Preparation of (Thiophene)manganese Tricarbonyl Cations for Nonlinear Optics

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Two series of organometallic complexes, **1**−**6** and **7**−**11,** which contain a (thiophene)Mn-$(CO)_3^+$ fragment in the end group were synthesized for nonlinear optical chromophores, and their second-order nonlinear optical properties were measured by the HRS method. These complexes were found to possess promising hyperpolarizabilities.

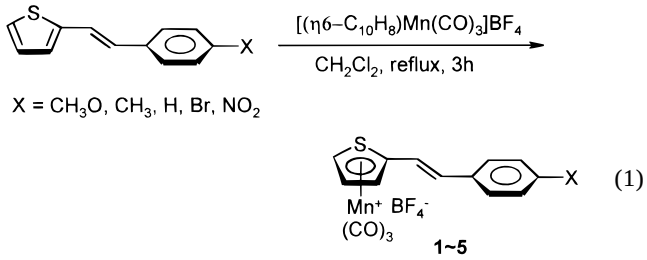
Introduction

Molecules based on thiophenes have attracted much attention due to their role in nonlinear optical (NLO) materials.[1] Thiophene derivatives used as conjugating units provide electron delocalization pathways more efficient than those of benzene.[2] Thiophene moieties are important in enhancing the molecular hyperpolarizabilities of charge-transfer compounds.[3] Due to the extended π-conjugation, polythiophenes have recently been recognized as an important class of third-order NLO media.[4] Incorporation of metal moieties with oligothiophenes or thienyl entities in the conjugation chain has been used to improve the NLO properties.[5]

Here we report the synthesis and nonlinear optical study of several new (thiophene)manganese tricarbonyl cations. Chart 1 shows the compounds which have been studied.

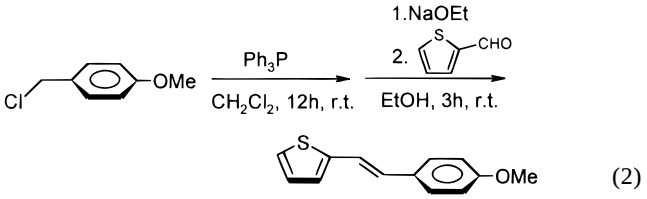
Results and Discussion

Synthesis. Complexes **1**−**5**, which have the same organic structural frame except for X, have been prepared according to eq 1, in which $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]BF_4$ is used as a $Mn(CO)_3^+$ transfer reagent.[6] Complex

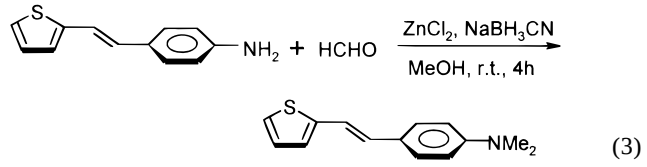


(1)

6 was prepared by the same method and found to have the $Mn(CO)_3^+$ moiety coordinated to the arene ring. Complex **5-2** was synthesized by the reaction of **5** and PPh_3 in the presence of Me_3NO. The coordination site in **1** and **6** was verified by X-ray crystallography (vide infra). The organic frames for **2**−**4** were made by known procedures,[7,8] and those for **1** and **6** were newly prepared according to eqs 2 and 3.



(2)



(3)

Complexes **7**−**11** have almost the same frame except for the spacer and the position of substituent. The syntheses of the ferrocene derivatives used in the preparation of **7**−**9** and **11** were previously reported.[9−11]

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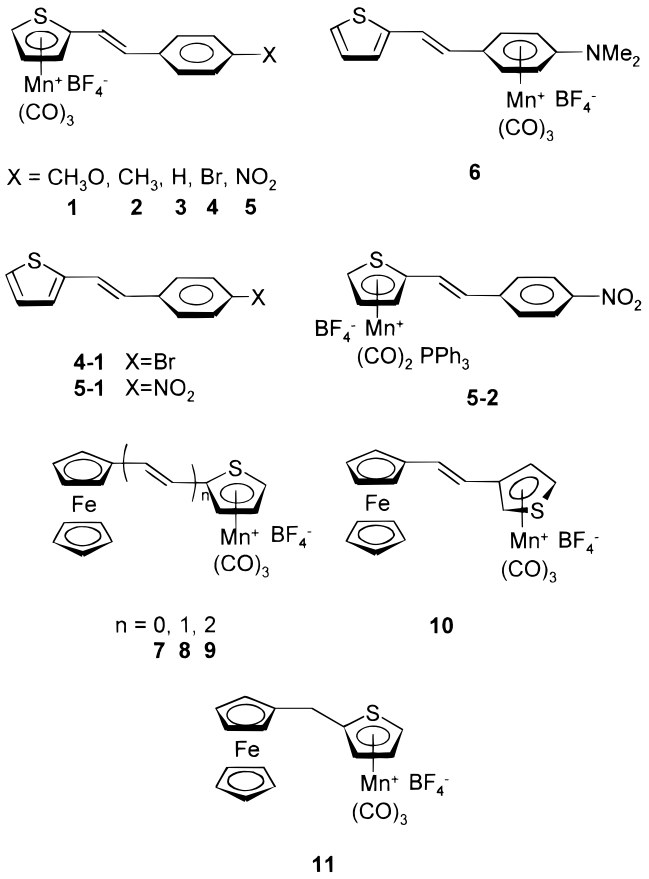
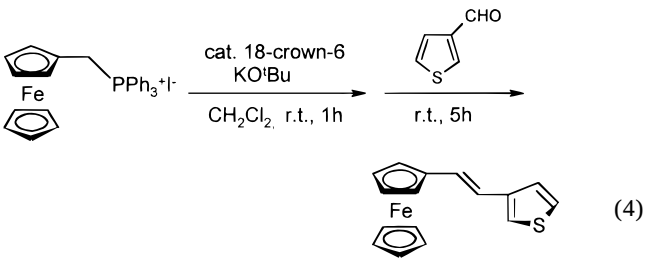
Chart 1



