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Preparation, Characterization and Electric Conductivity of CT Adducts of Crystalline Poly(1,1'-ferrocenylene) with Electron Acceptors

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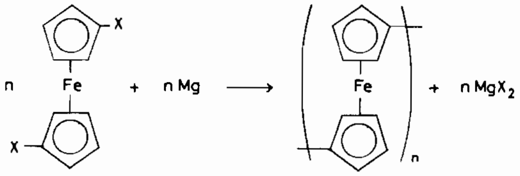
Crystalline poly(1,1'-ferrocenylene) forms adducts with various electron acceptors such as iodine, 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis-propanedinitrile (TCNQ), and tetracyanoethylene (TCNE). Magnetic susceptibilities, color, and Mössbauer spectra of the adducts indicate partial oxidation of Fe(II) in poly(1,1'-ferrocenylene) to Fe(III). The adducts of crystalline poly(1,1'-ferrocenylene) with the electron acceptors show much higher electric conductivities (by a factor of 10^2*–*10^6*) than the previously reported adducts of amorphous poly(1,1'-ferrocenylene). Among the adducts studied, a TCNQ adduct shows the highest electric conductivity;* $\sigma = 4.1 \times 10^{-2}$ *S cm*$^{-1}$ *for a 1:0.64 adduct of the polymer with TCNQ at 295 K. An X-ray diffraction pattern of the crystalline poly(1,1'-ferrocenylene) shows peaks at 11.8°, 19.2°, 23.5°, and 25.2°, whereas the TCNQ adducts gives rise to new sharp peaks at quite different positions. In contrast to a high crystallinity of the TCNQ adduct, the adducts of other electron acceptors are amorphous as revealed by their X-ray diffraction patterns which show no peaks. Both the peaks assigned to Fe(II) and Fe(III) found in the Mössbauer spectrum of the TCNQ adduct become broad on raising the temperature from 78 K to 310 K, suggesting the occurrence of a rapid intervalence electron exchange between Fe(II) and Fe(III) on the Mössbauer time scale at higher temperatures.*

Introduction

Previously we reported the preparation of crystalline poly(1,1'-ferrocenylene) using a highly selective dehalogenative polycondensation of 1,1'-dihaloferrocene with magnesium [1]:



The paper included a brief report on electric conductivities of adducts of the polymer with iodine and 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis-propanedinitrile (TCNQ).

Although various methods to prepare poly(1,1'-ferrocenylene) have been developed [2–5], most poly(1,1'-ferrocenylene) prepared before our work were not crystalline, presumably due to contamination with units other than the recurring 1,1'-ferrocenylene unit in the polymer chain. The pioneering work of Pittman and his co-workers [3] on the electric conductivities of poly(1,1'-ferrocenylene)–electron acceptor adducts was carried out using amorphous poly(1,1'-ferrocenylene) which was prepared by poly-recombination of ferrocene radicals generated by the thermal decomposition of di-*ter*-butyl peroxide in the presence of ferrocene. The polymer thus prepared is considered to contain some fragments other than the 1,1'-ferrocenylene unit (for example, 1,2-ferrocenylene, $-CH_2-$, and $-O-$ units) in the main chain [2g, 2h].

The crystallinity of a compound strongly affects its electric conductivity [6] and the possible delocalization of electrons along the poly(1,1',-ferrocenylene) main chain (which may be crucial for a polymer to have such a high electric conductivity as those observed with π-conjugated polymers [7–11]), seems to be disturbed in the amorphous poly(1,1′-ferrocenylene) containing units other than 1,1′-ferrocenylene. Therefore, we have examined the electric conducting properties of the adducts of our crystalline poly(1,1′-ferrocenylene) with electron acceptors, expecting that the adducts of crystalline poly(1,1′-ferrocenylene) with the electron acceptors would show higher electric conductivities than similar adducts of amorphous poly-(1,1′-ferrocenylene).

