

# Preparation of Thiophene-Coordinated Ruthenium Complexes for Nonlinear Optics

In Su Lee,<sup>†</sup> Dae Seung Choi,<sup>†</sup> Dong Mok Shin,<sup>†</sup> Young Keun Chung,<sup>\*,†</sup> and Cheol Ho Choi<sup>\*,‡</sup>

*School of Chemistry and Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea, and Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea*

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The new organometallic compounds [ $\{(E)\text{-}2\text{-SC}_4\text{H}_3\text{CH=CHC}_6\text{H}_4\text{-X-}p\}\text{Ru}(\text{C}_6\text{Me}_6)[\text{CF}_3\text{SO}_3]_2$  ( $\text{X} = \text{MeO}$  (**1**),  $\text{Me}$  (**2**),  $\text{H}$  (**3**),  $\text{Br}$  (**4**),  $\text{NO}_2$  (**5**)), bearing a (thiophene) $\text{Ru}(\text{C}_6\text{Me}_6)^{2+}$  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 ( $\beta_0$ ) values of the complexes increase as the electron-acceptor power of the substituent  $\text{X}$  increases ( $\text{MeO} < \text{Me} < \text{H} < \text{Br} < \text{NO}_2$ ). Replacement of hexamethylbenzene with pentamethylcyclopentadienyl resulted in [ $\{(E)\text{-}2\text{-SC}_4\text{H}_3\text{CH=CHC}_6\text{H}_4\text{-NO}_2\text{-}p\}\text{Ru}(\text{C}_5\text{Me}_5)[\text{CF}_3\text{SO}_3]$  (**7**), showing a significant increase in the hyperpolarizability. The substituent effects on  $\beta_0$  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.<sup>1,2</sup> Since the report in 1987 by Green et al.,<sup>3</sup> in which good second-harmonic

generation efficiency was revealed for ferrocenyl derivatives, group 8 metallocene complexes have been studied extensively in this field.<sup>4,5</sup> 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.<sup>6</sup> Many other  $\pi$ -coordinated transition-metal complexes are also highly polarizable and show strong MLCT absorption, but nevertheless relatively few studies have been carried out on them.<sup>7</sup>

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

\* To whom correspondence should be addressed. E-mail: ykchung@plaza.snu.ac.kr (Y.K.C.); cchoi@knu.ac.kr (C.H.C.). Tel: 82-2-880-6662 (Y.K.C.); 82-53-950-5332 (C.H.C.). Fax: 82-2-889-0310 (Y.K.C.).

<sup>†</sup> Seoul National University.

<sup>‡</sup> Kyungpook National University.

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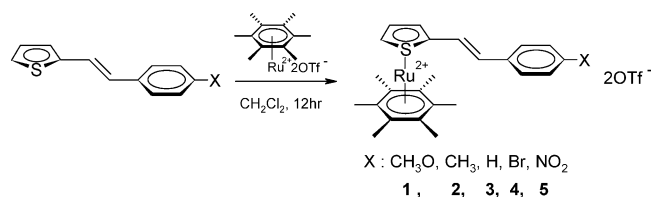
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## Scheme 1. Synthesis of 1–5



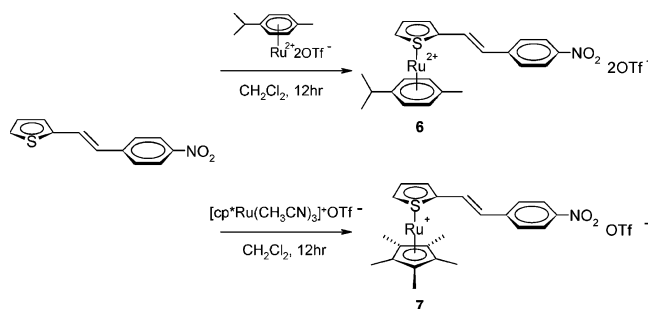
continuing study on the transition-metal  $\pi$  complexes of thiophenes, we herein report the synthesis of ruthenium cation complexes of thiophenes and their nonlinear optical properties. There exist a few examples of non-acetylide Ru(II) complexes acting as nonlinear optical materials.<sup>11</sup>

