

# $\pi$ -Conjugated Poly(aryleneethynylene)s Consisting of Salophen and Ni–Salophen Units in the $\pi$ -Conjugated Main Chain: Preparation and Chemical Properties

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**ABSTRACT:**  $\pi$ -Conjugated poly(aryleneethynylene)s consisting of *N,N'*-bis(salicylidene)-1,2-phenylenediamine (salophen) units (**Poly-1–Poly-3**) and salophen–nickel complex units (**Poly-1–Ni**) were prepared in high yields by the palladium-catalyzed polycondensation of  $\text{H}-\equiv\text{Ar}-\equiv\text{H}$  (Ar = fluorene or 2,5-dialkoxy-*p*-phenylene) with dibromo compounds of salophen (**Br<sub>2</sub>–Salophen**) and its nickel complex (**Br<sub>2</sub>–Salophen–Ni**), respectively. The Ni-free polymers (**Poly-1–Poly-3**) showed good solubility in  $\text{CHCl}_3$  and THF, had high thermal stability, and exhibited number-average molecular weights ( $M_n$ ) of 9200–14000 in GPC analysis. The UV–vis spectra of the polymers showed  $\pi-\pi^*$  transition peaks at about 420 nm, which was comparable to those of poly(*p*-phenyleneethynylene)s. The UV–vis spectrum of **Poly-1–Ni** exhibited additional intermediate and small peaks at about 480 and 600 nm, which were assigned to a charge-transfer (CT) electronic transition and a d–d transition, respectively. The complexation of **Poly-1** with  $\text{Ni}^{2+}$  proceeded clearly and quantitatively to give **Poly-1–Ni**, as monitored by UV–vis spectroscopy. Both the Ni-free and Ni-containing polymers were electrochemically active, and CV (cyclic voltammetry) scans of the polymers showed a reduction peak of the salophene unit at approximately  $-2.2$  V vs  $\text{Ag}^+/\text{Ag}$  and an oxidation peak of the salophene unit at about 0.8 V vs  $\text{Ag}^+/\text{Ag}$ .

## Introduction

Metal complexes of  $\pi$ -conjugated polymer ligands (e.g.,  $\text{Ru}^{2+}$  complex of poly(2,2'-bipyridine-5,5'-diyl)s) have been the subject of many studies.<sup>1,2</sup> Since  $\pi$ -conjugated polymers have mobile electrons along the polymer main chain, metal-containing  $\pi$ -conjugated polymers show interesting chemical and physical properties such as high catalytic activity,<sup>1,2a–2d</sup> electrical conductivity,<sup>2d–f</sup> and metal-controlled light-emitting<sup>1,2g</sup> properties.

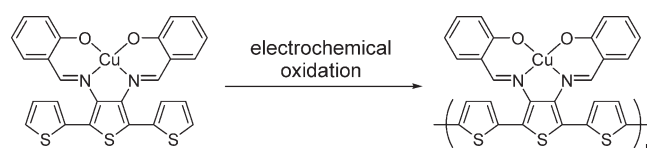
Bis(salicylidene)ethylenediamine (salen) and salophen shown in Chart 1 are typical metal-complex-forming ligands and their metal complexes have long been studied. Some of the metal complexes of salen and salophen have been used as catalysts for organic synthesis.<sup>3</sup>

The synthesis of polymers containing the salen or salophen unit<sup>4a,b</sup> or their metal complexes<sup>4a,c–k,5</sup> in aromatic main chains has been reported as shown in Chart 2.

Most of the salen or salophen unit in the reported polymers is connected at the *p*-positions of the phenolic groups, and  $\pi$ -conjugation is not thought to be extended along the polymer main chain. Actually, UV–vis data of the polymers have shown no expanded  $\pi$ -conjugated system along the polymer main chain. When the salophen unit is linked at *m*-positions of the phenolic groups, expansion of  $\pi$ -conjugated system become possible;<sup>4c</sup> however, examples of expansion of the  $\pi$ -conjugation system through the salophen unit in polymers are not many.

By contrast, connecting salophen at the 3- and 6-positions (cf. Chart 1) can give a fully  $\pi$ -conjugated poly(*p*-phenylene) type polymer. Reynolds and co-workers reported the synthesis of the

following polythiophenes with salophen–Cu complex side chains by electrochemical polymerization:<sup>5</sup>



This polymer possesses a thiophene analogue of the salophene unit at the center of the terthiophene unit and has extended  $\pi$ -conjugation along the polymer main chain. To reveal basic chemical properties of  $\pi$ -conjugated polymers consisting of the salophen unit or its metal complex, we have synthesized the following poly(aryleneethynylene)<sup>6</sup> polymers (Chart 3) as well as their dialkoxy-*p*-phenylene analogues.

We now report results of the synthesis and chemical properties of the polymers.

## Experimental Section

**Materials and Measurements.** 3,6-Dibromo-1,2-diaminobenzene (**1**),<sup>7</sup> 2,7-diethynyl-9,9-dioctylfluorene,<sup>8</sup> 3-bromo-4,5-diaminotoluene,<sup>9</sup> and  $\text{Pd}(\text{PPh}_3)_4$ <sup>10</sup> were prepared according to the literature.  $^1\text{H}$  NMR spectra were recorded on a JEOL EX-400 or a JEOL Lambda-300 spectrometer. UV–vis and photoluminescence (PL) spectra were measured with a Shimadzu UV-3100PC spectrometer and a Hitachi F-4010 spectrometer, respectively. The quantum yield ( $\Phi$ ) of the PL was calculated using a quinine sulfate standard ( $\Phi = 54.6\%$  at ca.  $10^{-5}$  M solution in 0.5 M  $\text{H}_2\text{SO}_4$ ). IR spectra were recorded on a JASCO FT/IR 460 PLUS spectrometer. High-resolution mass spectra

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(HRMS) were obtained with a JEOL JMS-700 analyzer. TGA curves were taken using a Shimadzu thermometric TGA-50 system. Elemental analysis was carried out using a LECO CHNS-932 analyzer and a Yanako YS-10 SX-Elements microanalyzer. Gel permeation chromatography (GPC) was performed with a Toso HLC-8120 system using THF as the eluent, and molecular weights were estimated using polystyrene standards. The microanalysis of Ni in **Poly-1-Ni** was carried out using a Shimadzu ICPS-8100 sequential plasma spectrometer at the Center for Advanced Materials Analysis (Suzukakedai), Technical Department, Tokyo Institute of Technology. **Poly-1-Ni** was decomposed in fuming nitric acid, and an aqueous solution for Ni analysis was obtained. Cyclic voltammetry (CV) was performed with a Toyo Technica Solartron SI-1287 electrochemical interface. Spectro-electrochemical measurements were carried out using a polymer film-coated ITO (indium–tin-oxide) working electrode, a Pt counter electrode, and an  $\text{Ag}^+/\text{Ag}$  reference electrode; the measuring system was controlled by using a Hokuto Denko HSV-100 electrochemical

interface and the spectroscopic changes were followed with a Shimadzu UV-3100PC spectrometer.

**Synthesis of Monomers (cf. Scheme 1).** **Br<sub>2</sub>–Salophen.** To an ethanol solution (10 mL) of **1** (2.00 g, 7.5 mmol) salicylaldehyde (1.85 g, 15.1 mmol) was added at 70 °C, and the mixture was stirred at 80 °C for 2 h. After cooling to room temperature (rt), a yellow precipitate was collected by filtration and dried under reduced pressure to give a precursor compound **2** for **Br<sub>2</sub>–Salophen**. Yield = 2.38 g (86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.29 (s, 1H, OH), 8.56 (s, 1H,  $-\text{CH}=\text{N}-$ ), 7.45 (ddd, 1H,  $J$  = 7.8, 7.3, and 1.5 Hz), 7.39 (dd, 1H,  $J$  = 7.8 and 1.5 Hz), 7.15 (d, 1H,  $J$  = 8.3 Hz), 7.07 (dd, 1H,  $J$  = 7.8 and 1.1 Hz), 6.99 (ddd, 1H,  $J$  = 7.8, 7.3, and 1.1 Hz), 6.92 (d, 1H,  $J$  = 8.3 Hz), 4.24 (s, 2H,  $\text{NH}_2$ ). Anal. Calcd for C<sub>13</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O: C, 42.20; H, 2.72; Br, 43.19; N, 7.57. Found: C, 42.31; H, 2.69; Br, 43.59; N, 7.60. HRMS calcd for C<sub>13</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O: 368.9238 ( $M + \text{H}^+$ ). Found: 368.9229 ( $M + \text{H}^+$ ). FT-IR (KBr): 3484, 3385, 1624, 1457, 1269, 1151, 1054, 916, 755 cm<sup>-1</sup>.

