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Preparation of Thiophene-Coordinated Ruthenium Complexes for Nonlinear Optics

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The new organometallic compounds $[\{(E)\text{-}2\text{-}SC_4H_3CH{=}CHC_6H_4\text{-}X\text{-}p\}Ru(C_6Me_6)][CF_3SO_3]_2$ (X = MeO (**1**), Me (**2**), H (**3**), Br (**4**), NO_2 (**5**)), bearing a (thiophene)$Ru(C_6Me_6)^{2+}$ fragment in the end group, have been prepared for nonlinear optical chromophores, and their hyperpolarizabilities have been measured by the HRS method. The static hyperpolarizability (β_0) values of the complexes increase as the electron-acceptor power of the substituent X increases (MeO < Me < H < Br < NO_2). Replacement of hexamethylbenzene with pentamethylcyclopentadienyl resulted in $[\{(E)\text{-}2\text{-}SC_4H_3CH{=}CHC_6H_4\text{-}NO_2\text{-}p\}]Ru(C_5Me_5)]CF_3SO_3$ (**7**), showing a significant increase in the hyperpolarizability. The substituent effects on β_0 were studied by time-dependent DFT calculations.

Introduction

During the last several decades, interest in organometallic chemistry for the development of novel NLO materials has increased considerably. Thus, various classes of metal complexes have been explored in terms of new and optimized NLO materials.[1,2] Since the report in 1987 by Green et al.,[3] in which good second-harmonic generation efficiency was revealed for ferrocenyl derivatives, group 8 metallocene complexes have been studied extensively in this field.[4,5] Numerous systematic studies have shown that their large nonlinear optical efficiencies are mainly due to the facile charge transition from the Fe or Ru center to cyclopentadienyl ligands and the consequent difference between ground-state and excited-state dipole moments.[6] Many other π-coordinated transition-metal complexes are also highly polarizable and show strong MLCT absorption, but nevertheless relatively few studies have been carried out on them.[7]

The thiophene moiety has been successfully used in organic chromophores.[8] Moreover, the incorporation of metal moieties with oligothiophene or thienyl entities in the conjugation chain has been used to improve the NLO properties.[9] Recently, we have published the NLO performance of manganese tricarbonyl cations of thiophenes.[10] Complexes containing the (thiophene)$Mn(CO)_3^+$ fragment in the end group were found to possess substantial molecular nonlinearities. As part of our

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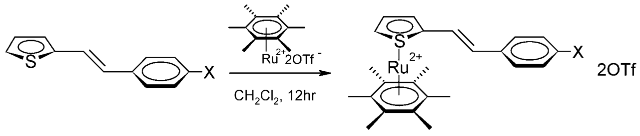
Scheme 1. Synthesis of 1−5



X : CH$_3$O, CH$_3$, H, Br, NO$_2$
1, **2**, **3**, **4**, **5**

continuing study on the transition-metal π complexes of thiophenes, we herein report the synthesis of ruthenium cation complexes of thiophenes and their nonlinear optical properties. There exist a few examples of non-acetylide Ru(II) complexes acting as nonlinear optical materials.[11]

Results and Discussion

Synthesis. The syntheses of thiophene derivatives used in the preparation of complexes **1**−**5**, $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4H_3SCH{=}CHC_6H_5\text{-}4\text{-}X)](CF_3SO_3)_2$ (**1**, X = MeO; **2**, X = Me; **3**, X = H; **4**, X = Br; **5**, X = NO$_2$), have been previously reported.[10,12] Complexes **1**−**5**, having the same organic structural frame except for X, have been prepared according to Scheme 1. The reaction of $[(\eta^6\text{-}C_6Me_6)Ru](CF_3SO_3)_2$, generated in situ from $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ and $AgCF_3SO_3$ with the corresponding thiophene derivatives, readily affords the thiophene-coordinated ruthenium complexes in a yield of 63−83%.[13]

Complexes **6** and **7** were prepared by the same method except for the use of $[(\eta^6\text{-}p\text{-cymene})Ru](CF_3SO_3)_2$ and $[(\eta^5\text{-}C_5Me_5)Ru(CH_3CN)_3]CF_3SO_3$, respectively, instead of $[(\eta^6\text{-}C_6Me_6)Ru]CF_3SO_3$ (Scheme 2).[14] Complexes **1**−**7** were characterized by a combination of ^{1}H NMR and satisfactory microanalyses.