The ferrocene derivative used in the preparation of **10** is outlined in eq 4. Reactions of those ferrocene derivatives with [(naphthalene)$Mn(CO)_3$]BF_4 afforded high yields (77−94%) of **7**−**8** and **10**−**11** and a 40% yield of **9**.



X-ray Crystal Structures of 1 and 6. Single crystals for **1** and **6** were grown in nitromethane and diethyl ether, respectively. X-ray structure determinations of **1** and **6** confirmed their centrosymmetric nature (space group $P2_1/n$) of **1** and **6** (Figures 1 and 2). Crystal data and structure refinement details are given in Table 1 and selected bond lengths and angles in Table 2. Usually, the manganese carbonyl unit prefers to coordinate to the thiophene ring rather than the arene ring, as in the case of **1**. However, in **6**, the $Mn(CO)_3^+$ moiety coordinates to the arene ring. For **1**, there are two isomers **A** and **B** in an asymmetric unit. Due to the disorder of the anion, structure **A** was more disturbed than structure **B**. Interestingly, isomers **A** and **B** are π-stacked between the thiophene ring of **A** and the arene ring of **B** and between the thiophene ring of **B** and the arene ring of **A**. The thiophene ring of **A** is parallel to the arene ring of **B** (tilt angle 1.8(0.6)°), and the distance between the centroids of the two rings is 3.60 Å. The tilt angle between thiophene ring of **B** and arene ring of **A** is 7.2(0.4)°, and the distance between the centroids of the two rings is 3.60 Å. In general, bond distances and angles in the thiophene and arene rings in **1** are in agreement with the structures of other transition-metal complexes.[12] The fragment 2-$SC_4H_3CH{=}CHC_6H_4OCH_3$-*p* in **1** is roughly planar with a dihedral angle of 5.9(0.4)° (for **A**) and 3.6(0.6)° (for **B**) between two aromatic rings, but the fragment 2-$SC_4H_4CH{=}CHC_6H_4NMe_2$-*p* in **6** is slightly twisted with a dihedral angle of 26.6(0.2)° between two aromatic rings. In addition, the arene ring (C1−C2−C3−C4−C5−C6) and the thiophene ring (S−C9−C10−C12−C11) are twisted out of the ethenediyl plane (C1−C7−C8−C9) by 19.3(0.6) and 7.6(0.7)°, respectively. Thus, in the solid state, electronic coupling in **1** may be greater than in **6**. Due to the anion disorder, however, any detailed discussion of the structural parameters in **1** and **6** is unwarranted.

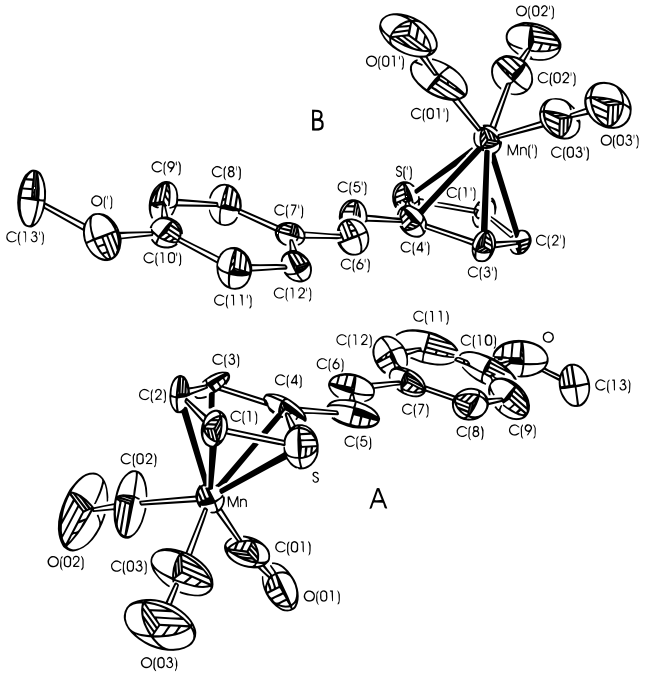


Figure 1. ORTEP drawing of **1** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