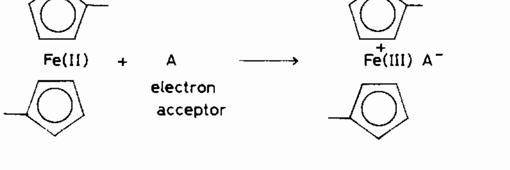
It has been revealed by several groups that Mössbauer spectroscopy provides invaluable information concerning intervalence electron transfer in mixed valence ferrocene compounds [12–14]. Recently it was reported that the Mössbauer spectroscopic studies of *trans*-μ-(*as*-indacene)bis-(cyclopentadienyliron) and 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenium triiodides show temperature-dependent mixed-valence state [13].

We now report the formation reactions, characeterization, Mössbauer spectroscopic analysis, and electric conducting properties of the adducts of the crystalline poly(1,1′-ferrocenylene) with electron acceptors.

Results and Discussion

Formation of Adducts with Electron Acceptors

The crystalline poly(1,1′-ferrocenylene), similarly to the amorphous poly(1,1′-ferrocenylene) [2i, 3], absorbs various electron acceptors including iodine, 2,2′-(2,5-cyclohexadiene-1,4-diylidene)-bispropanedinitrile (TCNQ), tetracyanoethylene (TCNE), 4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile (DDQ), and 2,3,5,6,-tetrachloro-2,5-cyclohexadiene-1,4-dione (*p*-CA). The initial orange color of the polymer turned to dark brown or black on adduct formation with the electron acceptor, indicating the occurrence of partial oxidation of the polymer [3, 15].



(1)

The magnetic susceptibilities and Mössbauer spectra of the adducts also confirm the partial oxidation of the polymer (*vide infra*).

Most of the absorption bands in the IR spectrum of poly(1,1′-ferrocenylene) are broadened and weakened on adduct formation. When the molar ratio of the electron acceptor absorbed to the 1,1′-ferrocenylene unit is below *ca.* 0.2, the broadening and weakening of the bands are not so remarkable, but when the ratio reaches about 0.5 most of the original peaks of poly(1,1′-ferrocenylene) disappear and even such strong bands as δ(C–H) of the monosubstituted cyclopentadienyl group (Cp) (1110, 1030, 995, and 795 cm^{-1}) and ν(Fe–Cp) (480 cm^{-1}) become very weak, despite the remaining 50% of the 1,1′-ferrocenylene units in the adduct, considered to be not oxidized. These results indicate that oxidation of half of the 1,1′-ferrocenylene units causes severe change in the vibrational modes of the whole polymer molecule. The ν(C≡N) bands of TCNQ and DDQ shift to lower frequencies by 50–100 cm^{-1} on adduct formation with poly(1,1′-ferrocenylene), and this is taken as evidence for the formation of anion radicals [16] of TCNQ and DDQ according to eqn. 1.

The poly(1,1′-ferrocenylene)–electron acceptor adducts described above have high stabilities against oxygen and moisture in air, but their thermal stabilities are somewhat lower than pure poly(1,1′-ferrocenylene); among the adducts, the DDQ adduct has the highest thermal stability (d.p. = 300 °C) and the iodine adduct has the lowest (d.p. = 115 °C). The adducts are insoluble in organic solvents.

The poly(1,1′-ferrocenylene) has a strong affinity toward SO_3 and absorbs 2.9 mol of SO_3 per 1,1′-ferrocenylene unit on exposure to vapors of SO_3 at room temperature. However, the high hygroscopic character of the SO_3 adduct prevented measuring its electric conductivity and other physical properties.

Electric Conductivity and Other Physical Properties Related to the Electric Conductivity

Table I shows magnetic susceptibilities (χ), electric conductivities (σ), and the activation energy (E_a) for the electric conduction of the poly(1,1′-ferrocenylene)-electron acceptor adducts.