Scheme 2. Synthesis of 6 and 7

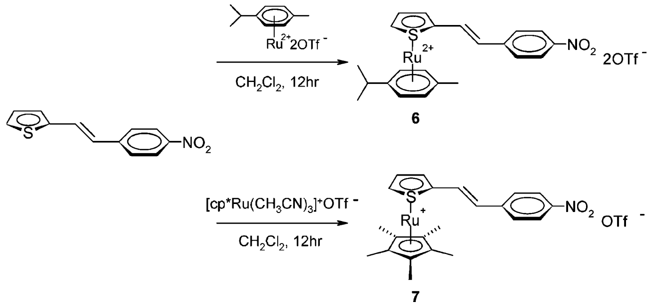
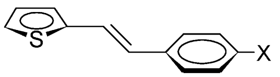


Chart 1. Molecular Components Used in This Work



X : Br , NO$_2$
4-1 , **5-1**

Table 1. Quadratic Hyperpolarizability Values for 1−7[a]

	1	**2**	**3**	**4**	**4-1**	**5**	**5-1**	**6**	**7**
λ (nm)[b]	447	416	386	412	n.r.[d]	410	383	407	408
λ (nm)[f]	424	417	408	379		403		406	404
β (10^{-30}esu)	68	61	66	98	ca. 0	226	54	226	389
β_0 (10^{-30}esu)[c]	16	20	27	33	n.c.[e]	78	23	80	137

[a] All the measurements were carried out in nitromethane solvent. [b] Lowest charge transition band in the 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. [f] Theoretical predictions.

Hyperpolarizability Measurements. Chart 1 shows the compounds studied. All the ruthenium compounds studied have one absorption in the UV−vis spectrum. The hyperpolarizability values of all complexes were determined by hyper-Rayleigh scattering (HRS) in nitromethane solution using *p*-nitroaniline in chloroform as an external standard.[15] For the correction to the resonance enhancement effect, static hyperpolarizabilities (β_0) are estimated from the experimental β values using the two-level dispersion model, as previously proposed.[16] Experimental errors on β values are estimated to be on the order of 10%. The β and β_0 values are summarized in Table 1.

The hyperpolarizability values of complexes **1**−**3** are almost the same within experimental error, and the β values of complexes **4** and **5** increase in the order **4** < **5**. The static hyperpolarizabilities (β_0) of **1**−**5** increase in the order **1** < **2** < **3** < **4** < **5**. Since the (thiophene)$Ru(C_6Me_6)^{2+}$ fragment possesses a double positive charge, the differences in the β_0 values for **1**−**5** are not as great as would be expected from the differences in the electron-acceptor power of the substituent X. In any case, the values follow the electron-acceptor power of the substituent X (MeO < Me < H < Br < NO$_2$), which represents a trend similar to that shown in (thiophene)$Mn(CO)_3^+$ complexes.[10] This observation implies that

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the (thiophene)Ru(C_6Me_6)$^{2+}$ fragment behaves like the (thiophene)Mn(CO)$_3$$^+$ fragment. This is also confirmed by a DFT calculation of complexes **1** and **5** and their manganese congeners (see below and the Supporting Information).

In our earlier paper, the β_0 value of free ligand **4-1** is too small to be detected and the β_0 value of free ligand **5-1** is ca. 23 × 10^{-30} esu.[10] When ligands **4-1** and **5-1** are coordinated to Mn(CO)$_3$$^+$, the β_0 values increase to 35 × 10^{-30} and 38 × 10^{-30} esu, respectively. When ligands **4-1** and **5-1** are coordinated to (C_6Me_6)Ru^{2+}, the β_0 values increase to 33 × 10^{-30} and 78 × 10^{-30} esu, respectively. Thus, the coordination of Mn(CO)$_3$$^+$ or (C_6Me_6)Ru^{2+} to ligand **4-1** has almost the same effect on the β_0 value, but for ligand **5-1** the coordination of (C_6Me_6)Ru^{2+} shows a greater effect on the β_0 value than that of Mn(CO)$_3$$^+$ does. The larger β_0 value of **5** is presumably due to the good donor ability and weak acceptor ability of the hexamethylbenzene ligand compared to the three carbonyl ligands.