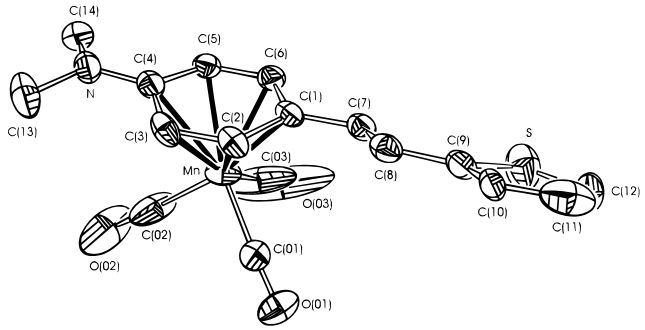


Figure 2. ORTEP drawing of **6** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

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Table 1. Crystal Data and Structure Refinement Details for 1 and 6

	1	6
empirical formula	$C_{32}H_{24}B_2F_8Mn_2O_8S_2$	$C_{17}H_{15}BF_4MnNO_3S$
fw	884.13	455.11
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	10.0627(12)	12.209(2)
b, Å	19.404(2)	10.440(2)
c, Å	19.769(4)	14.993(3)
β, deg	101.526(14)	94.78(2)
V, Å^3	3782(10)	1904.4(7)
Z	4	4
d(calcd), Mg/m^3	1.553	1.587
2θ range, deg	4.2−50	4.1−50
total no. of data collected	7044	3511
no. of unique data	6566	3337
no. of params refined	584	290
R1	0.0846	0.0608
wR2	0.1265	0.1356
GOF	0.763	1.046

Hyperpolarizability Measurements. Chart 1 shows compounds for which hyperpolarizability measurements were made, and Table 3 shows the results. The hyperpolarizability (β) values of complexes **1**−**5** increase in the order **1** < **2** < **3** < **4** < **5**, similar to the electron-acceptor power of the substituent X (MeO < Me < H < Br < NO_2). The static hyperpolarizabities (β_0) of **1**−**5** also increase in the order **1** < **2** < **3** < **4** < **5**. With the assumption that the β value of **6** follows the electron acceptibility of the amino group as seen in **1**−**5**, the β value of **6** is predicted to be negligible. This, however, is not the case (Table 3), possibly because the $Mn(CO)_3^+$ unit is coordinated to the arene instead of the thiophene ring (as in **1**−**5**).

According to Cheng et al.,[13] the chromium tricarbonyl fragment in (arene)$Cr(CO)_3$ functions as a ground-state acceptor but as an excited-state donor. The β values of substituted (benzene)chromium tricarbonyls are small in magnitude and quite insensitive to the electronic influence of the substituents. This phenomenon was ascribed to poor conjugation between the metal center and the benzene substituents.

If we follow the aforementioned discussion, the differences in dipole moments for **1**−**5** in the ground state may not be great and the (thiophene)$Mn(CO)_3^+$ fragment functions as a ground-state acceptor but an excited-state donor. When an electron-withdrawing substituent is appended to the arene ring, the energy of the arene π^* orbital is lowered, thereby increasing β. Electron-donating substituents will have the opposite effect, thereby decreasing β. Introduction of electron-donating groups such as PPh_3 should destabilize the HOMO, thereby decreasing the electron-withdrawing ability in the ground state and increasing the electron-donating ability in the excited state. The β value of **5-2** is larger than that of **5**, and this may originate from the presence of high-lying filled metal orbitals and a large electronic asymmetry around the metal center. In contrast to those of (C_6H_5X)$Cr(CO)_3$, the β values for **1**−**5** are large, probably due to good conjugation between the metal center and the benzene substituents. This was confirmed by comparing **4** to **4-1** and **5** to **5-1**. The β value of **4-1** is almost negligible, but the β value of **5-1** is 326 × 10^{-30} esu. When compounds **4-1** and **5-1** are coordinated to $Mn(CO)_3^+$, the β values increases to 534 × 10^{-30} and 613 × 10^{-30} esu, respectively. Ratner and Marks[14] reported theoretical studies on the quadratic hyperpolarizabilities in organotransition-metal chromophores. According to their calculation, the β_{vec} values for chromium arene complexes are significantly less than those for the $Cr(CO)_3$-free analogues. Those calculated results are quite different from our experimental results. In a recent study, Marks and Ratner[15] reported that electron-rich heterocyclic bridges act as auxiliary donors while electron-deficient heterocyclic bridges act as auxiliary acceptors, significantly enhancing the NLO response. Compounds **4-1** and **5-1** contain an electron-rich thiophene, and it is expected that their β values would be larger than those of metal-free phenyl analogues. The large difference in the β values of **4-1** and **5-1** may originate from the different electron acceptabilities of the bromo and nitro groups. The large β values for **1**−**5** may be due to the electronic asymmetry around the metal center and/or the presence of a thiophene ring instead of a phenyl ring.[5,16]