Salicylaldehyde (1.22 g, 10.0 mmol) was added to an ethanol solution (10 mL) of **2** (1.86 g, 5.0 mmol) at 90 °C, and the mixture was stirred at 90 °C for 1 h. After cooling to room temperature, a yellow precipitate was separated by filtration and recrystallized from chloroform–methanol at 0 °C to afford a bright yellow solid of **Br<sub>2</sub>–Salophen** (1.54 g, 65%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.68 (s, 2H, OH), 8.75 (s, 2H,  $-\text{CH}=\text{N}-$ ), 7.56 (dd, 2H,  $J$  = 7.8 and 1.5 Hz), 7.52 (s, 2H), 7.39 (ddd, 2H,  $J$  = 8.3, 7.8, and 1.5 Hz), 6.91 (dt, 2H,  $J$  = 7.8 and 1.0 Hz), 6.90 (dd, 2H,  $J$  = 8.3 and 1.0 Hz). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 50.66; H, 2.98; Br, 33.70; N, 5.91. Found: C, 50.45; H, 3.12; Br, 34.05; N, 5.94. FT-IR (KBr): 1618, 1270, 907, 750 cm<sup>-1</sup>.

**Br<sub>2</sub>–Salophen–Ni.** To an ethanol solution (10 mL) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.262 g, 1.1 mmol) a THF (2 mL) solution of **Br<sub>2</sub>–Salophen** (0.430 g, 0.91 mmol) was added at 70 °C, and the reaction mixture was stirred at 70 °C for 10 min. Cooling to room temperature gave dark green microcrystals. They were collected by filtration and dried under reduced pressure. Yield = 0.46 g (96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.04 (s, 2H,  $-\text{CH}=\text{N}-$ ), 7.32 (ddd, 2H,  $J$  = 8.8, 7.8, and 2.0 Hz), 7.28 (dd, 2H,  $J$  = 7.8 and 2.0 Hz), 7.24 (s, 2H), 7.11 (dd, 2H,  $J$  = 8.8 and 1.0 Hz), 6.63 (dt, 2H,  $J$  = 7.8 and 1.0 Hz). Anal. Calcd for C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>NiO<sub>2</sub>: C, 45.25; H, 2.28; Br, 30.11; N, 5.28. Found: C, 45.10; H, 2.46; Br, 29.62; N, 5.33. FT-IR (KBr): 1606, 1517, 1443, 1189, 1153, 956, 567, 463 cm<sup>-1</sup>.

The one-pot reaction of salicylaldehyde (2.83 g, 23.2 mmol), **1** (2.98 g, 11.2 mmol), and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (3.04 g, 12.2 mmol) in ethanol (10 mL) at 70 °C for 40 min also gave **Br<sub>2</sub>–Salophen–Ni** in 90% (5.3 g) yield. <sup>1</sup>H NMR data of **Br<sub>2</sub>–Salophen–Ni** prepared by this one-pot reaction agreed with that of the Ni complex obtained by the reaction of **Br<sub>2</sub>–Salophen** and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O.

Chart 1. Salen and Salophen

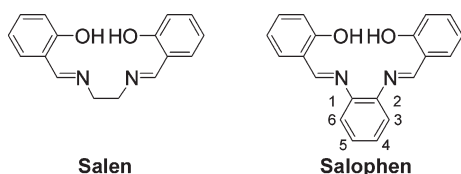


Chart 2. Reported Polymers of Salen and Salophen

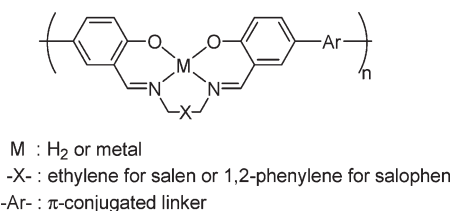
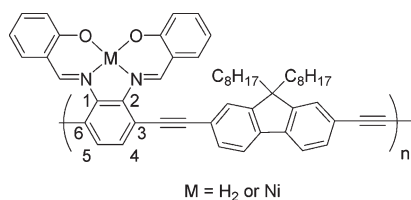
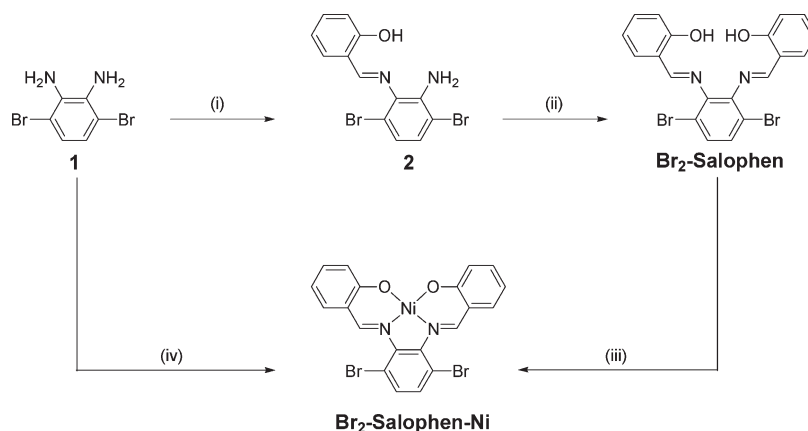


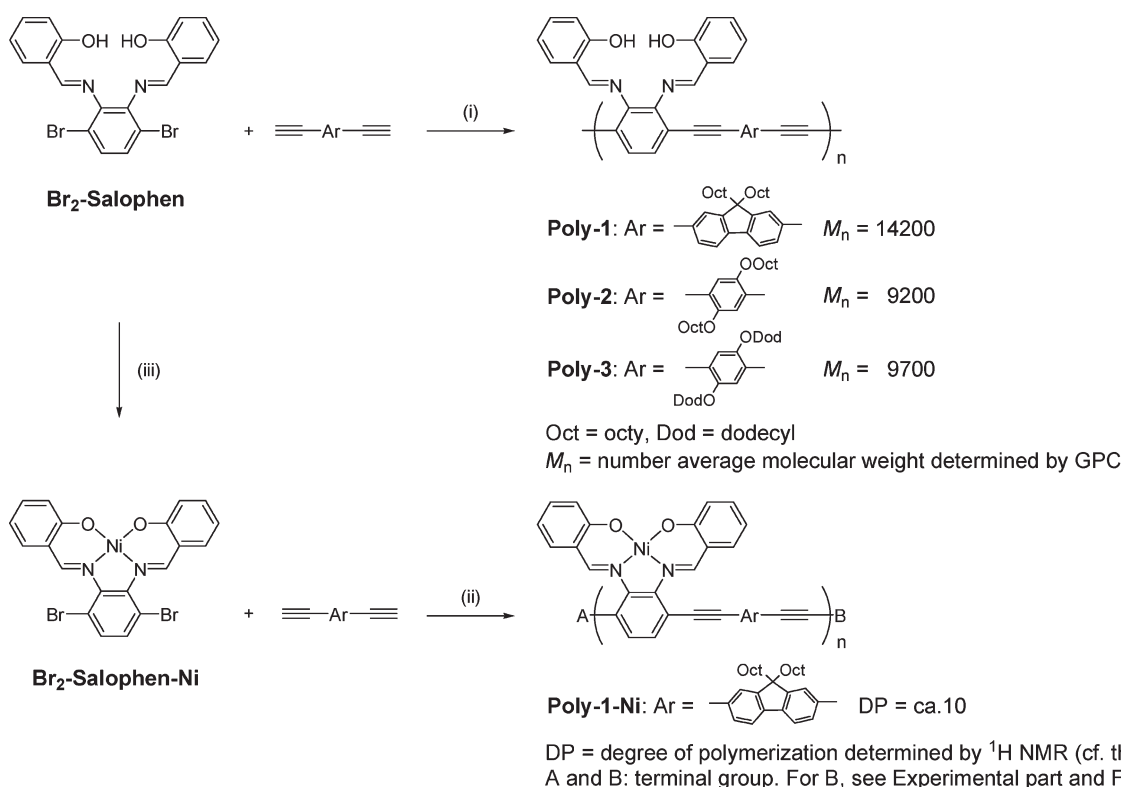
Chart 3. Synthesized  $\pi$ -Conjugated Salophen Polymers



Scheme 1. Synthetic Routes to the Monomers<sup>a</sup>



<sup>a</sup> Key: (i) salicylaldehyde (2 equiv), EtOH, 80 °C, 2 h; (ii) salicylaldehyde (2 equiv), EtOH, 90 °C, 1 h; (iii) Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, EtOH, 70 °C, 10 min; (iv) salicylaldehyde (2 equiv), Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, EtOH, 70 °C, 40 min.