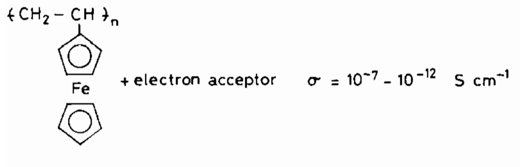
It is seen in Table I that

i) All the adducts show paramagnetism, presumably due to the formation of the ferricinium cation, $\text{-}(C_5H_4Fe(III)^+C_5H_4)\text{-}$, and anion radical of the electron acceptor (eqn. 1).

ii) The poly(1,1′-ferrocenylene)–electron acceptor adducts have high electric conductivities for a range of semiconductors. The σ values shown in Table I are larger by a factor of 10^2–10^6 than are the electric conductivities of similar adducts of amorphous poly(1,1′-ferrocenylene) with the electron acceptors reported by Pittman and his coworkers [3], who reported that poly(1,1′-ferrocenylene)–electron acceptor adducts had almost the same conductivities as those of poly(vinylferrocene)–electron acceptor adducts:

TABLE I. Magnetic Susceptibility χ and Electric Conductivity σ of $(-C_5H_4FeC_5H_4 \cdot xA-)$ (A = electron acceptor).

A	x	χ $cm^3\ g^{-1}$	σ, Electric conductivity $S\ cm^{-1}$	Temp. K	Activation energy, E_a kcal mol^{-1}
I_3	0.32	4.8×10^{-5}	1.3×10^{-4}	292	5.0 (σ_0 = 0.74 S cm^{-1})
			2.6×10^{-5}	248	
			8.7×10^{-6}	223	
			2.0×10^{-6}	197	
p-CA	0.46	1.0×10^{-4}	2.2×10^{-7}	290	8.3 (σ_0 = 0.42 S cm^{-1})
			8.9×10^{-8}	273	
			2.7×10^{-8}	253	
			5.7×10^{-9}	231	
TCNQ	0.98		1.4×10^{-2}	298	2.3 (σ_0 = 0.69 S cm^{-1})
			8.6×10^{-3}	264	
			5.5×10^{-3}	239	
			3.8×10^{-3}	221	
			2.3×10^{-3}	195	
TCNQ	0.64	8.0×10^{-5}	4.1×10^{-2}	295	1.7 (σ_0 = 1.0 S cm^{-1})
			3.1×10^{-2}	271	
			1.2×10^{-2}	220	
			6.9×10^{-3}	195	
TCNQ	0.19	1.4×10^{-4}	3.5×10^{-3}	300	2.1 (σ_0 = 0.19 S cm^{-1})
			2.5×10^{-3}	274	
			1.9×10^{-3}	253	
TCNE	0.56	1.2×10^{-4}	1.5×10^{-6}	301	6.9 (σ_0 = 0.23 S cm^{-1})
			4.7×10^{-7}	275	
			1.6×10^{-7}	254	
			4.9×10^{-8}	233	
DDQ	0.55	1.0×10^{-4}	3.2×10^{-7}	297	8.2 (σ_0 = 0.36 S cm^{-1})
			6.5×10^{-8}	266	
			4.0×10^{-8}	258	
			2.3×10^{-8}	249	



On the basis of their observation Pittman [3] claimed that increase of the delocalization of electrons along a polymer chain on going from poly(vinylferrocene) to poly(1,1′-ferrocenylene) did not affect the electric conductivity. However, the present observation clearly indicates that the adducts of poly(1,1′-ferrocenylene) with electron acceptors have markedly higher electric conductivities than similar adducts of poly(vinylferrocene), and consequently the presence of delocalized electrons along the polymer chain is crucial for the high electric conductivity.

iii) Moderately oxidized poly(1,1′-ferrocenylene) with a composition of $\leftarrow C_5H_4FeC_5H_4 \cdot 0.68\text{-}TCNQ \rightarrow_n$ has a higher electric conductivity than either a strongly oxidized polymer of composition $-(C_5H_4FeC_5H_4 \cdot 0.98TCNQ)-_n$ and a weakly oxi-