The hyperpolarizability values of **7**−**9** and **11** increase in the order **7** < **11** < **8** < **9**, reflecting the increase of the π-conjugation length and the removal of the electronic pseudosymmetry around the metal center. It is well-known[17] that the ferrocene moiety acts as a moderate donor. Both experiment[17] and theory[18] suggest that the donor strength of ferrocene is comparable to that of a methoxyphenyl group. Thus, we expected that the β value of **8** would be similar to that of **1**, but in fact the β of **8** is 2 times greater than that of **1**. The reason for this difference is not clear.

The hyperpolarizability depends on where the double bond on the vinylferrocene is linked to the thiophene ring (see **8** and **10** in Table 3). Complexes **8** and **9** display high β values that may be attributed to resonance enhancement, which becomes important whenever the fundamental frequency and/or the doubled frequency is close to the charge-transfer excitation.[19] The latter is the case for **8** and **9**. A similar interpretation was applied to the unusually large β values (320 × 10^{-30} and 570 × 10^{-30} esu) for bimetallic (Fe−Cr) sesquifulvalene complexes.[20] These sesquifulvalene complexes were shown to exhibit static hyperpolarizabities (β_0) of (105−113) × 10^{-30} esu, depending on the spacer. Calculation of the static hyperpolarizability β_0 for **7**−**10**

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 1 and 6

Compound **1**										
Mn−S	2.285(3)	Mn−C1	2.075(11)	Mn−C3	2.182(10)	C4−C5	1.57(2)			
C5−C6	1.168(13)	C7−C8	1.357(14)	Mn−C01	1.66(2)	C01−O01	1.22(2)			
O01−C01−Mn	173.1(12)	C1−S−C4	89.6(6)	C1−C2−C3	119.7(10)					
Compound **6**										
S−C9	1.692(6)	S−C12	1.678(9)	C11−C12	1.346(12)	C7−C8	1.321(9)			
Mn−C1	2.213(5)	Mn−C01	1.794(7)	C01−O01	1.140(6)	N−C14	1.441(8)			
Mn−C01−O01	177.1(6)	C9−S−C12	91.8(4)	S−C9−C10	111.9(5)					
C7−C8−C9	126.8(6)	C6−C1−C2	115.3(5)	C1−C2−C3	121.5(5)					

Table 3. Quadratic Hyperpolarizability Values Measured by the HRS Method[a]

	1	**2**	**3**	**4**	**4-1**	**5**	**5-1**	**5-2**	**6**	**7**	**8**	**9**	**10**	**11**
λ (nm)[b]	415	405	390	393	n.r.[d]	400	383	384	470	514	536	548	480	n.r.
β (10^{-30}esu)	252	355	413	534	2	613	326	700	377	260	670	771	305	220
β_0 (10^{-30}esu)[c]	84	127	165	209	n.c.[e]	229	137	292	67	13	−8	−34	45	n.c.

[a] All the measurements were carried out in nitromethane solvent. [b] Lowest charge transition band in UV region. [c] Corrected using the two-level model with $\beta_0 = \beta[1 - (2\lambda_{max}/1064)^2][1 - (\lambda_{max}/1064)^2]$. [d] Not resolved. [e] Not calculated.

gives β_0(**7**) = 13 × 10^{-30} esu, β_0(**8**) = −8 × 10^{-30} esu, β_0(**9**) = −34 × 10^{-30} esu, and β_0(**10**) = 45 × 10^{-30} esu. The β_0 values for **7**−**10** are relatively small compared to those of **1**−**5**. In comparison to neutral chromium complexes, the cationic manganese complexes **8** and **9** led to a substantial increase in the resonance-enhanced hyperpolarizability.

In conclusion, we have synthesized several potential NLO materials and measured their hyperpolarizabilities by the HRS method. All the (thiophene)manganese complexes studied show substantial β values. A rationale is provided which is based on the assumption that the (thiophene)$Mn(CO)_3^+$ moiety acts as an excited-state donor. The largest β value was obtained for **9** and is ascribed to resonance enhancement.