Scheme 2. Synthetic Routes to Polymers<sup>a</sup>

<sup>a</sup> Key: (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>3</sub>N, THF, 70 °C, 24 h; (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>3</sub>N, toluene, 70 °C, 48 h; (iii) Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, EtOH, 70 °C, 10 min. A monobromo salophen-Ni group is considered to be a major terminal group (A and B) of **Poly-1-Ni** (cf. the text).

**Synthesis of Polymers (cf. Scheme 2).** **Poly-1.** A mixture of **Br<sub>2</sub>-Salophen** (0.25 g, 0.53 mmol), 2,7-diethynyl-9,9-dioctylfluorene (0.23 g, 0.52 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol), CuI (5 mg, 0.03 mmol), triethylamine (10 mL), and THF (25 mL) was stirred at 70 °C for 24 h. The reaction mixture was cooled to room temperature and poured into methanol to obtain a precipitate, which was collected by filtration and dissolved in THF. The THF solution was poured into methanol, and the precipitate was collected. The precipitate was dissolved in THF again, and the THF solution was poured into an aqueous solution of EDTA·2Na (EDTA = ethylenediaminetetraacetate). The brown precipitate was separated by filtration, washed with acetone repeatedly, and dried under reduced pressure to yield a brown powder of **Poly-1** (0.38 g, 96%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 12.77 (2H, OH), 8.95 (2H, -CH=N-), 7.50–6.97 (16H), 1.70 (4H), 1.10 (20 H), 0.81 (6H), 0.49 (4H). Anal. Calcd for (C<sub>53</sub>H<sub>54</sub>N<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 84.76; H, 7.25; N, 3.73. Found: C, 83.33; H, 7.25; N, 4.01; Br, 0.00. FT-IR (KBr): 2924, 2852, 2200, 1616, 1465, 1278, 1183, 1150, 901, 819, 753 cm<sup>-1</sup>.  $M_n$  (number-average molecular weight) = 14200. PDI (=  $M_w/M_n$ ;  $M_w$ , weight-average molecular weight) = 3.5. **Poly-2** and **Poly-3** were prepared analogously.

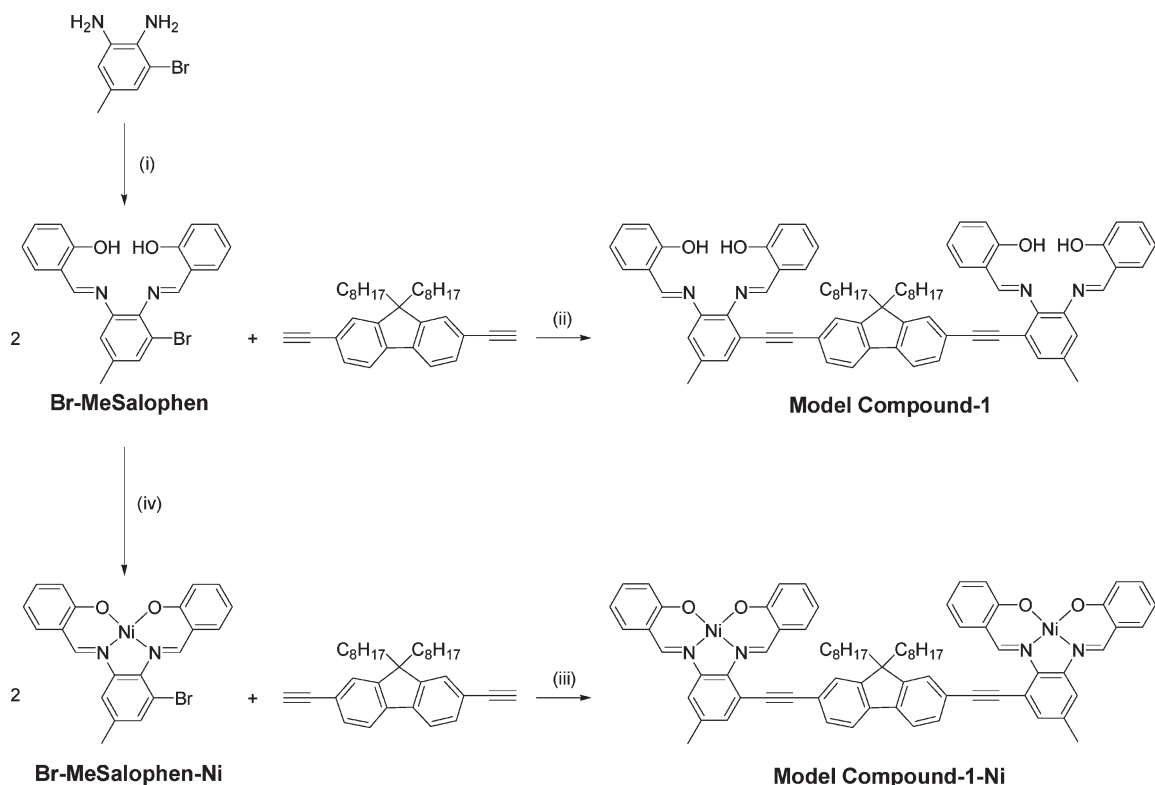
**Poly-2.** Brown solid. 95% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 12.75 (2H, OH), 8.87 (2H, -CH=N-), 7.61–7.3 (6H), 7.09–6.90 (6H), 3.74 (4H), 1.25 (24 H), 0.89 (6H). Anal. Calcd for Br-C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>-(C<sub>46</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub>)<sub>11</sub>-Br: C, 77.82; H, 7.00; N, 4.14; Br, 1.97.  $M_n$  = 8120. Found: C, 76.53; H, 7.25; N, 4.03; Br, 1.96.  $M_n$  = 9200. PDI = 3.7. FT-IR (KBr): 2924, 2854, 2196, 1617, 1508, 1458, 1277, 1216, 1030, 754 cm<sup>-1</sup>.

**Poly-3.** Red solid. 97% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 12.67 (2H, OH), 8.67 (2H, -CH=N-), 7.61–7.3 (6H), 7.09–6.90 (6H), 3.59 (4H), 1.26 (40 H), 0.86 (6H). Anal. Calcd for Br-C<sub>20</sub>H<sub>14</sub>-N<sub>2</sub>O<sub>2</sub>-(C<sub>54</sub>H<sub>66</sub>N<sub>2</sub>O<sub>4</sub>)<sub>10</sub>-Br: C, 78.70; H, 7.95; N, 3.60; Br, 1.89.  $M_n$  = 8540. Found: C, 77.01; H, 8.34; N, 3.42; Br, 2.20.  $M_n$  = 9700. PDI = 2.9. FT-IR (KBr): 2921, 2851, 2192, 1615, 1506, 1464, 1277, 1215, 1029, 753 cm<sup>-1</sup>.