When *p*-cymene is used instead of hexamethylbenzene, the β and β_0 values (226 × 10^{-30} and 80 × 10^{-30} esu, respectively) of **6** are almost the same as those of **5**. Thus, the β and β_0 values are not highly sensitive to the number of electron-donating groups on the arene ring. When pentamethylcyclopentadienyl (Cp*) is used instead of hexamethylbenzene, the β and β_0 values of **7** noticeably increase to 389 × 10^{-30} and 137 × 10^{-30} esu, respectively. Thus, it is expected that the negative charge of pentamethylcyclpentadienyl activates orbitals of the ruthenium center. Large amounts of charge donation from the pentamethylcyclopentadienyl ligand to the ruthenium center have been reported in NLO systems.[19] Thus, the increased β and β_0 values of **7** may be partly due to the high-lying filled set of metal orbitals. It has already been suggested that the presence of a high-lying filled set of metal orbitals is required in order to produce large β values.[6] While complex **7** has a structure quite similar to that of ruthenocene, **7** has a much larger β_0 value than its ruthenocenyl analogue.

Orbital Analysis on the Basis of TD-DFT Calculations. According to the simple two-level model,[16b] to a first approximation, the trends in β_0 can be inferred from the knowledge of excited- and ground-state dipole moments as well as the transition energy and transition dipole moments. Thus, molecules with low-lying intense charge-transfer transitions are expected to have large β_0 values.

To better understand the substituent effects on β_0, time-dependent DFT calculations were carried out on the representative compounds **1**, **5**, and **7**. Calculated λ_{max} values are presented in Table 1. The theoretical linear optical λ_{max} values closely reproduce the experimental values, substantiating the quality of current theories. On the basis of these agreements, orbital analysis for these particular optical transitions of representative compounds **1**, **5**, and **7** were attempted, and the results are presented in Table 2. According to Table 2, the HOMO orbitals of **1** are mostly composed of conjugated bridge (π) and small thiophene moieties, while the next highest occupied orbitals are composed of the metal region (***M***). In the case of **5**, the acceptor orbital (***A***, the substituent orbital) appears between the π and ***M*** orbitals. For both **1** and **5,** the LUMO orbitals are mostly composed of the conjugated bridge (π*****), while the next lowest unoccupied orbitals are composed of metal (***M****). However, in the case of **7**, the next lowest unoccupied orbitals are mostly composed of the acceptor (***A*****), the substituents.

Table 2. TD-DFT Singlet Excitation Calculations of 1, 5, and 7 for the Largest Band[a] in the UV Region

molecule	λ_{calcd}	λ_{exptl}	contribns[b]	assignts
1	424	447	HOMO − 4 → LUMO (9)	$\boldsymbol{M}^c \rightarrow \pi^*$
			HOMO − 4 → LUMO + 1(4)	$\boldsymbol{M} \rightarrow \boldsymbol{M}^*$
			HOMO − 4 → LUMO + 2 (1)	$\boldsymbol{M} \rightarrow \boldsymbol{M}^*$
			HOMO − 2 → LUMO (3)	$\pi^d \rightarrow \pi^*$
			HOMO − 2 → LUMO + 1 (4)	$\pi \rightarrow \boldsymbol{M}^*$
			HOMO − 1 → LUMO (5)	$\pi \rightarrow \pi^*$
			HOMO − 1 → LUMO + 1 (4)	$\pi \rightarrow \boldsymbol{M}^*$
			HOMO → LUMO (3)	$\pi \rightarrow \pi^*$
			HOMO → LUMO + 1 (6)	$\pi \rightarrow \pi^*$
5	403	410	HOMO − 8 → LUMO (3)	$\boldsymbol{M} \rightarrow \pi^*$
			HOMO − 7→ LUMO (3)	$\boldsymbol{M} \rightarrow \pi^*$
			HOMO − 7 → LUMO + 1 (4)	$\boldsymbol{M} \rightarrow \boldsymbol{M}^*$
			HOMO − 5 → LUMO (5)	$\boldsymbol{M} \rightarrow \pi^*$
			HOMO − 5 → LUMO + 1 (7)	$\boldsymbol{M} \rightarrow \boldsymbol{M}^*$
			HOMO − 3 → LUMO + 1 (12)	$\boldsymbol{A}^e \rightarrow \boldsymbol{M}^*$
			HOMO − 1 → LUMO (2)	$\pi \rightarrow \pi^*$
			HOMO − 1 → LUMO + 1 (7)	$\pi \rightarrow \boldsymbol{M}^*$
7	404	408	HOMO − 5 → LUMO + 2 (2)	$\boldsymbol{M} \rightarrow \boldsymbol{A}^*$
			HOMO-3→ LUMO + 1 (6)	$\boldsymbol{M} \rightarrow \boldsymbol{A}^*$
			HOMO-3 → LUMO + 2 (7)	$\boldsymbol{M} \rightarrow \boldsymbol{A}^*$
			HOMO-1 → LUMO + 1 (2)	$\boldsymbol{M} \rightarrow \boldsymbol{A}^*$
			HOMO-1 → LUMO + 2 (2)	$\boldsymbol{M} \rightarrow \boldsymbol{A}^*$
			HOMO → LUMO (10)	$\pi \rightarrow \pi^*$
			HOMO → LUMO + 1 (7)	$\pi \rightarrow \boldsymbol{A}^*$
			HOMO → LUMO + 2 (5)	$\pi \rightarrow \boldsymbol{A}^*$

