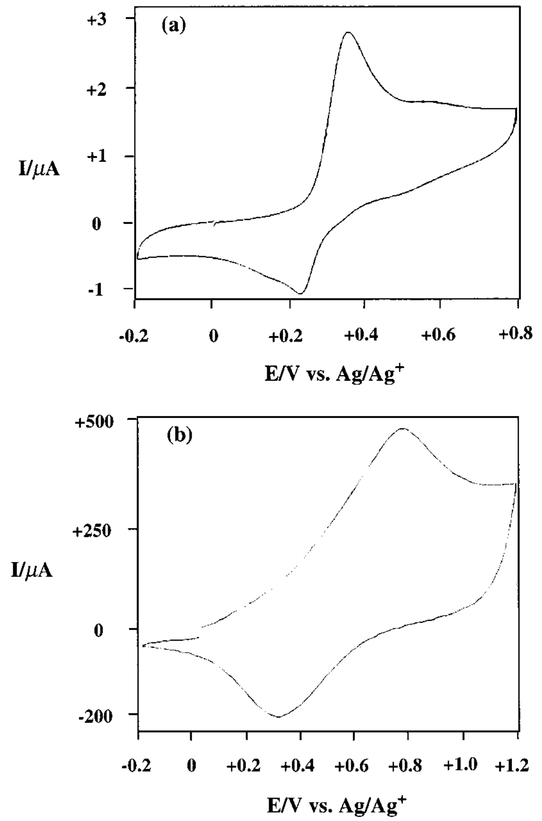
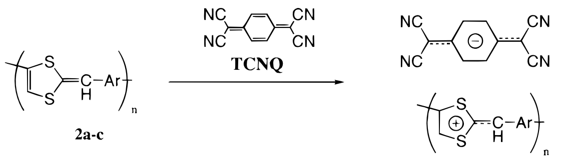


Figure 3. Cyclic voltammogram of (a) **3** (4×10^{-4} M; platinum working electrode) and (b) a film of **2a** (thickness = 12 μm) on indium−tin−oxide (ITO) coated glass electrode, measured in CH_3CN solutions of 0.1 M $[NEt_4]BF_4$ at 300 mV/s.

(**5**) as benzene analogue (λ_{max} = 352 nm)[5a,b] suggested a unique electronic state related to the donor−acceptor pair between the dithiafulvene unit and the pyridine unit. The smaller bathochromic shift of **2b** from λ_{max} of **3**, compared with the bathochromic shift observed with **2a**, was due to a steric distortion of the side alkyl chain of the thiophene moiety.[10]

The electrochemical redox behavior of the donors was studied by cyclic voltammetry. As shown in Figure 3, **3** showed a single oxidation peak at 0.36 V vs Ag/Ag$^+$. The value of the oxidation peak was less positive by 0.04 V than that of 5 (E_{pa} = 0.40 V),[5b] indicating that the electron-donating ability of **3** increased by the π-excessive thiophene moiety. The cast film of **2a** gave a single broad oxidation peak at 0.78 V and a reduction peak at 0.30 V vs Ag/Ag$^+$. The oxidation peak of **2a** was largely anodic shifted and broadened in comparison with that of **3**. Such an anodic shift and broadening of the peak have been reported for several electrochemically active π-conjugated polymers.[9d,11] The fairly higher oxidation potential of **2a** compared with that of **2d** was also observed, whereas **3** shows the stronger electron-donating property than its benzene analogue. This result indicated that the dithiafulvene unit in **2a** caused a higher stabilization against oxidation than that in **2d**, due to the fact that the π-electron delocalization of **2a** was enhanced in comparison with that of **2d**.

Scheme 2



π-conjugated polymer CT complex 6a-c

The cast film of **2b** showed a lower oxidation peak than that of **2a**, suggesting that π-conjugation between dithiafulvene units through the thiophene having a side alkyl chain was not so effective as that through the thiophene with no alkyl group. This behavior is consistent with the UV absorption analysis described above. Moreover, **2b** gave a lower oxidation potential compared with the corresponding benzene polymer. The unusual high oxidation potential of the dithiafulvene unit of **2c** was caused by the effect of the π-deficient pyridine unit.

The polymers **2a**−**c** formed complexes with TCNQ in DMSO (Scheme 2). To a solution of **2a**−**c** in DMSO, an excess amount of TCNQ against the repeating dithiafulvene unit of **2a**−**c** was added and the mixture was stirred for 15 min. TCNQ itself is hardly soluble in DMSO. After unreacted TCNQ was filtered off, the filtrates were evaporated to obtain dark green powders. The resulting CT complexes (**6a**−**c**) were soluble in common organic solvents such as DMSO, DMF, acetonitrile, acetone, and methanol.