**Synthesis of Polymers Containing Ni.** **Poly-1-Ni.** Toluene (47 mL) and triethylamine (18 mL) were added to a mixture of **Br<sub>2</sub>-Salophen-Ni** (0.25 g, 0.47 mmol) and 2,7-diethynyl-9,9-dioctylfluorene (0.21 g, 0.48 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (27 mg, 0.023 mmol), and CuI (4.5 mg, 0.023 mmol), and the reaction mixture was stirred at 70 °C for 48 h. After cooling to room temperature, the reaction mixture was poured into methanol to obtain a reddish-brown precipitate. The product was collected by filtration, washed with an aqueous solution of EDTA·2Na and acetone repeatedly, and dried under reduced pressure to afford a reddish-brown powder of **Poly-1-Ni** (0.35 g, 92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.86, 9.77, and 9.08 (2H; for detail, see Figure 3b and the text), 7.71 (2H), 7.54 (2H), 7.49 (2H), 7.35–7.28 (6H), 7.13 (2H), 6.61 (2H), 2.00 (4H), 1.08 (20 H), 0.78 (6H), 0.61 (4H). Anal. Calcd for Br-C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>NiO<sub>2</sub>-(C<sub>53</sub>H<sub>52</sub>N<sub>2</sub>NiO<sub>2</sub>)<sub>11</sub>-Br: C, 76.93; H, 6.24; Br, 1.70; N, 3.57; Ni, 7.48. Found: C, 75.35; H, 6.38; Br, 1.93; N, 3.57; Ni, 8.0. FT-IR (KBr): 2921, 2849, 2193, 1607, 1578, 1519, 1437, 1375, 1186, 816, 750, 534, 445 cm<sup>-1</sup>.

**Synthesis of Model Compounds (cf. Scheme 3).** **Br-MeSalophen.** Salicylaldehyde (1.9 g, 15 mmol) was added to an ethanol solution (10 mL) of 3-bromo-4,5-diaminotoluene (1.49 g, 7.4 mmol) at room temperature, and the reaction mixture was stirred at 80 °C for 1 h. After cooling to room temperature, a yellow precipitate was collected by filtration and purified by recrystallization from chloroform-methanol to give a yellow powder of **Br-MeSalophen** (1.97 g, 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 12.79 (s, 1H, OH), 12.48 (s, 1H, OH), 8.66 (s, 1H, -CH=N-), 8.51 (s, 1H, -CH=N-), 7.44 (d, 1H,  $J$  = 0.9 Hz), 7.42–7.33 (m, 3H), 7.30 (dd, 1H,  $J$  = 7.7 and 1.5 Hz), 7.04 (d, 1H,  $J$  = 7.7 Hz), 6.98 (d, 1H,  $J$  = 0.9 Hz), 6.97–6.88 (m, 3H), 2.41 (s, 3H). Anal. Calcd for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 61.63; H, 4.19; Br, 19.52; N, 6.84. Found: C, 61.86; H, 4.26; Br, 20.03; N, 6.81.

**Br-MeSalophen-Ni.** A mixture of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.27 g, 5.1 mmol), 3-bromo-4,5-diaminotoluene (1.02 g, 5.1 mmol), and salicylaldehyde (1.31 g, 10.7 mmol) in ethanol (25 mL) was stirred at 80 °C for 30 min to obtain a red solid. The red precipitate was collected by filtration and dried under reduced pressure to afford

Scheme 3. Synthetic Routes to Model Compounds<sup>a</sup>

<sup>a</sup> Key: (i) salicylaldehyde (2 equiv), EtOH, 80 °C, 1 h; (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>3</sub>N, THF, 70 °C, 24 h; (iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>3</sub>N, toluene, 70 °C, 24 h; (iv) Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, EtOH, 80 °C, 30 min.

**Br-MeSalophen-Ni** (2.13 g, 90%) as a dark red solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.21 (s, 1H, -CH=N-), 8.15 (s, 1H, -CH=N-), 7.48 (s, 1H), 7.27–7.24 (m, 5H), 7.12 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 8.4 Hz), 6.64 (t, 1H, *J* = 7.2 Hz), 6.59 (d, 1H, *J* = 7.2 Hz), 2.32 (s, 3H). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>BrN<sub>2</sub>NiO<sub>2</sub>: C, 54.13; H, 3.24; Br, 17.15; N, 6.01. Found: C, 54.22; H, 3.66; Br, 16.77; N, 5.94. FT-IR (KBr): 1609, 1523, 1449, 1190, 987, 750, 563, 437 cm<sup>-1</sup>.

**Model Compound-1.** A mixture of **Br-MeSalophen** (0.20 g, 0.49 mmol), 2,7-diethynyl-9,9-dioctylfluorene (0.11 g, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (60 mg, 0.05 mmol), CuI (20 mg, 0.1 mmol), triethylamine (4 mL), and THF (10 mL) was stirred at 70 °C for 24 h. After the reaction mixture was cooled to room temperature, the solvent was removed by evaporation. The crude product was purified by column chromatography on silica (eluent = ethyl acetate/chloroform (1/1 in volume)) to yield **Model Compound-1** (0.19 g, 71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 13.11 (s, 2H, OH), 12.83 (s, 2H, OH), 8.86 (s, 2H, -CH=N-), 8.69 (s, 2H, -CH=N-), 7.42–7.32 (m, 16 H), 7.10 (d, 2H, *J* = 8.1 Hz), 7.02 (s, 2H), 7.00 (d, 2H, *J* = 8.1 Hz), 6.94 (t, 4H, *J* = 7.2 Hz), 2.44 (s, 6H), 2.20–1.70 (m, 4H), 1.30–0.90 (m, 20H), 0.80 (t, 6H, *J* = 7.0 Hz), 0.54 (brs, 4H). Anal. Calcd for C<sub>75</sub>H<sub>74</sub>N<sub>4</sub>O<sub>4</sub>: C, 82.23; H, 6.81; N, 5.12. Found: C, 81.88; H, 6.85; N, 4.92. FT-IR (KBr): 2924, 2852, 2200, 1614, 1465, 1278, 1186, 1150, 901, 820, 754 cm<sup>-1</sup>.

**Model Compound-1-Ni.** Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg, 0.05 mmol), CuI (9.9 mg, 0.05 mmol), and triethylamine (20 mL) were added to a toluene (50 mL) solution containing **Br-MeSalophen-Ni** (0.47 g, 1.00 mmol) and 2,7-diethynyl-9,9-dioctylfluorene (0.12 g, 0.28 mmol), and the mixture was stirred at 70 °C for 24 h. After the reaction mixture was cooled to room temperature, the mixture was poured into methanol to obtain a precipitate. The precipitate was collected by filtration and purified by recrystallization from chloroform to give a red powder of **Model Compound-1-Ni** (0.33 g, 97%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.95 (s, 2H, -CH=N-), 8.26 (s, 2H, -CH=N-), 7.74 (d, 2H, *J* = 7.9 Hz),

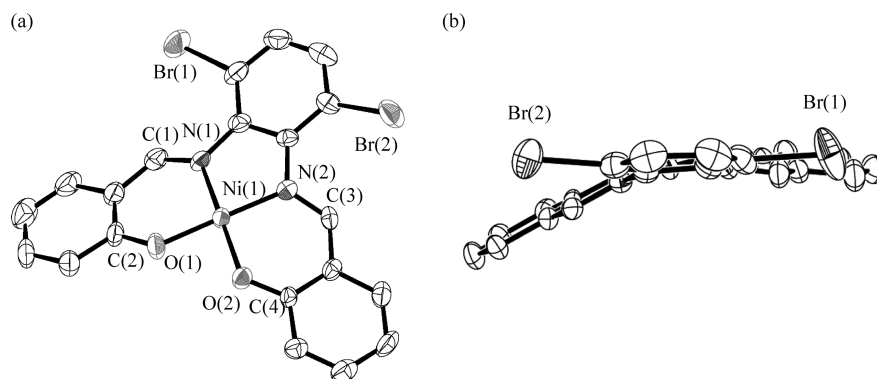
7.58–7.52 (m, 6H), 7.35–7.28 (m, 10H), 7.20 (d, 2H, *J* = 7.2 Hz), 7.18 (d, 2H, *J* = 7.2 Hz), 6.66 (t, 2H, *J* = 7.2 Hz), 6.64 (t, 2H, *J* = 7.3 Hz), 2.44 (s, 6H), 2.01 (m, 4H), 1.25–1.00 (m, 20H), 0.78 (t, 6H, *J* = 7.0 Hz), 0.64 (br, 4H). Anal. Calcd for C<sub>75</sub>H<sub>70</sub>N<sub>4</sub>NiO<sub>4</sub>: C, 74.52; H, 5.84; N, 4.64. Found: C, 74.11; H, 5.88; N, 4.64. FT-IR (KBr): 2923, 2825, 1608, 1524, 1445, 1186, 1147, 841, 822, 748, 734, 547, 417 cm<sup>-1</sup>.