[a] Corresponding bands are also given in Table 1. [b] The numbers in parentheses are values of |coeff.|^2 × 100. [c] d orbitals of metal. [d] Bridge π orbitals. [e] The acceptor, substituent's orbitals.

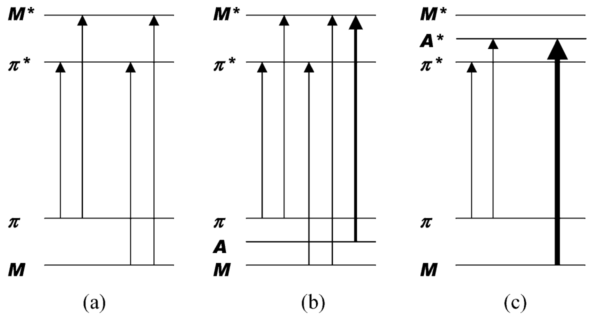

Figure 1. Illustrations of excitation characters of compounds (a) **1**, (b) **5,** (c) and **7**, where ***M***, ***A***, and π correspond to the orbitals of metal, acceptor (substituent), and conjugated bridge, respectively. A thicker line represents a larger contribution.

The relative orbital levels as well as the magnitudes of contributions (the numbers given in parentheses in Table 2) are illustrated in Figure 1, where thicker arrows indicate larger contributions. In the case of compound **1,** the excitation is composed of the contributions from ***M*** → ***M****, π → π*****, ***M*** → π*****, and π → ***M****, which are effectively canceled, yielding a small total transition dipole moment.

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A similar situation can be seen in **5**, except for the large contribution of $\boldsymbol{A} \rightarrow \boldsymbol{M^*}$, which would increase the transition dipole moments to yield a β_0 value relatively larger than that of **1**. The origin of the $\boldsymbol{A} \rightarrow \boldsymbol{M^*}$ can be reasoned as follows. Since the substituent of **5** is an electron acceptor, the substituent region is electron rich in its ground state and it becomes an electron donor in its excited state, especially because of the doubly charged metal center. Thus, the reason **5** has a larger β_0 **value** than **1** is due to this particular effect of the substituent, which acts as a ground-state acceptor and an excited-state donor.

In the case of **7**, it is clear that the peak is mostly composed of $\boldsymbol{M} \rightarrow \boldsymbol{A^*}$ and $\pi \rightarrow \boldsymbol{A^*}$. Therefore, one would expect a large transition dipole moment. In contrast to **5**, the substituent acts as an excited-state acceptor, which may be due to the smaller charge on the metal center, which can act as a strong electron donor.

For a comparison between complexes **1** and **5** and their manganese congeners, a DFT calculation of manganese complexes was performed (see the Supporting Information). The calculation shows that the (thiophene)Ru(C_6Me_6)$^{2+}$ fragment behaves like the (thiophene)Mn(CO)$_3^+$ fragment.