## Results and Discussion

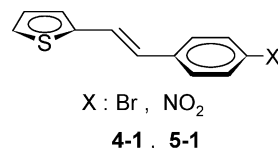
**Synthesis.** The syntheses of thiophene derivatives used in the preparation of complexes **1–5**,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{-Ru}(\eta^5\text{-C}_4\text{H}_3\text{SCH=CHC}_6\text{H}_5\text{-4-X})(\text{CF}_3\text{SO}_3)_2]$  (**1**, X = MeO; **2**, X = Me; **3**, X = H; **4**, X = Br; **5**, X = NO<sub>2</sub>), have been previously reported.<sup>10,12</sup> Complexes **1–5**, having the same organic structural frame except for X, have been prepared according to Scheme 1. The reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}](\text{CF}_3\text{SO}_3)_2$ , generated in situ from  $[(\eta^6\text{-C}_6\text{Me}_6)\text{-RuCl}_2]_2$  and  $\text{AgCF}_3\text{SO}_3$  with the corresponding thiophene derivatives, readily affords the thiophene-coordinated ruthenium complexes in a yield of 63–83%.<sup>13</sup>

Complexes **6** and **7** were prepared by the same method except for the use of  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}](\text{CF}_3\text{SO}_3)_2$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CH}_3\text{CN})_3]\text{CF}_3\text{SO}_3$ , respectively, instead of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}]\text{CF}_3\text{SO}_3$  (Scheme 2).<sup>14</sup> Complexes

## Scheme 2. Synthesis of 6 and 7



## Chart 1. Molecular Components Used in This Work

Table 1. Quadratic Hyperpolarizability Values for 1–7<sup>a</sup>

	1	2	3	4	4-1	5	5-1	6	7
$\lambda$ (nm) <sup>b</sup>	447	416	386	412	n.r. <sup>d</sup>	410	383	407	408
$\lambda$ (nm) <sup>f</sup>	424	417	408	379		403		406	404
$\beta$ (10 <sup>−30</sup> esu)	68	61	66	98	ca. 0	226	54	226	389
$\beta_0$ (10 <sup>−30</sup> esu) <sup>c</sup>	16	20	27	33	n.c. <sup>e</sup>	78	23	80	137

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

**1–7** were characterized by a combination of <sup>1</sup>H NMR and satisfactory microanalyses.

**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.<sup>15</sup> For the correction to the resonance enhancement effect, static hyperpolarizabilities ( $\beta_0$ ) are estimated from the experimental  $\beta$  values using the two-level dispersion model, as previously proposed.<sup>16</sup> Experimental errors on  $\beta$  values are estimated to be on the order of 10%. The  $\beta$  and  $\beta_0$  values are summarized in Table 1.

The hyperpolarizability values of complexes **1–3** are almost the same within experimental error, and the  $\beta$  values of complexes **4** and **5** increase in the order **4** < **5**. The static hyperpolarizabilities ( $\beta_0$ ) of **1–5** increase in the order **1** < **2** < **3** < **4** < **5**. Since the (thiophene)-Ru(C<sub>6</sub>Me<sub>6</sub>)<sup>2+</sup> fragment possesses a double positive charge, the differences in the  $\beta_0$  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<sub>2</sub>), which represents a trend similar to that shown in (thiophene)-Mn(CO)<sub>3</sub><sup>+</sup> complexes.<sup>10</sup> This observation implies that

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the (thiophene)Ru(C<sub>6</sub>Me<sub>6</sub>)<sup>2+</sup> fragment behaves like the (thiophene)Mn(CO)<sub>3</sub><sup>+</sup> 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  $\beta_0$  value of free ligand **4-1** is too small to be detected and the  $\beta_0$  value of free ligand **5-1** is ca.  $23 \times 10^{-30}$  esu.<sup>10</sup> When ligands **4-1** and **5-1** are coordinated to Mn(CO)<sub>3</sub><sup>+</sup>, the  $\beta_0$  values increase to  $35 \times 10^{-30}$  and  $38 \times 10^{-30}$  esu, respectively. When ligands **4-1** and **5-1** are coordinated to (C<sub>6</sub>Me<sub>6</sub>)Ru<sup>2+</sup>, the  $\beta_0$  values increase to  $33 \times 10^{-30}$  and  $78 \times 10^{-30}$  esu, respectively. Thus, the coordination of Mn(CO)<sub>3</sub><sup>+</sup> or (C<sub>6</sub>Me<sub>6</sub>)Ru<sup>2+</sup> to ligand **4-1** has almost the same effect on the  $\beta_0$  value, but for ligand **5-1** the coordination of (C<sub>6</sub>Me<sub>6</sub>)Ru<sup>2+</sup> shows a greater effect on the  $\beta_0$  value than that of Mn(CO)<sub>3</sub><sup>+</sup> does. The larger  $\beta_0$  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  $\beta$  and  $\beta_0$  values ( $226 \times 10^{-30}$  and  $80 \times 10^{-30}$  esu, respectively) of **6** are almost the same as those of **5**. Thus, the  $\beta$  and  $\beta_0$  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  $\beta$  and  $\beta_0$  values of **7** noticeably increase to  $389 \times 10^{-30}$  and  $137 \times 10^{-30}$  esu, respectively. Thus, it is expected that the negative charge of pentamethylcyclopentadienyl 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.<sup>19</sup> Thus, the increased  $\beta$  and  $\beta_0$  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  $\beta$  values.<sup>6</sup> While complex **7** has a structure quite similar to that of ruthenocene, **7** has a much larger  $\beta_0$  value than its ruthenocenyl analogue.