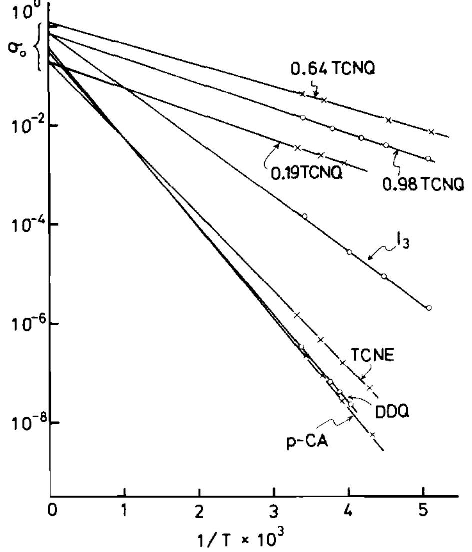


Fig. 1. Plot of σ given in Table I against 1/T.

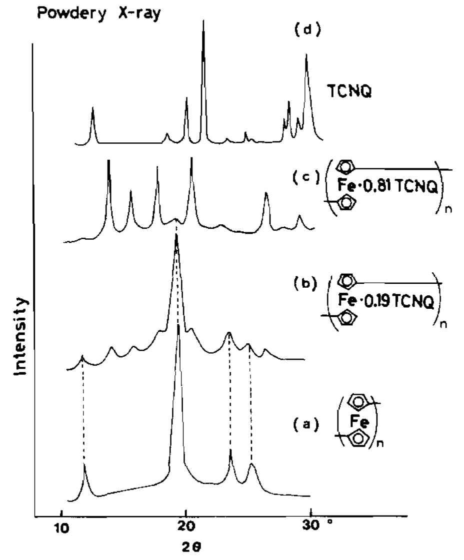


Fig. 2. Powder X-ray diffraction spectra of poly(1,1′-ferrocenylene) and its TCNQ adducts.

dized polymer, $-(C_5H_4FeC_5H_4 \cdot 0.19TCNQ)-_n$, indicating the importance of a mixed valent Fe(II) Fe(III) state for the electric conduction, in agreement with Pittman's observation concerning the electric conductivities of the amorphous poly(1,1′-ferrocenylene)–electron acceptor adducts and poly(vinylferrocene)–electron acceptor adducts [3].

iv) The temperature dependence of the electric conductivity, obeys the following equation (Fig. 1),

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (2)$$

As shown in Table I, an adduct having a higher electric conductivity has a lower activation energy, and the σ_0 (Fig. 1) values calculated for the adducts listed in Table I have the same order of magnitude in spite of large differences in σ and E_a values. Since no theory to elucidate the mechanism of the electric conduction in mixed valent polymer compounds has been established, a clear-cut discussion for the coincidence of the σ_0 values is not possible but the coincidence of the σ_0 values for the various adducts may be taken as an indication that the same factor controls the electric conduction in the various poly(1,1′-ferrocenylene)–electron acceptor adducts.

X-Ray Diffraction

Figure 2 shows powder X-ray diffraction patterns of poly(1,1′-ferrocenylene), its adduct with TCNQ, and TCNQ. These are the first reported data concerning the X-ray diffraction patterns of poly(1,1′-ferrocenylene) and its adduct with an electron acceptor. Among the poly(1,1′-ferrocenylene)–electron acceptor adducts, only the TCNQ adduct gives rise to sharp diffraction bands and the other adducts seem to be amorphous as judged from their powder X-ray diffraction patterns which showed no peak. The powder X-ray diffraction data of poly(1,1′-ferrocenylene) and its adduct with TCNQ are summarized in Table II. The strongest diffraction band of poly(1,1′-ferrocenylene) at 2θ = 19.2°, corresponding to a distance of 5.37 Å, is tentatively assigned to an Fe–Fe distance.