Conclusion

We have synthesized (hexamethylbenzene)ruthenium(II) complexes of thiophene and measured their hyperpolarizabilities by the HRS method. All of the complexes studied show substantial β values. Especially, the hyperpolarizabilities of **5**−**7** are among the largest found for organometallic chromophores with comparable molecular lengths. In addition, in comparison with σ-bonded ruthenium chromophores suffering from a nonlinearity−transparency tradeoff,[19,20] the λ_{max} values of **5**−**7** appear in a much shorter wavelength region and have better transparency in the visible region.

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under nitrogen using standard Schlenk techniques. Freshly distilled, dry, and 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 not corrected. The compounds (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene, (*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, [(η^6-C_6Me_6)RuCl$_2$]$_2$, [(η^6-*p*-cymene)RuCl$_2$]$_2$, and [(η^5-C_5Me_5)Ru(CH_3CN)$_3$]CF_3SO_3 were previously reported and prepared according to the modified procedures.[10,12,13,14]

Synthesis of 1. The complex [(η^6-C_6Me_6)RuCl$_2$]$_2$ (0.15 g, 0.22 mmol) and $AgCF_3SO_3$ (0.23 g, 0.89 mmol) were dissolved in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 2 h, and then the supernatant solution was transferred via syringe into another Schlenk flask without exposure to air. To the clear solution was added a solution of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene (0.14 g, 0.66 mmol) in 5 mL of CH_2Cl_2. The resulting solution was stirred at room temperature for 12 h. The precipitates were filtered off, washed with CH_2Cl_2 (20 mL × 2), and dried under vacuum. Yield: 0.26 g (75%). ^{1}H NMR (acetone-d_6): δ 7.80 (d, 16.3 Hz, 1 H), 7.75 (d, 8.8 Hz, 2 H), 7.43 (d, 3.1 Hz, 2 H), 7.25 (d, 16.3 Hz, 1 H), 7.22 (m, 2 H), 7.05 (d, 8.8 Hz, 2 H), 3.89 (s, 3 H), 2.61 (s, 18 H) ppm. Anal. Calcd for $C_{27}H_{30}F_6O_7RuS_3$: C, 41.70; H, 3.89; S, 12.37. Found: C, 41.55; H, 3.60; S, 12.64.

Synthesis of 2. The same procedure as for the synthesis of **1** was applied using (*E*)-2-[2-(4-methylphenyl)ethenyl]thiophene (0.13 g, 0.66 mmol) instead of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene. Yield: 0.24 g (73%). ^{1}H NMR (acetone-d_6): δ 7.82 (d, 16.2 Hz, 1 H), 7.67 (d, 7.9 Hz, 2 H), 7.47 (m, 1 H), 7.36 (d, 16.2 Hz, 1 H), 7.31 (d, 7.9 Hz, 2 H), 7.25 (m, 2 H), 2.62 (s, 18 H), 2.39 (s, 3 H) ppm. Anal. Calcd for $C_{27}H_{30}F_6O_6RuS_3$: C, 42.57; H, 3.97; S, 12.63. Found: C, 42.85; H, 4.01; S, 13.03.

Synthesis of 3. The same procedure as for the synthesis of **1** was applied using (*E*)-2-(2-phenylethenyl)thiophene (0.12 g, 0.66 mmol) instead of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene. Yield: 0.27 g (83%). ^{1}H NMR (acetone-d_6): δ 7.86 (d, 16.3 Hz, 1 H), 7.79 (m, 1 H), 7.77 (m, 1 H), 7.50 (m, 4 H), 7.42 (d, 16.3 Hz, 1 H), 7.28 (m, 2 H), 2.63 (s, 18 H) ppm. Anal. Calcd for $C_{26}H_{28}F_6O_6RuS_3$: C, 41.76; H, 3.77; S, 12.86. Found: C, 41.42; H, 3.53; S, 12.44.

Synthesis of 4. The same procedure as for the synthesis of **1** was applied using (*E*)-2-[2-(4-bromophenyl)ethenyl]thiophene (0.17 g, 0.64 mmol) instead of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene. Yield: 0.28 g (78%). ^{1}H NMR (acetone-d_6): δ 7.83 (d, 16.2 Hz, 1 H), 7.72 (d, 8.7 Hz, 2 H), 7.67 (d, 8.7 Hz, 2 H), 7.50 (d, 3.2 Hz, 1 H), 7.45 (d, 16.2 Hz, 1 H), 7.29 (m, 2 H), 2.63 (s, 18 H) ppm. Anal. Calcd for $C_{26}H_{27}BrF_6O_6RuS_3$: C, 37.78; H, 3.29; S, 11.64. Found: C, 37.59; H, 3.26; S, 11.97.