A degree of charge transfer can be determined by the frequency of the nitrile stretching band of TCNQ.[12] Neutral TCNQ shows at 2227 cm^{-1} and anion radical of TCNQ shows at 2180 cm^{-1}. IR spectra of **6a** showed two peaks in the C≡N stretching region at 2200 and 2180 cm^{-1}. This fact suggested that two different types of TCNQ interacted with polymer **2a**. The latter band was assignable to the anion radical of TCNQ. The former peak was shifted by 27 cm^{-1} from neutral TCNQ, indicating the partially charge transferred TCNQ was in the complex. The degree of charge transfer was estimated to be 0.63 from the value of the peak difference.[12a] IR spectra of **6b** and **6c** were similar to that of **6a**, both of which showed two C≡N stretching bands of anion radical and partially charge transferred TCNQ (2197 cm^{-1} in **6b** and 2202 cm^{-1} in **6c**). The calculated values of degree of charge transfer in **6b** and **6c** were 0.68 and 0.59, respectively.[12a] The degrees of charge transfer of TCNQ in **6** have the following order: **6b** > **6a** > **6c**. This observation might be explained by the oxidation potentials of polymers **2** determined from the CV analyses. When TCNQ formed a complex with dithiafulvene polymers, it could accept more charge from the stronger donor (**6b**, E_{pa} = 0.55) and less charge from the weaker one (**6c**, E_{pa} = 1.38), resulting in the difference of degrees of charge transfer.

UV−vis spectra of the CT complexes **6** in acetonitrile showed absorptions which were essentially a summation of the band characteristic of TCNQ and the anion radical. The appearances of the absorption bands between 650 and 900 nm were responsible for the anion radical of TCNQ.[13] The strong peaks at 390 nm were also observed in the spectra of **6**. Normal TCNQ shows an absorption at 395 nm. In the IR spectra of the polymer CT complexes **6**, the C≡N stretching bands due to neutral TCNQ could not be found so that the observed peaks at 390 nm in **6** should be corresponding to the partially charge transferred TCNQ.

In the ^{1}H NMR spectra of **6** in DMSO-d_6, comparison of the intensities of the absorption of the aromatic region and the dithiafulvene protons and the TCNQ protons with those of the terminal thioamide protons showed formations of both complexes containing about 1:1 ratio of dithiafulvene unit to TCNQ.[5a,c]

The conductivities of the polymers were investigated at room temperature by conventional two-probe technique. Undoped **2a** and **2c** exhibited electrical conductivities of 1.2×10^{-6} and 1.6×10^{-4} S/cm, respectively. Extremely high intrinsic conductivity of **2c** was achieved in an undoped state, due to an incorporation of a π-deficient pyridine unit into the dithiafulvene polymer. This unusual observation presumably resulted from the effective donor−acceptor pair of the dithiafulvene and the pyridine units. The CT complex **6a** had a conductivity of 1.0×10^{-4} S/cm, 2 orders of magnitude greater than that of the uncomplexed polymer **2a**; however, **6c** showed 2.9×10^{-4} S/cm, not much improved compared with the undoped polymer.

Conclusions

We presented the synthesis and properties of the polymers with the electron donating dithiafulvene and the heteroaromatic units. The UV absorption analysis indicated that π-conjugation in **2a**−**c** was more effectively expanded than that in the phenyl analogue polymer. Polymer **2** formed the CT complexes with TCNQ in DMSO. Two different types of TCNQ, anion radical of TCNQ and partially charge transferred TCNQ, interacted with the repeating dithiafulvene unit of the polymer, indicated by IR and UV spectra of **6**. The undoped **2c** showed unexpectedly high conductivity due to its donor−acceptor pair of the dithiafulvene and the pyridine units. The CT complexes **6** raised conductivities to exhibit the property as a semiconductor.

Experimental Section

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. 2,5-Diethynylthiophene,[14a,b] 2,5-diethynyl-3-hexylthiophene,[14a−c] and 2,5-diethynylpyridine[14a,b] were synthesized according to the literature.

Measurements. ^{1}H 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. Gel permeation chromatography was carried out on TSK gel α-3000 by using DMSO as an eluent at 50 °C after calibration with standard poly(ethylene glycol) samples. For cyclic voltammetry studies, thin polymer films (thickness, 10−20 μm) were deposited on an indium−tin−oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under 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 all CV measurements. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 source meter. The polymer film was prepared by dropping of a DMSO solution onto glass plates equipped with platinum electrodes, followed by drying in vacuo.