## Results and Discussion

Scheme 1 shows the synthetic route to the two types of monomers. The reaction of 3,6-dibromo-1,2-diaminobenzene **1**<sup>7</sup> with salicylaldehyde in a 1:2 molar ratio at 80 °C gave the mono-salicylidene compound **2** as the main product (86%) and **Br<sub>2</sub>-Salophen** as the minor product. **Br<sub>2</sub>-Salophen** was prepared by further reaction of isolated **2** with salicylaldehyde. The nickel-containing monomer, **Br<sub>2</sub>-Salophen-Ni**, was synthesized in 96% yield by the addition of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O to **Br<sub>2</sub>-Salophen**. The one-pot reaction of **1** with salicylaldehyde in the presence of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O also afforded **Br<sub>2</sub>-Salophen-Ni** in 90% yield. **Br<sub>2</sub>-Salophen-Ni** has a coplanar coordination geometry around Ni as determined by single-crystal X-ray crystallography (cf. Figure 1), similarly to the case of the reported salophen-nickel complex.<sup>11</sup> However, the plane of the phenolic group is distorted from that of the dibromophenylene unit, presumably due to the steric repulsion between bromine and hydrogen of the imine group.

The synthetic routes to the polymers are outlined in Scheme 2. Palladium-catalyzed polycondensation<sup>6</sup> of 2,7-diethynyl-9,9-dioctylfluorene with **Br<sub>2</sub>-Salophen** and **Br<sub>2</sub>-Salophen-Ni**, afforded **Poly-1** and **Poly-1-Ni** in 96% and 92% yields, respectively. **Poly-2** and **Poly-3** were also obtained in high yields. **Poly-1**, **Poly-2**, and **Poly-3** showed good solubility in organic solvents such as chloroform and THF; however, **Poly-1-Ni** was only partially soluble in chloroform and THF.





**Figure 1.** ORTEP drawing of **Br<sub>2</sub>-Salophen-Ni**. (a) Front view and (b) side view.

**Table 1.** Polymerization and Optical and Thermogravimetric Data of the Polymers

polymer	yield, %	$M_n$	$M_w$	$\lambda_{\max}$ , nm		$\lambda_{\text{PL}}$ , nm [in THF ( $\Phi$ , %)] <sup>d</sup>	$T_d$ , °C <sup>f</sup>
				in CHCl <sub>3</sub>	film		
<b>Poly-1</b>	96	14200 <sup>a</sup>	49700 <sup>a</sup>	419	427	526 (0.5)	369
<b>Poly-2</b>	95	9200 <sup>a</sup>	34000 <sup>a</sup>	461	485	518 (1.0)	c
<b>Poly-3</b>	97	9300 <sup>a</sup>	27000 <sup>a</sup>	457	494	521 (3.0)	346
<b>Poly-1-Ni</b>	92	9400 <sup>b</sup>	c	428	402	e	431

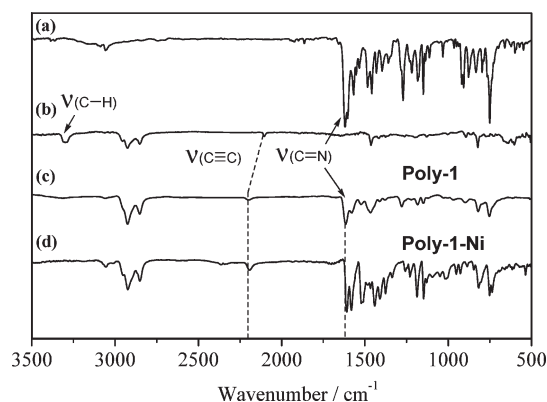
<sup>a</sup> Estimated by GPC (eluent: THF, polystyrene standards). <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy (cf. the text). <sup>c</sup> Not measured. <sup>d</sup> PL quantum yield calculated by comparing with the standard of quinine sulfate (ca. 10<sup>-3</sup> M solution in 0.5 M H<sub>2</sub>SO<sub>4</sub>, having a quantum yield of 54.6%). <sup>e</sup> Not observed. <sup>f</sup> 5 wt % loss temperature obtained by thermogravimetry.

The PAE-type polymers often have a polymer-C-Br group as the major terminal group, because of partial occurrence of Glaser coupling and/or higher reactivity of the -C≡CH group than that of the -C-Br group.<sup>6d-f</sup> However, **Poly-1** showed no bromine content, suggesting that the dehalogenation polycondensation proceeded smoothly. **Poly-1** showed  $M_n$  of 14,200 in GPC analysis (vs polystyrene standards), which corresponded to DP (degree of polymerization) of 19. **Poly-1**, **Poly-2**, and **Poly-3** showed unimodal GPC curves, and the PDIs ( $M_w/M_n$ ) were estimated to be about 3.

GPC analysis of **Poly-1-Ni** was not possible owing to the low solubility of the polymer or partial aggregation. **Poly-1-Ni** contained a small amount of bromine (1.93%; cf. Experimental Section). If both polymer ends (A and B in Scheme 2) of **Poly-1-Ni** contained Br, the DP of **Poly-1-Ni** was estimated to be about 10 from the Br content. This DP of **Poly-1-Ni** is consistent with <sup>1</sup>H NMR data of the polymer. The nickel content of **Poly-1-Ni** (8.0% of Ni) agreed with the calculated value (7.48%) within experimental error. **Poly-2** and **Poly-3** contained a small amount of bromine (ca. 2%). If both the polymer ends have a bromine group, the DP of **Poly-2** and **Poly-3** was estimated to be about 10, which agreed with the GPC  $M_n$  data for the polymers. All the polymers had good thermal stability under N<sub>2</sub>. For example, the TGA curves of **Poly-1** and **Poly-1-Ni** exhibited a 5% weight loss at 369 and 431 °C, respectively (Table 1).

To understand the nature of the polymers in detail, the corresponding model compounds depicted in Scheme 3 were also synthesized. 2,7-Diethynyl-9,9-dioctylfluorenes capped with two salophen terminal units and two nickel complexes, **Model Compound-1** and **Model Compound-1-Ni**, were synthesized by Pd-catalyzed reactions similar to those shown in Scheme 2. <sup>1</sup>H NMR spectra and data from elemental analyses agreed with their structures.

**IR and NMR Spectra.** The IR spectra of the polymers agree with their structures and are shown in Figure 2. The IR spectrum of **Poly-1** shows a  $\nu(\text{C}\equiv\text{C})$  peak of disubstituted acetylene at 2200 cm<sup>-1</sup> (Figure 2c). Absorption peaks due to  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{C}-\text{H})$  of terminal acetylenes of 2,7-diethynyl-9,9-dioctylfluorene at 2100 and 3300 cm<sup>-1</sup>, respectively, (Figure 2b) are not observed. The peak of **Poly-1** at