Synthesis of 5. The same procedure as for the synthesis of **1** was applied using (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene (0.15 g, 0.66 mmol) instead of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene. Yield: 0.22 g (63%). ^{1}H NMR (acetone-d_6): δ 8.33 (d, 8.8 Hz, 2 H), 8.05 (d, 8.8 Hz, 2 H), 7.98 (d, 16.3 Hz, 1 H), 7.66 (d, 16.3 Hz, 1 H), 7.57 (d, 3.2 Hz, 1 H), 7.34 (m, 2 H), 2.65 (s, 18 H) ppm. Anal. Calcd for $C_{26}H_{27}F_6NO_6RuS_3$: C, 39.39; H, 3.43; N, 1.77; S, 12.13. Found: C, 39.45; H, 3.26; N, 1.87; S, 12.15.

Synthesis of 6. The same procedure as for the synthesis of **1** was applied using [(η^6-*p*-cymene)RuCl$_2$]$_2$ (0.13 g, 0.21 mmol) instead of [(η^6-C_6Me_6)RuCl$_2$]$_2$ and (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene (0.15 g, 0.66 mmol) instead of (*E*)-2-[2-(4-methoxyphenyl)ethenyl]thiophene. Yield: 0.21 g (65%). ^{1}H NMR (acetone-d_6): δ 8.30 (d, 8.8 Hz, 2 H), 8.01 (d, 8.8 Hz, 2 H), 7.96 (d, 16.2 Hz, 1 H), 7.83 (d, 3.1 Hz, 1H), 7.64 (d, 16.2 Hz, 1 H), 7.55 (t, 3.3 Hz, 1 H), 7.48 (d, 7.32, 1H), 7.14 (d, 1.8, 2H), 7.08 (d, 1.8 2H), 3.11 (sept, 6.9, 1H), 2.48 (s, 3H), 1.37 (d, 6.8, 6H) ppm. Anal. Calcd for $C_{24}H_{23}F_6NO_8RuS_3$: C, 37.70; H, 3.03; N, 1.83; S, 12.58. Found: C, 37.72; H, 3.01; N, 1.88; S, 12.59.

Synthesis of 7. The complex [(η^5-C_5Me_5)Ru(CH_3CN)$_3$]CF_3SO_3 (0.35 g, 0.69 mmol) and (*E*)-2-[2-(4-nitrophenyl)ethenyl]thiophene (0.24 g, 1.05 mmol) were dissolved in 10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 12 h without exposure to air. The solution was then filtered, and 20 mL of diethyl ether was added to the filtrate. The yellow precipitate was isolated by filtration, washed with diethyl ether (20 mL × 2), and dried under vacuum. Yield: 0.29 g (69%). ^{1}H NMR (acetone-d_6): δ 8.26 (d, 8.9 Hz, 2 H), 7.91 (d, 8.8 Hz, 2 H), 7.45 (d, 16.2 Hz, 1 H), 7.36 (d, 16.2 Hz,

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1H), 6.55 (d, 3.1 Hz, 1H), 6.36 (m, 2H), 2.03 (s, 15H) ppm. Anal. Calcd for $C_{23}H_{24}F_3NO_5RuS_2$: C, 44.80; H, 4.23; N, 2.27. Found: C, 44.38; H, 4.23; N, 2.20.

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.[21] 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 Sys. SR250). The intensity of the HRS light was corrected for the sample absorption and flourescence,[22] and the β values were derived by using an external reference method with the known β value of *p*-nitroaniline in chloroform.[15]

Theoretical Calculations. Full geometry optimizations on **1**−**7** were performed with density functional theory (DFT). It is noted that the calculations were performed without the negative ions. The B3LYP[23] exchange-correlation functions in combination with LanL2DZ[24] basis sets were used throughout the calculations. The time-dependent DFT[25] calculations were performed to obtain the excitation wavelengths and oscillator strengths.

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Supporting Information Available: A table giving the results of time-dependent DFT calculations for (thiophene)-$Mn(CO)_3^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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