When poly(1,1′-ferrocenylene) absorbs 0.81 mol of TCNQ per 1,1′-ferrocenylene unit, the X-ray diffraction pattern ((c) in Fig. 2) shows new peaks due to the TCNQ adduct at 2θ = 7.0, 14.0, 15.8, 17.9, 20.6, 26.6, 28.4, 29.3, 30.7 and 32.8°, besides weak bands due to poly(1,1′-ferrocenylene). The powder X-ray diffraction pattern of the TCNQ adduct containinig 0.18 mol of TCNQ per 1,1′-ferrocenylene unit ((b) in Fig. 2) also shows the new peaks due to the TCNQ adduct at the same positions, although the relative intensities of the peaks are considerably weaker than those of peaks due to poly(1,1′-ferrocenylene). These X-ray diffraction data strongly suggest that poly(1,1′-ferrocenylene) does not absorb TCNQ randomly, but once a 1,1′-ferrocenylene unit in a polymer chain forms an adduct with TCNQ, 1,1′-ferrocenylene units near the TCNQ adduct preferentially absorb TCNQ until the TCNQ–1,1′-ferrocenylene adducts thus produced form new microcrystals. Thus, the TCNQ adduct formulated as $-(C_5H_4FeC_5H_4 \cdot xTCNQ)-_n$ does not become a random adduct between the 1,1′-ferrocenylene unit and TCNQ but a mixture of pure $-(C_5H_4FeC_5H_4)-_n$ and a polymeric adduct having a stoichio-

TABLE II. Powdery X-Ray Diffraction Data of Poly(1,1′-ferrocenylene) and Its TCNQ Adduct.[a]

Compound	2θ, °	d, Å	Intensity	
$-(C_5H_4FeC_5H_4)-_n$	11.8	8.70	26	
	19.2	5.37	100	
	23.5	4.39	24	
	25.2	4.10	13	
			x = 0.18	x = 0.81
$-(C_5H_4FeC_5H_4xTCNQ)-_n$	7.0	14.7	4	15
	11.8[b]	8.70	16	3
	14.0	7.34	26	99
	15.8	6.51	11	51
	17.9	5.75	26	86
	19.2[b]	5.37	100	9
	20.6	5.01	23	100
	23.5[b]	4.39	23	6
	25.2[b]	4.10	14	c
	26.6	3.89	7	53
	28.4	3.65	c	8
	29.3	3.54	c	20
	30.7	3.38	c	14
	32.8	3.17	c	8

[a] CoK_α was irradiated. [b] Peaks due to $-(C_5H_4FeC_5H_4)-_n$. [c] Not observable.

metric composition, in accord with the powder X-ray diffraction data. According to the Mössbauer data of the TCNQ adduct (*vide infra*), the microcrystal of the TCNQ adduct seems to have a composition of $\text{-}\!\!(C_5H_4Fe(II)C_5H_4{-}C_5H_4Fe(III)C_5H_4^{+}\ TCNQ^{-}\ (TCNQ)\!\!\text{-}_n$.

The observation that among the poly(1,1′-ferrocenylene)–electron acceptor adducts only the TCNQ adduct forms the microcrystals suggests an exceptionally good steric fitness between TCNQ and the poly(1,1′-ferrocenylene) chain.

Mössbauer Spectrum

Figure 3 shows Mössbauer spectra of poly(1,1′-ferrocenylene), $-(C_5H_4FeC_5H_4)-_n$, and its TCNQ adduct having a composition of $-(C_5H_4FeC_5H_4\cdot 0.81TCNQ)-_n$. The isomer shift (IS = 0.46 mm/s) and quadrupole splitting (QS = 2.22 mm/s) of $-(C_5H_4FeC_5H_4)-_n$ at room temperature are comparable to those of ferrocene and biferrocene [17]. The Mössbauer spectrum of $-(C_5H_4FeC_5H_4\cdot 0.81TCNQ)-_n$ at 78 K clearly shows two kinds of doublets, an inner doublet ascribed to Fe(III) and an outer doublet due to Fe(II), indicating that the $-C_5H_4Fe(II)C_5H_4-$ species is partly oxidized to $-C_5H_4Fe(III)C_5H_4-$ according to the reaction shown by eqn. 1.