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under nitrogen using standard Schlenk techniques. Freshly distilled dry, oxygen-free solvents were used throughout. Routine ^{1}H NMR spectra (300 and 500 MHz) were recorded with a Bruker 300 or 500 spectrometer. Elemental analyses were performed by the Analytical Center, College of Engineering, Seoul National University. UV−vis electronic absorption spectra were recorded on a Unikon 930 spectrophotometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus, Model 6427-H10, and were not corrected. (*E*)-2-(2-Phenylethenyl)thiophene, (*E*)-2-[2-(4-methylphenyl)ethenyl]-thiophene, (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene, (*E*)-2-[2-(4-bromophenyl)ethenyl]thiophene, 2-[$(C_5H_5)FeC_5H_4(CH{=}CH)_n$]-$C_4H_3S$ (n = 0−2), 2-[$(C_5H_5)FeC_5H_4CH_2$]C_4H_3S, and [$(C_5H_5)Fe$-$C_5H_4CH_2PPh_3$]I were previously reported[7−11,21] and prepared according to the modified procedures.

(*E*)-2-[2-(4-Methoxyphenyl)ethenyl]thiophene. 4-Methoxybenzyl chloride (2.35 g, 15 mmol) and PPh_3 (5.11 g, 19.5 mmol) were dissolved in 30 mL of CH_2Cl_2. The solution was stirred at room temperature for 1 day. After the solution was concentrated to 10 mL, Et_2O (200 mL) was added to the precipitate. After filtration, the corresponding phosphonium salt was obtained in 82.4% yield (5.28 g). The phosphonium salt (4.39 g, 10.5 mmol) and NaOEt (13.6 mmol, generated by the reaction of EtOH with Na metal) were dissolved in 30 mL of EtOH. To the solution was added 2-thiophenecarboxaldehyde (1.3 g, 11.5 mmol). After the solution was stirred at room temperature for 3 h and evaporated to dryness, excess Et_2O (50 mL × 2) was added to extract a product from the residue. After removal of the solvent, the crude product was obtained. Pure product was obtained by recrystallization from methanol. Yield: 0.77 g (33.8%). ^{1}H NMR ($CDCl_3$): δ 7.43 (d, 8.72 Hz, 2 H), 7.18 (d, 4.98 Hz, 1 H), 7.13 (d, 16.2 Hz, 1 H), 7.05 (d, 3.35 Hz, 1 H), 7.01 (m, 1 H), 6.91 (d, 8.46 Hz, 2 H), 6.91 (d, 15.9 Hz, 1 H), 3.85 (s, 3 H, CH_3) ppm. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.27; H, 5.47.

(*E*)-2-[2-(4-(Dimethylamino)phenyl)ethenyl]thiophene. (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene (1.07 g, 4.63 mmol), $Fe_3(CO)_{12}$ (2.7 g, 5.36 mmol), and absolute methanol (1.9 mL) were placed in 30 mL of benzene. The solution was heated at reflux overnight. After filtration, the filtrate was concentrated and chromatographed on a silica gel column with Et_2O and hexane (v/v, 1:1) as the eluent. After removal of the solvent, (*E*)-2-[2-(4-aminophenyl)ethenyl]thiophene was obtained in 95.4% yield (0.89 g). ^{1}H NMR ($CDCl_3$): δ 7.28 (d, 8.50 Hz, 2 H), 7.12 (d, 4.60 Hz, 1 H), 7.05 (d, 16.2 Hz, 1 H), 6.98 (d, 4.63 Hz, 1 H), 6.96 (d, 3.56 Hz, 1 H), 6.84 (d, 16.1 Hz, 1 H), 6.66 (d, 8.30 Hz, 2 H), 3.74 (br s, 2 H) ppm. Anal. Calcd for $C_{12}H_{11}NS$: C, 71.61; H, 5.51; N, 6.96; S, 15.93. Found: C, 71.52; H, 5.59; N, 6.90; S, 16.08. (*E*)-2-[2-(4-aminophenyl)-ethenyl]thiophene (0.85 g, 4.22 mmol) and formaldehyde (1.7 mL, 35% aqueous solution) were dissolved in 20 mL of MeOH. To the methanol solution were added a 10 mL methanol solution of $ZnCl_2$ (0.58 g, 4.25 mmol) and $NaBH_3CN$ (0.416 g, 6.38 mmol). The resulting solution was stirred at room temperature for 4 h and evaporated to dryness. Excess Et_2O was added to extract the product from the residue. Chromatography on a silica gel column with Et_2O and hexane (v/v, 1:3) as eluent gave the product in 42.9% yield (0.416 g). ^{1}H NMR ($CDCl_3$): δ 7.30 (d, 8.68 Hz, 2 H), 7.05 (d, 4.92 Hz, 1 H), 7.02 (d, 16.1 Hz, 1 H), 6.92 (d, 3.1 Hz, 1 H), 6.89 (dd, 3.50, 4.65 Hz, 1 H), 6.79 (d, 16.1 Hz, 1 H), 6.68 (d, 8.11 Hz, 2 H), 2.91 (s, 6 H, CH_3) ppm. Anal. Calcd for $C_{14}H_{15}N_2S$: C, 73.32; H, 6.59; S, 13.98. Found: C, 73.41; H, 6.36; S, 14.15.