Polymerization. A typical experimental procedure is as follows. To a solution of 2,5-diethynylthiophene (132 mg, 1.00 mmol) in Et_2O (1.5 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (1.25 mL, 2.00 mmol) at 0 °C. After the reaction was stirred for 0.5 h, sulfur powder (64 mg, 2.00 mmol) was added to the solution. The reaction mixture was stirred for 2 h and then cooled at −55 °C, and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise to room temperature, and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.3 mL), and the mixture was stirred for 0.5 h. The mixture was then poured into a large quantity of Et_2O. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a dark brown-colored polymer was obtained.

2a. Yield: 134 mg (65%). ^{1}H NMR (270 MHz, DMSO-d_6): δ 1.2−1.6 (CH_2 of piperidine unit), 3.7 ($N{-}CH_2$ of piperidine unit), 4.1 ($N{-}CH_2$ of piperidine unit), 4.4 ($CH_2C({=}S)N<$), 6.5−6.8 (benzylidene proton), 7.0 (protons of thiophene), 7.2 (1,3-dithiole ring proton). IR (KBr, cm^{-1}): 2835, 1628, 1576, 1540, 1496, 1428, 1284, 1240. Anal. Calcd: C, 49.1; H, 2.4. Found: C, 48.3; H, 2.6.

2b. ^{1}H NMR (270 MHz, DMSO-d_6): δ 0.8 ($-CH_2(CH_2)_4\mathit{CH_3}$) 1.0−1.7 ($-CH_2(\mathit{CH_2})_4CH_3$, and CH_2 of piperidine unit), 2.6 ($-\mathit{CH_2}(CH_2)_4CH_3$), (3.6 ($N{-}CH_2$ of piperidine unit), 4.2 ($N{-}CH_2$ of piperidine unit and $CH_2C({=}S)N<$), 6.4−7.4 (thiophene and dithiafulvene protons). IR (KBr, cm^{-1}): 2918, 2848, 1626, 1575, 1550, 1504, 1454, 1292. Anal. Calcd: C, 60.4; H, 6.1. Found: C, 59.8; H, 6.0.

2c. ^{1}H NMR (270 MHz, DMSO-d_6): δ 1.2−1.6 (CH_2 of piperidine unit), 3.2 ($N{-}CH_2$ of piperidine unit), 4.3 ($N{-}CH_2$ of piperidine unit and $CH_2C({=}S)N<$), 6.5−7.0 (dithiafulvene protons), 7.4 (pyridyl proton), 7.7−7.9 (pyridyl proton), 8.7 (pyridyl proton). IR (KBr, cm^{-1}): 1584, 1508, 1434, 1286, 1261. Anal. Calcd: C, 57.1; H, 3.1. Found: C, 57.3; H, 3.3.

Model Compounds. The model compounds **3** were prepared according to ref 6b,d.

2,6-Bis(2-thienyl)-1,4-dithiafulvene (3).[6d] ^{1}H NMR (270 MHz, ($CDCl_3$): δ 6.44 ($>C{=}CH{-}Ar$, s, 1H), 6.74 (dithiole ring proton, s, 1H), 6.93−7.08 (thiophene, m, 4H), 7.24 (thiophene, m, 2H). IR (KBr, cm^{-1}): 1574, 1568, 1416 cm^{-1}.

2,6-Bis(2-pyridyl)-1,4-dithiafulvene (4).[6d] ^{1}H NMR (270 MHz, ($CDCl_3$): δ 6.70−7.22 (dithiafulvene and pyridyl protons, m, 4H), 7.48 (pyridine, d, 1H), 7.50 (pyridine, d, 1H), 7.66 (pyridine, m, 2H), 8.59 (pyridine, q, 2H). IR (KBr, cm^{-1}): 1582, 1557, 1454 cm^{-1}.

CT Complexes of 2 with TCNQ. A typical experimental procedure is as follows. An excess amount of TCNQ against the repeating unit of **2** was added to a solution of **2** in DMSO, and the mixture was stirred for 15 min. The solution gradually became dark green. After the unreacted TCNQ was filtered off, the solvent was evaporated to obtain a dark green powder.

Acknowledgment. This work was partly supported by the Ogasawara Foundation for the Promotion of Science & Engineering and the Kinki-Area Innovation Center.

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