The isomer shifts and quadrupole splittings of the outer doublet due to Fe(II) (IS = 0.54 mm/s; QS = 2.00 mm/s at 78 K) and the inner doublet due to Fe(III) (IS = 0.57 mm/s; QS = 0.72 mm/s at 78 K) are comparable to those of outer and inner doublets observed in the Mössbauer spectra of mono cations

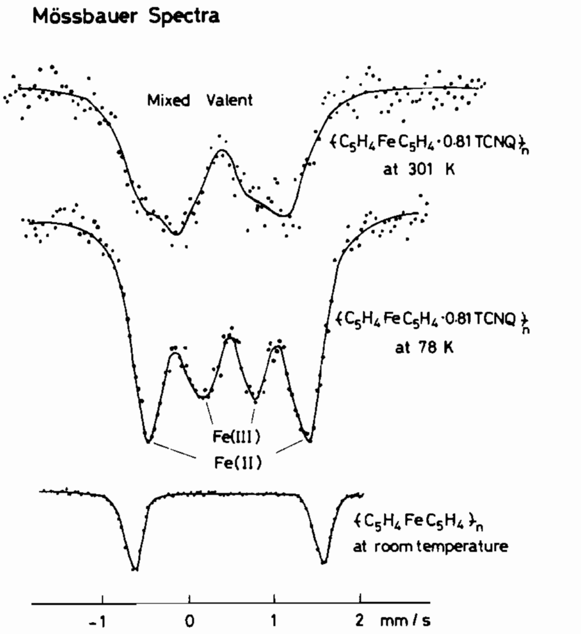
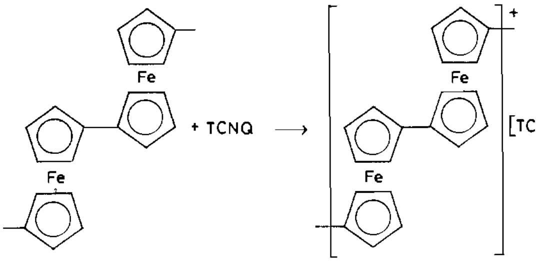


Fig. 3. Mössbauer spectra of poly(1,1′-ferrocenylene) and its 1:0.81 adduct with TCNQ at 78 K and 301 K.

of biferrocene and its derivatives [14b]. The relative intensity of the Fe(III) species to the Fe(II) species in Fig. 3 indicates that roughly 40% of the starting Fe(II) species is oxidized to the Fe(III) species in $-\!(C_5H_4FeC_5H_4\cdot 0.81(TCNQ)\!)\!-_n$. These results and the fact that poly-(1,1′-ferrocenylene) did not absorb more than 1 mol of TCNQ per unit $-C_5H_4FeC_5H_4-$ under experimental conditions may be taken as an indication that only half of the TCNQ in the adduct forms the salt with the bis(ferrocenylene) unit in poly(1,1′-ferrocenylene),



(3)

and the remaining half of TCNQ exists as a neutral molecule like a solvent of crystallization. It is known that only one Fe(II) of the two Fe(II)s in biferrocene, $C_5H_5FeC_5H_4-C_5H_4FeC_5H_5$, is oxidized by interaction with electron acceptors according to a reaction similar to that expressed by eqn. 3 and the adduct of biferrocene with the electron acceptor sometimes absorbs additional molecule(s) of the electron acceptor as the solvent of crystallization [14b].

The Mössbauer spectral peaks of $-\!(C_5H_4FeC_5H_4\cdot 0.81TCNQ\!)\!-_n$ are somewhat broadened even at 78 K compared with those of $-\!(C_5H_4FeC_5H_4\!)\!-_n$, suggesting the occurrence of a rapid electron migration between Fe(II) and Fe(III) [12–14] at that temperature. On raising the temperature the peaks become broader and each of the two peaks at low and high energy regions collapses at 301 K showing a relaxation phenomenon between Fe(II) and Fe(III) as in the case of *trans-μ-*(*as*-indacene)bis(cyclopentadienyliron) [13]. This indicates that a very rapid exchange of electrons between Fe(II) and Fe(III) on the Mössbauer time scale (10^{-7} s) takes place at that temperature.