(*E*)-3-[$(C_5H_5)FeC_5H_4CH{=}CH$]C_4H_3S. To 30 mL of a THF solution of [$C_5H_4FeC_5H_4CH_2PPh_3$]I (3.60 g, 6.03 mmol) and 18-crown-6 (catalytic amount) was added KO*t*Bu (0.750 g, 6.68 mmol). The solution was stirred for 1 h. To this solution was added 3-thiophenecarboxaldehyde (0.53 mL, 6.05 mmol). The resulting solution was stirred for 5 h. Excess water (50 mL) and diethyl ether (50 mL) were added to quench the solution. The ethereal layer was collected, concentrated, and chromatographed on a silica gel column with hexane as eluent. Removal of the solvent gave the product in 44.9% yield (0.833 g, 2.71 mmol). ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 2 H), 7.11 (s, 1H), 6.89 (m, 2 H), 4.46 (s, 2 H), 4.30 (s, 2 H), 4.15 (s, 5 H) ppm. Anal. Calcd for $C_{16}H_{14}FeS$: C, 65.32; H, 4.80; S, 10.90. Found: C, 65.36; H, 4.62; S, 10.99.

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[{(*E*)-2-[2-(4-Bromophenyl)ethenyl]thiophene}Mn(CO)$_3$]-BF$_4$ (4). In a Schlenk flask (*E*)-2-[2-(4-bromophenyl)ethenyl]-thiophene (0.61 g, 2.3 mmol) and [(naphthalene)Mn(CO)$_3$]BF$_4$ (0.895 g, 2.53 mmol) were dissolved in 20 mL of CH_2Cl_2. The solution was heated at reflux under N_2 for 3 h. After filtration of any solids, the filtrate was evaporated and redissolved in CH_3NO_2. The CH_3NO_2 solution was dropped slowly into a stirred Et_2O solution. After filtration, the yellow manganese salt was obtained in 37.4% yield (0.42 g). Mp: 129 °C. IR (CD_3NO_2): ν(CO) 2072, 2008 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.61 (d, 8.6 Hz, 2 H), 7.52 (d, 8.6 Hz, 2 H), 7.33 (d, 16.5 Hz, 1 H), 7.15 (d, 16.1 Hz, 1 H), 6.78 (d, 3.5 Hz, 1 H), 6.75 (m, 2 H) ppm. Anal. Calcd for $C_{15}H_9BBrF_4MnO_3S$: C, 36.70; H, 1.85; S, 6.53. Found: C, 36.68; H, 1.83; S, 6.60.

Synthesis of 1. The same procedure as the synthesis of **4** was applied, using (*E*)-2-[2-(4-methoxylphenyl)ethenyl]thiophene. A yellow solid, with mp 148 °C dec, was obtained. Yield: 58.9%. IR (CD_3NO_2): ν(CO) 2064, 2016 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.53 (d, 8.79 Hz, 2 H), 7.27 (d, 16.1 Hz, 1 H), 6.95 (d, 8.67 Hz, 1 H), 6.95 (d, 5.11 Hz, 1 H), 6.93 (d, 15.9 Hz, 1 H), 6.68 (d, 2.14 Hz, 1 H), 6.61 (dd, 2.01, 2.15 Hz, 1 H), 3.81 (s, 3 H, CH_3) ppm. Anal. Calcd for $C_{16}H_{12}BF_4MnO_4S$: C, 43.47; H, 2.74; S, 7.25. Found: C, 43.20; H, 2.67; S, 7.45.

Synthesis of 2. The same procedure as the synthesis of **4** was applied, using (*E*)-2-[2-(4-methylphenyl)ethenyl]thiophene. A yellow solid, with mp 168 °C, was obtained. Yield: 79.8%. IR (CD_3NO_2): ν(CO) 2080, 2008 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.54 (d, 8.17 Hz, 2 H), 7.38 (d, 16.1 Hz, 1 H), 7.32 (d, 7.97 Hz, 2 H), 7.11 (d, 16.1 Hz, 1 H), 6.78 (m, 2 H), 6.73 (m, 1 H), 2.41 (s, 3 H, CH_3) ppm. Anal. Calcd for $C_{16}H_{12}BF_4MnO_3S$: C, 45.10; H, 2.84; S, 7.52. Found: C, 44.75; H, 2.57; S, 7.84.