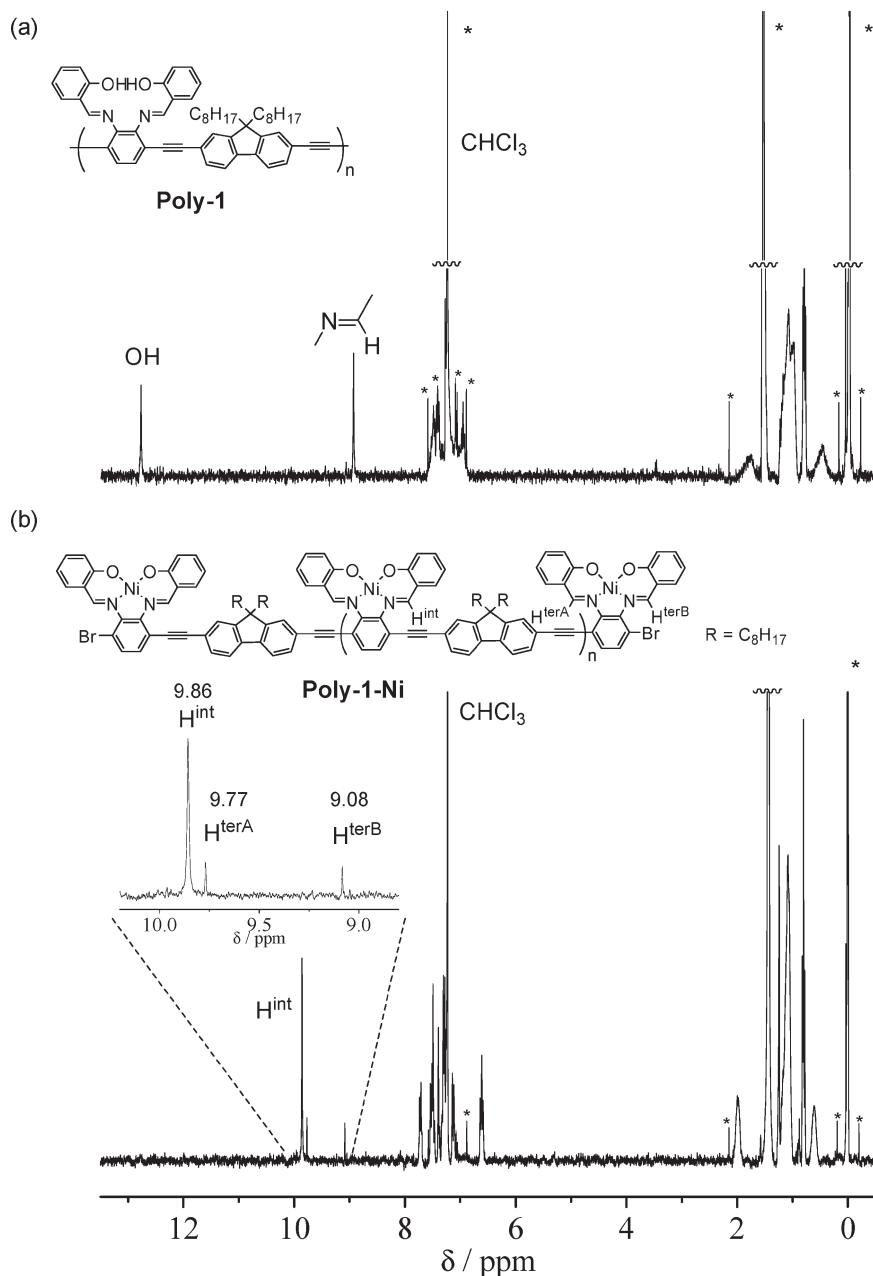
**Figure 2.** IR spectra of (a) **Br<sub>2</sub>-Salophen**, (b) 2,7-diethynyl-9,9-dioctylfluorene, (c) **Poly-1**, and (d) **Poly-1-Ni**.

1616 cm<sup>-1</sup> is assigned to a  $\nu(\text{C}=\text{N})$  peak of the imine group in the salophen unit and is located near that (1618 cm<sup>-1</sup>) of **Br<sub>2</sub>-Salophen** (Figure 2a). **Poly-1-Ni** (Figure 2d) gives rise to an IR spectrum similar to that of **Poly-1**. The IR spectra of **Poly-2** and **Poly-3** also exhibit a  $\nu(\text{C}\equiv\text{C})$  peak at about 2100 cm<sup>-1</sup> and a  $\nu(\text{C}=\text{N})$  peak at approximately 1610 cm<sup>-1</sup>.

Figure 3 shows the <sup>1</sup>H NMR spectra of **Poly-1** and **Poly-1-Ni** in CDCl<sub>3</sub>. Hydroxy and imine proton signals of **Poly-1** are clearly observed at  $\delta$  12.7 and 8.95, respectively (Figure 3a). The ratios of the area of these signals to that of aliphatic signals agree with the structure of **Poly-1**. **Poly-2**, and **Poly-3** give the hydroxy and imine proton signals at approximately  $\delta$  12.7 and 8.7, respectively.

In the <sup>1</sup>H NMR spectrum of **Poly-1-Ni**, the -OH signal completely disappears. These <sup>1</sup>H NMR data and the Ni content (see above) of **Poly-1-Ni** reveal that the nickelated structure of the salophen unit is maintained during polymerization.

**Poly-1-Ni** gives rise to three <sup>1</sup>H NMR peaks in the region between  $\delta$  9.0 and 10.0. The major peak at  $\delta$  9.86 is assigned to an imine -CH=N- proton of inner salophen units



**Figure 3.**  $^1\text{H}$  NMR spectra of (a) **Poly-1** and (b) **Poly-1-Ni** in  $\text{CDCl}_3$ . Peaks with \* are due to impurities in the solvent ( $\text{CHCl}_3$  and  $\text{H}_2\text{O}$ ) and TMS. Spinning side bands of the impurities and TMS are also marked with \*.

( $\text{H}^{\text{int}}$ ; cf. Figure 3b), and the two small peaks at  $\delta$  9.77 and 9.08 in a 1:1 ratio are considered to be due to imine protons of the terminal salophen–Ni unit as shown in Figure 3b. The magnetic deshielding effect of the  $-\text{C}\equiv\text{C}-$  group<sup>12</sup> seems to bring about a shift of the  $-\text{CH}=\text{N}-$  signal to a lower magnetic field from that of **Br<sub>2</sub>–Salophen–Ni** at  $\delta$  9.04. The  $^1\text{H}$  NMR data of **Model Compound-1–Ni** also shows a large chemical shift difference (1.69 ppm, cf. Experimental Section) between the  $\text{H}^{\text{terA}}$  and  $\text{H}^{\text{terB}}$  peaks. The ratio of the peak area of  $\text{H}^{\text{int}}$  to that of  $\text{H}^{\text{terA}}$  (or  $\text{H}^{\text{terB}}$ ) is approximately 10:1, which agrees with the DP (ca.10) estimated from the Br content.

**UV–Vis and Photoluminescence (PL) Spectra.** Figure 4 shows the UV–vis spectra of **Poly-1**, **Model Compound-1**, and the starting materials (**Br<sub>2</sub>–Salophen** and **Br–MeSalophen**) for the synthesis in  $\text{CHCl}_3$ . The UV–vis spectra of **Br<sub>2</sub>–Salophen** (Figure 4b) and **Br–MeSalophen** (Figure 4a) exhibit peaks at about  $\lambda_{\text{max}} = 335$  nm, which are principally assigned to the  $\pi-\pi^*$  transition in the salophen unit.<sup>13</sup> The  $\lambda_{\text{max}}$  of

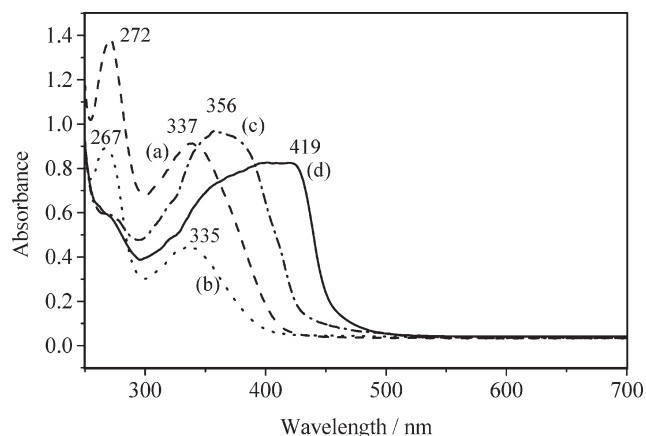
**Model Compound-1** (Figure 4c) shifts to a longer wavelength by about 20 nm because of the extension of the  $\pi$ -conjugation system (cf. Scheme 3). **Poly-1** (Figure 4d) seems to give overlapping  $\pi-\pi^*$  transition peaks at about 350 nm and a new  $\pi-\pi^*$  absorption peak at about 420 nm.