The iodine adduct of poly(1,1′-ferrocenylene), $-\!(C_5H_4FeC_5H_4\cdot 0.32I_3\!)\!-_n$ at 78 K also shows peaks due to Fe(II) (IS = 0.55 mm/s; QS = 1.97 mms) and Fe(III) (IS = 0.52 mm/s; QS = 0.65 mm/s), but the broadening of the peaks at higher temperature was not clearly observed. That the rapid intervalence exchange between Fe(II) and Fe(III) occurs only in the crystalline poly(1,1′-ferrocenylene)–TCNQ adduct suggests the presence of a special interaction between Fe(II) and Fe(III) in the microcrystals. The rapid exchange may be responsible for the high electric conductivity of the TCNQ adduct.

Experimental

Materials

The crystalline poly(1,1′-ferrocenylene) was prepared according to the method reported in our previous paper [1]. A benzene-insoluble fraction having a molecular weight of 4600 [1] was employed in this study. Solvents were dried over CaH_2, distilled under N_2, and stored under N_2. The electron acceptors other than I_2 and SO_3 were purified by recrystallization or sublimation.

Preparation of the Adducts

Preparation of the adducts of poly(1,1′-ferrocenylene) was carried out under an atmosphere of N_2. In all cases, the reaction proceeded heterogeneously and almost quantitative yields were attained.

When 97 mg of powdery poly(1,1′-ferrocenylene) containing 0.53 mmol of the 1,1′-ferrocenylene unit was added into a benzonitrile solution (3 cm^3) of TCNQ (220 mg, 1.08 mmol) at room temperature, the color of the polymer immediately changed from orange to black. After stirring the reaction mixture for 3 h at 60 °C, 20 cm^3 of acetonitrile was added. The black TCNQ adduct was obtained by filtration and washed repeatedly with acetonitrile. *Anal.* Found: C, 67.2; H, 3.1; N, 12.9%. The analytical data correspond to a composition of $-\!(C_5H_4FeC_5H_4\cdot 0.81\text{-}TCNQ\!)\!-_n$; Calcd. for the composition: C, 67.8; H, 3.2; N, 13.0%. A part of the difference between the observed and the calculated values is attributed to Br at the terminal of the poly(1,1′-ferrocenylene) [1]. IR (KBr, cm^{-1}): 2180s, 2110s, 1590w, 1500m, 1300s,br, 1100–1020br, 820m, 680m. When a similar reaction between poly(1,1′-ferrocenylene) (123 mg, 0.67 mmol of the 1,1′-ferrocenylene unit) and TCNQ (272 mg, 1.34 mmol) was carried out in 3 cm^3 of benzonitrile at room temperature, the reaction gave the adduct containing a somewhat less amount of TCNQ, $-\!(C_5H_4FeC_5H_4\cdot 0.64TCNQ\!)\!-_n$. When a more dilute benzonitrile (4 cm^3) solution of TCNQ (35 mg, 0.17 mmol) was used in the reaction with poly(1,1′-ferrocenylene) (110 mg, 0.60 mmol of the 1,1′-ferrocenylene unit) at room temperature, the reaction afforded the adduct having a composition of $-\!(C_5H_4FeC_5H_4\cdot 0.19TCNQ\!)\!-_n$. On the contrary, addition of more TCNQ (300 mg, 1.45 mmol in 3 cm^3 of benzonitrile) in the reaction with poly(1,1′-ferrocenylene) (88 mg, 0.48 mmol of the 1,1′-ferrocenylene unit) at 100 °C resulted in the formation of the adduct having a composition of $-\!(C_5H_4FeC_5H_4\cdot 0.96\ TCNQ\!)\!-_n$.