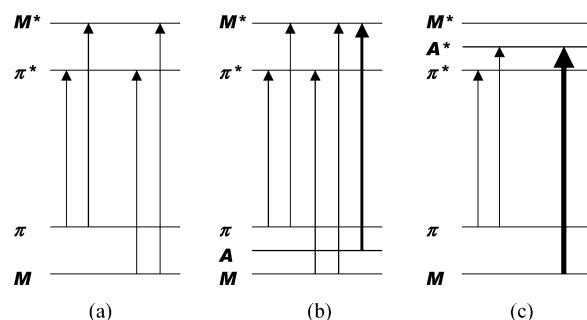
**Orbital Analysis on the Basis of TD-DFT Calculations.** According to the simple two-level model,<sup>16b</sup> to a first approximation, the trends in  $\beta_0$  can be inferred from the knowledge of excited- and ground-state dipole moments as well as the transition energy and transition dipole moments. Thus, molecules with low-lying intense charge-transfer transitions are expected to have large  $\beta_0$  values.

To better understand the substituent effects on  $\beta_0$ , time-dependent DFT calculations were carried out on the representative compounds **1**, **5**, and **7**. Calculated  $\lambda_{\max}$  values are presented in Table 1. The theoretical linear optical  $\lambda_{\max}$  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,

**Table 2. TD-DFT Singlet Excitation Calculations of **1**, **5**, and **7** for the Largest Band<sup>a</sup> in the UV Region**

molecule	$\lambda_{\text{calcd}}$	$\lambda_{\text{exptl}}$	contribns <sup>b</sup>	assignts
<b>1</b>	424	447	HOMO - 4 → LUMO (9)	$M^c \rightarrow \pi^*$
			HOMO - 4 → LUMO + 1 (4)	$M \rightarrow M^*$
			HOMO - 4 → LUMO + 2 (1)	$M \rightarrow M^*$
			HOMO - 2 → LUMO (3)	$\pi^d \rightarrow \pi^*$
			HOMO - 2 → LUMO + 1 (4)	$\pi \rightarrow M^*$
			HOMO - 1 → LUMO (5)	$\pi \rightarrow \pi^*$
			HOMO - 1 → LUMO + 1 (4)	$\pi \rightarrow M^*$
			HOMO → LUMO (3)	$\pi \rightarrow \pi^*$
			HOMO → LUMO + 1 (6)	$\pi \rightarrow \pi^*$
<b>5</b>	403	410	HOMO - 8 → LUMO (3)	$M \rightarrow \pi^*$
			HOMO - 7 → LUMO (3)	$M \rightarrow \pi^*$
			HOMO - 7 → LUMO + 1 (4)	$M \rightarrow M^*$
			HOMO - 5 → LUMO (5)	$M \rightarrow \pi^*$
			HOMO - 5 → LUMO + 1 (7)	$M \rightarrow M^*$
			HOMO - 3 → LUMO + 1 (12)	$A^e \rightarrow M^*$
			HOMO - 1 → LUMO (2)	$\pi \rightarrow \pi^*$
			HOMO - 1 → LUMO + 1 (7)	$\pi \rightarrow M^*$
<b>7</b>	404	408	HOMO - 5 → LUMO + 2 (2)	$M \rightarrow A^*$
			HOMO - 3 → LUMO + 1 (6)	$M \rightarrow A^*$
			HOMO - 3 → LUMO + 2 (7)	$M \rightarrow A^*$
			HOMO - 1 → LUMO + 1 (2)	$M \rightarrow A^*$
			HOMO - 1 → LUMO + 2 (2)	$M \rightarrow A^*$
			HOMO → LUMO (10)	$\pi \rightarrow \pi^*$
			HOMO → LUMO + 1 (7)	$\pi \rightarrow A^*$
			HOMO → LUMO + 2 (5)	$\pi \rightarrow A^*$

<sup>a</sup> Corresponding bands are also given in Table 1. <sup>b</sup> The numbers in parentheses are values of  $|\text{coeff.}|^2 \times 100$ . <sup>c</sup> d orbitals of metal. <sup>d</sup> Bridge  $\pi$  orbitals. <sup>e</sup> The acceptor, substituent's orbitals.