**Poly-1** essentially has a poly(*p*-phenyleneethynylene) **PPE** main chain,<sup>6,14</sup> and reported **PPEs** show  $\lambda_{\text{max}}$  (at about 420 nm) near the  $\lambda_{\text{max}}$  of **Poly-1**. Thus, the new peaks of **Poly-1** at about 420 nm are thought to arise essentially from the  $\pi-\pi^*$  transition along the polymer main chain.

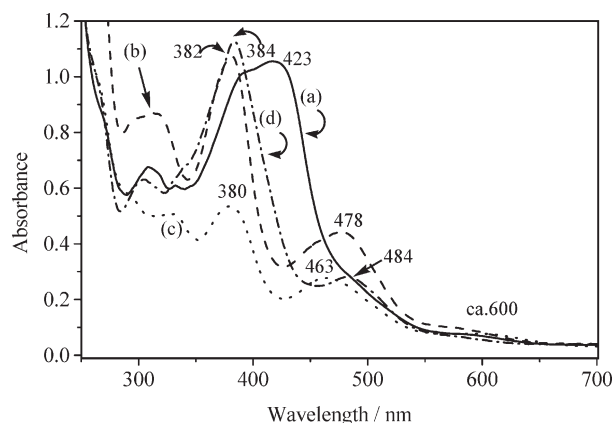
For the previously reported salen or salophen polymers shown in Chart 2, the  $\pi-\pi^*$  transition peak shows no distinct shift from that of the corresponding starting monomers<sup>4c–k</sup> because they lack formally extended  $\pi$ -conjugation system along the polymer chain. By contrast, the large bathochromic shift ( $\Delta\lambda_{\text{max}} = 84$  nm) observed between **Poly-1** and **Br<sub>2</sub>–Salophen** indicates the presence of an extended  $\pi$ -conjugated system along the polymer chain. Such large red-shifts of  $\lambda_{\text{max}}$

were also found in the UV-vis spectra of **Poly-2** ( $\lambda_{\text{max}} = 461$  nm,  $\Delta\lambda_{\text{max}} = 126$  nm) and **Poly-3** ( $\lambda_{\text{max}} = 457$  nm,  $\Delta\lambda_{\text{max}} = 122$  nm) to support the presence of extended  $\pi$ -conjugation systems along the polymer main chain.

Figure 5 shows the UV-vis spectra of **Poly-1-Ni**, **Br-MeSalophen-Ni**, **Br<sub>2</sub>-Salophen-Ni**, and **Model Compound-1-Ni**. In addition to the strong  $\pi$ - $\pi^*$  absorption peak, these Ni complexes show a medium UV-vis peak in the range of about 460–490 nm. Ni-salen and Ni-salophen complexes<sup>13</sup> reportedly show analogous absorption bands, and the contribution of a charge transfer (CT) electronic transition to the absorption band has been suggested.<sup>13</sup> A weak peak at approximately 600 nm (with  $\epsilon$  of about  $100 \text{ M}^{-1}\text{cm}^{-1}$ ) is considered to originate from d-d transition.<sup>13b,c</sup> Comparison of UV-vis spectra of **Poly-1** and **Poly-1-Ni** indicates that the  $\pi$ - $\pi^*$  transitions in the single salophen unit and in the



**Figure 4.** UV-vis spectra of (a) **Br-MeSalophen** (dashed line), (b) **Br<sub>2</sub>-Salophen** (dotted line), (c) **Model Compound-1** (dashed dot line), and (d) **Poly-1** (solid line) (solvent =  $\text{CHCl}_3$ ).



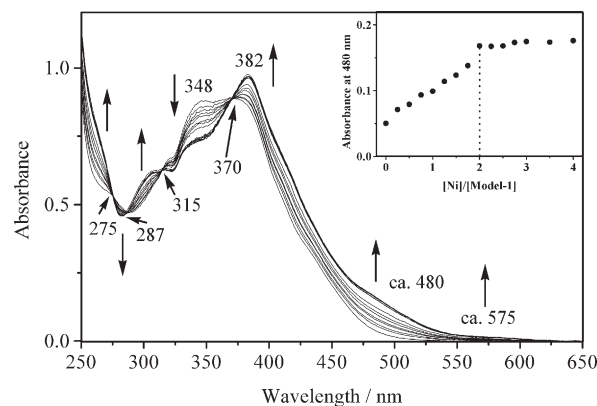
**Figure 5.** UV-vis spectra of (a) **Poly-1-Ni** (solid line), (b) **Br-MeSalophen-Ni** (dashed line), (c) **Br<sub>2</sub>-Salophen-Ni** (dotted line), and (d) **Model Compound-1-Ni** (dashed dot line) in  $\text{CHCl}_3$ .

$\pi$ -conjugated main chain are not significantly affected by the nickelation of the salophen side chain.

A cast film of **Poly-1** and **Poly-1-Ni** on a quartz glass showed essentially the same UV-vis spectra as those in Figure 5, suggesting that there was no significant electronic interaction between the polymer molecules. Two octyl side chains in the fluorene unit seem to prevent the intermolecular electronic interactions from taking place, similarly to the cases of poly(fluorene)s reported. By contrast, the  $\lambda_{\text{max}}$  values of **Poly-2** (485 nm) and **Poly-3** (494 nm) in cast films shift to a longer wavelength by 20–30 nm from those in  $\text{CHCl}_3$ . These data suggest that the polymers have intermolecular electronic interaction in the solid state because of a weak steric repulsion between the polymer molecules. When  $\pi$ -conjugated polymers assemble in the solid state, it often brings about intermolecular electronic interactions and a shift of the UV-vis peak to a longer wavelength.<sup>14,15</sup>

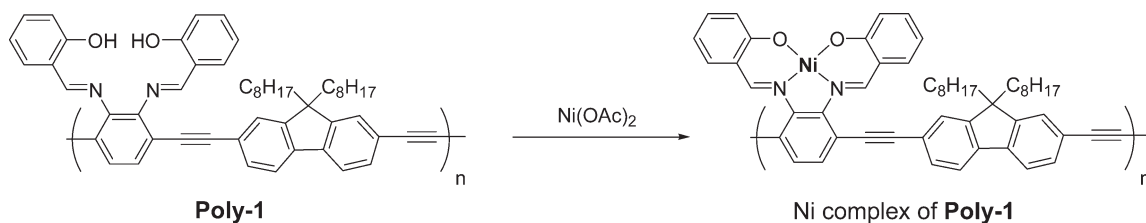
The PL spectra of **Poly-1**, **Poly-2**, and **Poly-3** showed a weak emission peak at approximately 520 nm in THF with quantum yields of 0.5–3.0%. OH compounds often show only a weak PL due to the quenching effect of the OH group<sup>16</sup> which is thought to originate from vibronic coupling. **Poly-1-Ni** showed no observable PL in either a THF solution or a film. Such a quenching effect of the transition metal was reported for some  $\pi$ -conjugated polymer ligands.<sup>17</sup>

**Nickelation of Poly-1.** As described earlier, **Poly-1-Ni** was synthesized directly from **Br<sub>2</sub>-Salophen-Ni**. A similar Ni(II) complex can be obtained by the reaction of **Poly-1** and  $\text{Ni}(\text{OAc})_2$  (cf. Scheme 4). Figures 6 and 7 show changes in the UV-vis spectra of **Model Compound-1** and **Poly-1** upon the addition of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ . As shown in Figure 6, the nickelation of **Model Compound-1** proceeds with clear isosbestic points, and changes in the peak intensity of the new peak at 480 nm vs  $[\text{Ni}^{2+}]/[\text{Model Compound-1}]$  are shown in