Synthesis of 3. The same procedure as the synthesis of **4** was applied, using (*E*)-2-(2-phenylethenyl)thiophene. A yellow solid, with mp 144 °C, was obtained. Yield: 75.4%. IR (CD_3NO_2): ν(CO) 2068, 2016 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.60 (m, 2 H), 7.47 (m, 3 H), 7.38 (d, 16.1 Hz, 1 H), 7.15 (d, 16.2 Hz, 1 H), 6.76 (m, 3 H) ppm. Anal. Calcd for $C_{15}H_{10}BF_4MnO_3S$: C, 43.72; H, 2.45; S, 7.78. Found: C, 43.53; H, 2.17; S, 8.07.

Synthesis of 5. The same procedure as the synthesis of **4** was applied using (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene. A reddish orange solid, with mp 43 °C dec, was obtained. Yield: 33%. IR (CD_3NO_2): ν(CO) cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 8.27 (d, 8.85 Hz, 2 H), 7.83 (d, 8.84 Hz, 2 H), 7.46 (d, 16.24 Hz, 1 H), 7.34 (d, 16.25 Hz, 1 H), 6.85 (m, 2 H), 6.79 (dd, 3.46, 3.51 Hz, 1 H) ppm. Anal. Calcd for $C_{31}H_{21}F_8Mn_2N_3O_{12}S_2$ ([[{(*E*)-2-[2-(4-nitrophenyl)ethenyl)thiophene}Mn(CO)$_3$][BF$_4$]]$_2$·CH_3NO_2): C, 38.18; H, 2.17; N, 4.31; S, 6.58. Found: C, 38.27; H, 2.06; N, 4.64; S, 6.91.

Synthesis of 5-2. Compounds **5** (0.20 g, 0.438 mmol) and PPh_3 (0.17 g, 0.648 mmol) were dissolved in 15 mL of CH_2Cl_2. To the solution was added Me_3NO (36 mg, 0.479 mmol), and the mixture was stirred at room temperature for 2 h. After the solution was filtered, the filtrate was precipitated by addition of excess Et_2O (50 mL). A dark blue solid (0.26 g, 85.8%) was obtained. Mp: 115 °C dec. IR (CD_3NO_2): ν(CO) 1993, 1936 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 8.18 (d, 8.3 Hz, 2 H), 7.53 (m, 11 H), 7.31 (m, 6 H), 6.95 (d, 16.2 Hz, 1 H), 6.80 (br s, 1 H), 6.66 (m, 2 H), 6.43 (br s, 1 H) ppm. Anal. Calcd for $C_{32}H_{24}BF_4MnNO_4PS$: C, 55.60; H, 3.50; N, 2.03; S, 4.64. Found: C, 55.98; H, 3.28; N, 2.21; S, 5.02.

Synthesis of 6. The same procedure as the synthesis of **4** was applied, using (*E*)-2-[2-(4-(dimethylamino)phenyl)ethenyl]-thiophene. An orange solid, with mp 187 °C, was obtained. Yield: 79.2%. IR (CD_3NO_2): ν(CO) 2056, 2004 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.54 (d, 16.05 Hz, 1 H), 7.41 (d, 4.93 Hz, 1 H), 7.24 (d, 3.43 Hz, 1 H), 7.05 (dd, 3.60, 3.65 Hz, 1 H), 6.79 (d, 7.82 Hz, 2 H), 6.70 (d, 16.09 Hz, 1 H), 5.57 (d, 7.83 Hz, 2 H), 3.21 (s, 6 H, CH_3) ppm. Anal. Calcd for $C_{17}H_{15}BF_4MnN_2O_3S$: C, 44.87; H, 3.32; N, 3.08; S, 7.04. Found: C, 44.61; H, 3.00; N, 3.37; S, 6.73.

Synthesis of 7. 2-[(C_5H_5)FeC_5H_4]C_4H_3S (0.35 g, 1.3 mmol) and [(naphthalene)Mn(CO)$_3$]BF$_4$ (0.50 g, 1.41 mmol) were dissolved in 20 mL of CH_2Cl_2. The solution was heated at reflux for 3 h. After removal of the solvent, the residue was dissolved in 3 mL of CH_3NO_2 and the solution passed through a Celite pad. Addition of excess Et_2O (50 mL) gave a violet precipitate in 90% yield. Mp: 110 °C dec. IR (CD_3NO_2): ν(CO) 2052, 2004 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.15 (dd, 1.1, 3.2 Hz, 1 H), 7.09 (m, 2 H), 5.16 (br s, 1 H), 4.95 (br s, 1 H), 4.80 (br s, 1 H), 4.76 (br s, 1 H), 4.35 (s, 5 H) ppm. Anal. Calcd for $C_{17}H_{12}BF_4FeMnO_3S$: C, 41.30; H, 2.45; S, 6.47. Found: C, 41.49; H, 2.60; S, 6.31.