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

and the results are presented in Table 2. According to Table 2, the HOMO orbitals of **1** are mostly composed of conjugated bridge ( $\pi$ ) 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  $\pi$  and **M** orbitals. For both **1** and **5**, the LUMO orbitals are mostly composed of the conjugated bridge ( $\pi^*$ ), 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.

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  $M \rightarrow M^*$ ,  $\pi \rightarrow \pi^*$ ,  $M \rightarrow \pi^*$ , and  $\pi \rightarrow M^*$ , 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  $A \rightarrow M^*$ , which would increase the transition dipole moments to yield a  $\beta_0$  value relatively larger than that of **1**. The origin of the  $A \rightarrow M^*$  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  $\beta_0$  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  $M \rightarrow A^*$  and  $\pi \rightarrow A^*$ . 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<sub>6</sub>Me<sub>6</sub>)<sup>2+</sup> fragment behaves like the (thiophene)Mn(CO)<sub>3</sub><sup>+</sup> 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  $\beta$  values. Especially, the hyperpolarizabilities of **5**–**7** are among the largest found for organometallic chromophores with comparable molecular lengths. In addition, in comparison with  $\sigma$ -bonded ruthenium chromophores suffering from a nonlinearity–transparency tradeoff,<sup>19,20</sup> the  $\lambda_{\max}$  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 <sup>1</sup>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, [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub>, [( $\eta^6$ -*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>, and [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(CH<sub>3</sub>CN)<sub>3</sub>]CF<sub>3</sub>SO<sub>3</sub> were previously reported and prepared according to the modified procedures.<sup>10,12,13,14</sup>

**Synthesis of 1.** The complex [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> (0.15 g, 0.22 mmol) and AgCF<sub>3</sub>SO<sub>3</sub> (0.23 g, 0.89 mmol) were dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. 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<sub>2</sub>Cl<sub>2</sub>. The resulting solution was stirred at room temperature for 12 h. The precipitates were filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  2), and dried under vacuum. Yield: 0.26 g (75%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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<sub>27</sub>H<sub>30</sub>F<sub>6</sub>O<sub>7</sub>RuS<sub>3</sub>: 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%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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<sub>27</sub>H<sub>30</sub>F<sub>6</sub>O<sub>6</sub>RuS<sub>3</sub>: 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%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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<sub>26</sub>H<sub>26</sub>F<sub>6</sub>O<sub>6</sub>RuS<sub>3</sub>: 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%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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<sub>26</sub>H<sub>27</sub>BrF<sub>6</sub>O<sub>6</sub>RuS<sub>3</sub>: 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%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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<sub>26</sub>H<sub>27</sub>F<sub>6</sub>NO<sub>6</sub>RuS<sub>3</sub>: 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 [( $\eta^6$ -*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.13 g, 0.21 mmol) instead of [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> 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%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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, 1 H), 7.64 (d, 16.2 Hz, 1 H), 7.55 (t, 3.3 Hz, 1 H), 7.48 (d, 7.32, 1 H), 7.14 (d, 1.8, 2 H), 7.08 (d, 1.8, 2 H), 3.11 (sept, 6.9, 1 H), 2.48 (s, 3 H), 1.37 (d, 6.8, 6 H) ppm. Anal. Calcd for C<sub>24</sub>H<sub>23</sub>F<sub>6</sub>NO<sub>6</sub>RuS<sub>3</sub>: 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 [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(CH<sub>3</sub>CN)<sub>3</sub>]CF<sub>3</sub>SO<sub>3</sub> (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<sub>2</sub>Cl<sub>2</sub>. 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  $\times$  2), and dried under vacuum. Yield: 0.29 g (69%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  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.<sup>21</sup> 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 ( $\leq 30$  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  $0.2 \mu\text{m}$  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 fluorescence,<sup>22</sup> and the  $\beta$  values were derived by using an external reference method with the known  $\beta$  value of *p*-nitroaniline in chloroform.<sup>15</sup>

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**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<sup>23</sup> exchange-correlation functions in combination with LanL2DZ<sup>24</sup> basis sets were used throughout the calculations. The time-dependent DFT<sup>25</sup> 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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