The iodine adduct of poly(1,1′-ferrocenylene), $-\!(C_5H_4FeC_5H_4\cdot 0.32I_3\!)\!-_n$ was prepared as described in our previous paper [1]. IR (KBr, cm^{-1}): 610 s, 1030m, 820s, 670s, 600s, 480m.

Poly(1,1′-ferrocenylene) (80 mg, 0.43 mmol of the 1,1′-ferrocenylene unit) was added into a benzonitrile (4 cm^3) solution of 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione (210 mg, 0.85 mmol), *p*-CA, at room temperature, and the suspension was stirred for 24 h at room temperature. After heating the reaction mixture for 4 h at 100 °C, 20 cm^3 of acetonitrile was added. The dark brown adduct was separated by filtration, washed repeatedly with acetonitrile, and dried in vacuum to yield a compound having a composition of $-(C_5H_4FeC_5H_4\cdot 0.46p\text{-}CA)-_n$. *Anal.* Found: C, 51.4; H, 2.6. Calcd.: C, 51.6; H, 2.7. IR (KBr, cm^{-1}): 1515 m, 1405s, 1270w, 1200w, 1100w, 1030w, 920m, 820w, 750w, 710w, 670w, 480m.

Poly(1,1′-ferrocenylene) (100 mg, 0.54 mmol of the 1,1′-ferrocenylene unit) was added into a benzonitrile (3 cm^3) solution of tetracyanoethylene (140 mg, 1.1 mmol), TCNE, at room temperature. After stirring the mixture for 24 h at room temperature, 20 cm^3 of acetonitrile was added. The dark brown adduct was separated, washed, and dried in a similar manner as applied to the TCNQ or *p*-CA adduct. *Anal.* Found: C, 62.0; H, 3.9; N, 12.2. Calcd. for $-(C_5H_4FeC_5H_4\cdot 0.56TCNE)-_n$: C, 62.7; H, 3.2; N, 12.3. IR (KBr, cm^{-1}): 2200s, 2160s, 1600br, 1500br, 1300w, 1200w, 1010br, 920w, 820w, 790w.

Poly(1,1′-ferrocenylene) (114 mg, 0.62 mmol of the 1,1′-ferrocenylene unit) was added into a benzonitrile (3 cm^3) solution of 4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile (282 mg, 1.24 mmol), DDQ, at room temperature. Stirring the mixture for 3 h at room temperature gave a black solid, which was separated by filtration, washed with acetonitrile repeatedly, and dried in vacuum. *Anal.* Found: C, 55.0; H, 2.7; N, 4.8. Calcd. for $-(C_5H_5FeC_5H_4\cdot 0.55DDQ)-_n$: C, 56.0; H, 2.6; N, 5.0. IR (KBr, cm^{-1}): 2210m, 1680–1620br, 1520s, 1405s, 1220m, 1030s, 995s, 900s, 830br, 790m, 755m, 680m.

Instruments

The magnetic susceptibility was measured with the aid of a Shimadzu MB-100 magnetic balance. X-ray diffraction patterns were obtained with a Phillips PW-1051 X-ray diffractometer. IR spectra were recorded on a Hitachi Model 295 infrared spectrometer. The electric conductivity was measured by a Takeda Riken TR-8651 electrometer after molding the adduct into a disk (ϕ = 13 mm, d = 1–2 mm). From the disk we obtained a bar by cutting off other parts of the disk, and the electric conductivity was measured with the bar using a four-point method. Microanalysis of C, H, and N was performed by Mr. T. Saito of Tokyo Institute of Technology ,with a Yanagimoto CHN Autocorder Type MT2. Mössbauer spectra were recorded with an Austin-600 Mössbauer spectrometer by using a $^{57}Co(Pt)$ source moving in a constant acceleration mode at room temperature. The isomer shifts are determined relative to metallic iron foil.

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