Synthesis of 8. The same procedure as the synthesis of **7** was applied, using (*E*)-2-[(C_5H_5)FeC_5H_4CH=CH]C_4H_3S. A purple solid, with mp 68 °C dec, was obtained. Yield: 94%. IR (CD_3NO_2): ν(CO) 2064, 2008 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.34 (d, 15.9 Hz, 1 H), 6.71 (br s, 2 H), 6.67 (d, 16.0 Hz, 1 H), 6.54 (br s, 1 H), 4.60 (br s, 2 H), 4.33 (br s, 2 H), 4.27 (s, 5 H) ppm. Anal. Calcd for $C_{19}H_{14}BF_4FeMnO_3S$: C, 43.89; H, 2.71; S, 6.34. Found: C, 43.78; H, 2.40; S, 6.81.

Synthesis of 9. The same procedure as the synthesis of **7** was applied using (*E*,*E*)-2-[(C_5H_5)FeC_5H_4CH=CHCH=CH)]-C_4H_3S. A deep violet solid, with mp 105 °C dec, was obtained. Yield: 41%. IR (CD_3NO_2): ν(CO) 2080, 2002 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.90 (m, 1 H), 7.52 (m, 1 H), 7.46 (d, 16.3 Hz, 1 H), 6.96 (m, 3 H), 6.63 (d, 16.0 Hz, 1 H), 4.93 (s, 1 H), 4.64 (s, 1 H), 4.38 (s, 1 H) ppm (other peaks are overlapped with the peak (4.33 ppm) of the solvent). Anal. Calcd for $C_{21}H_{16}BF_4$-$FeMnO_3S$: C, 46.20; H, 2.95; S, 5.87. Found: C, 46.15; H, 3.12; S, 6.0.

Synthesis of 10. The same procedure as the synthesis of **7** was applied, using (*E*)-3-[(C_5H_5)FeC_5H_4CH=CH]C_4H_3S. A deep violet solid, with mp 85 °C dec, was obtained. Yield: 77%. IR (CD_3NO_2): ν(CO) 2064, 2010 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.48 (d, 15.6 Hz, 1 H), 6.97 (m, 2 H), 6.64 (d, 15.8 Hz, 1 H), 6.47 (br s, 1 H), 4.67 (br s, 1 H), 4.58 (br s, 1 H) ppm (other peaks are overlapped with the peak (4.33 ppm) of the solvent). Anal. Calcd for ($C_{19}H_{14}BF_4FeMnO_3S)_3$·$CH_2Cl_2$: C, 42.35; H, 2.70; S, 5.85. Found: C, 42.34; H, 2.72; S, 6.0.

Synthesis of 11. The same procedure as the synthesis of **7** was applied, using 2-[(C_5H_5)Fe$C_5H_4CH_2$)]C_4H_3S. A yellowish brown solid, with mp 123 °C dec, was obtained. Yield: 90%. IR (CD_3NO_2): ν(CO) 2064, 2008 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.10 (d, 3.4 Hz, 1 H), 6.96 (br, 1 H), 6.82 (br, 1 H), 4.79 (m, 9H), 4.43 (s, 2 H) ppm. Anal. Calcd for $C_{18}H_{14}BF_4FeMnO_3S$: C, 42.56; H, 2.78. Found: C, 42.75; H, 2.69.

Crystal Structure Determination of 1 and 6. Crystals of **1** and **6** were grown by slow diffusion of diethyl ether into nitromethane. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer by the $\omega/2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 1. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using a riding model with values equal to 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

Hyperpolarizability Measurements. A nanosecond laser pulse of 1064 nm from a Q-switched Nd:YAG laser (Spectron SL803G) was used as an excitation source for the hyper-Rayleigh scattering (HRS) measurement. After any residual flash light around the HRS frequency was filtered out with a high-pass filter (RG640), the laser beam was focused by using a long focal length plano-convex lens (f = 320 nm) and the repetition rate of the laser was 10 Hz. To avoid nonlinear processes such as stimulated Raman scattering, stimulated Brillouin scattering, and dielectric breakdown, the laser pulse (≤30 mJ) was focused at 70 mm after passing through the

sample cell. Quadratic power dependence of the HRS signal on the fundamental laser intensity was also confirmed.

Sample solutions were filtered with 0.2 μm filters to eliminate dust and undissolved solutes. A glass rather than quartz cuvette (3.5 mL in volume) was used for the sample cell to minimize second-harmonic generation (SHG) from the cuvette walls. HRS signals were collected by using a camera lens (f/1.2) followed by a plano-convex lens (f = 200 nm). A 532 nm band-pass filter (fwhm 3 nm) was used for the HRS signal detection. The output signal from a photomultiplier tube (Hamamatsu R955) was sampled by a boxcar signal averager (Stanford Research Systems, Model SR250). The intensity of the HRS light was corrected for the sample absorption,[22] and the β values were derived by using an internal reference method[23] with the known β value of nitromethane.

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Supporting Information Available: Tables of atomic coordinates, displacement parameters, and bond distances and angles for **1** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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