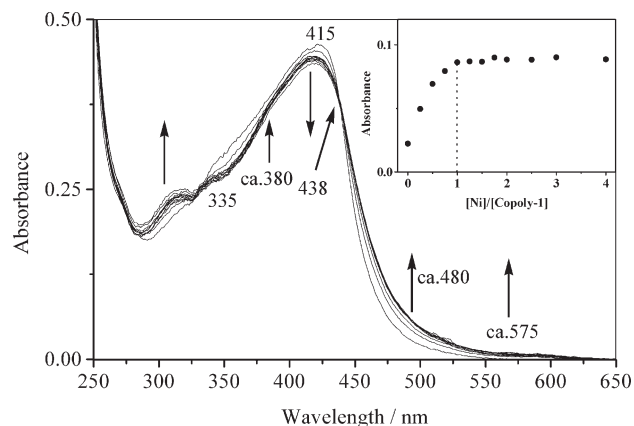
**Figure 6.** Changes in UV-vis spectrum of **Model Compound-1** ( $1.15 \times 10^{-5} \text{ M}$ ) in  $\text{CHCl}_3$ -MeOH (62.5:1 v/v) at various concentrations of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .  $[\text{Ni}] = 0, 2.88 \times 10^{-6}, 5.77 \times 10^{-6}, 8.65 \times 10^{-6}, 1.15 \times 10^{-5}, 1.44 \times 10^{-5}, 1.73 \times 10^{-5}, 2.02 \times 10^{-5}, 2.31 \times 10^{-5}, 2.60 \times 10^{-5}, 2.88 \times 10^{-5}, 3.17 \times 10^{-5}, 3.46 \times 10^{-5}, 4.04 \times 10^{-5},$  and  $4.61 \times 10^{-5} \text{ M}$ . The inset indicates the dependence of the absorbance of the shoulder peak at 480 nm on the addition of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .

**Scheme 4.** Response to  $\text{Ni}(\text{OAc})_2$

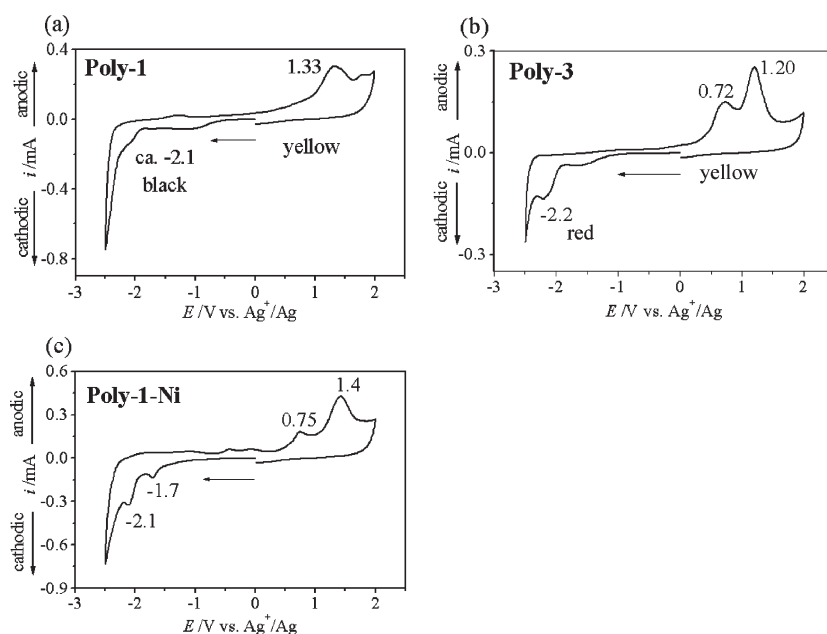


the inset of Figure 6. The absorbance increases smoothly with the  $[\text{Ni}^{2+}]/[\text{Model Compound-1}]$  ratio and saturates at a ratio of 2. Plots of data at 382 nm gave analogous results. Because **Model Compound-1** has two coordination sites, these data indicate that the nickelation of the salophen unit proceeds smoothly and quantitatively.

Similar UV-vis changes are observed in the reaction of **Poly-1** with  $\text{Ni}(\text{OAc})_2$ , as shown in Figure 7. Isosbestic points are observed at 438 and 335 nm, and the absorbance at 480 nm saturates at a  $[\text{Ni}]/[\text{Poly-1-Ni}]$  ratio of 1 (molarity of **Poly-1-Ni** is based on the repeating unit) as shown in the inset of Figure 7. These data indicate that every salophen unit in **Poly-1** smoothly participates in the reaction with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  to give **Poly-1-Ni**. It is reported that nickelation of salophen proceeds smoothly, and the product has a very large stability constant.<sup>18</sup> From the onset (approximately 550 nm) of the UV-vis absorption band of **Poly-1**, the band gap ( $E_g(\text{opt})$ ) of **Poly-1** is estimated at 2.3 eV.



**Figure 7.** Changes in UV-vis spectrum of **Poly-1** [ $1.14 \times 10^{-5}$  M (repeating unit)] in  $\text{CHCl}_3$ -MeOH (50:1 v/v) at various concentrations of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .  $[\text{Ni}] = 0, 2.87 \times 10^{-6}, 5.75 \times 10^{-6}, 8.62 \times 10^{-6}, 1.15 \times 10^{-5}, 1.44 \times 10^{-5}, 1.72 \times 10^{-5}, 2.01 \times 10^{-5}, 2.30 \times 10^{-5}, 3.45 \times 10^{-5}, 4.11 \times 10^{-5}$ , and  $5.13 \times 10^{-5}$  M. The inset indicates the increase in the absorbance of the shoulder peak at 480 nm on addition of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .



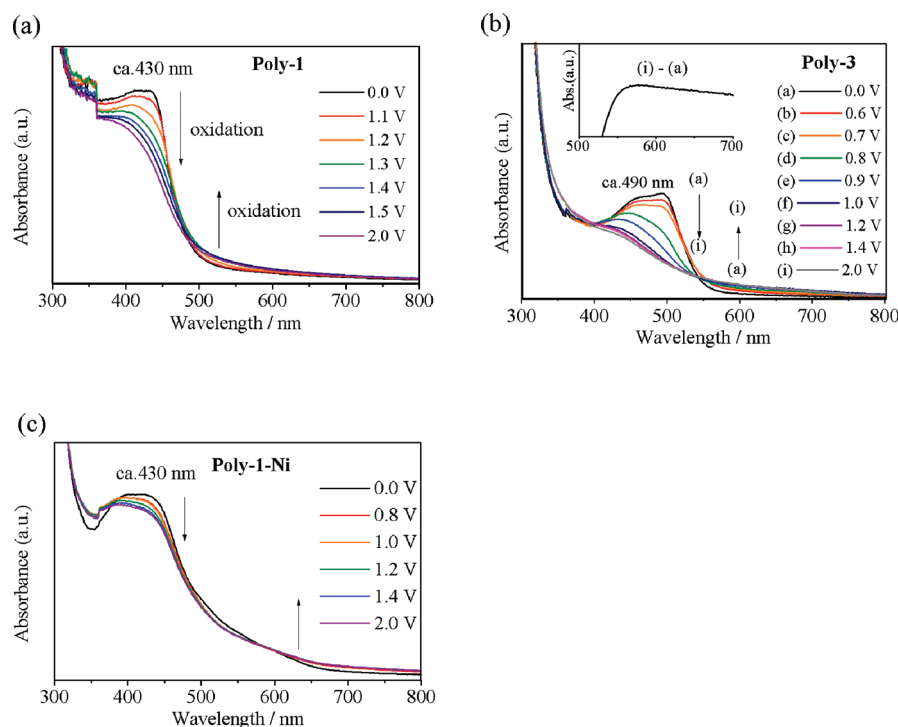
**Figure 8.** Cyclic voltammograms of the cast film of polymers on Pt electrode (1 cm  $\times$  1 cm) in a  $\text{CH}_3\text{CN}$  solution containing  $[\text{Bu}_4\text{N}]\text{PF}_6$  (0.1 M): (a) **Poly-1**; (b) **Poly-3**; (c) **Poly-1-Ni**. Sweep rate =  $50 \text{ mV s}^{-1}$ .

**Electrochemical Behavior.** *CV Data.* The salophen polymers and the Ni-salophen polymer are electrochemically active. Figure 8 shows CV charts of cast films of the polymers on Pt plates immersed in a  $\text{CH}_3\text{CN}$  solution of  $[\text{Bu}_4\text{N}]\text{PF}_6$ . **Poly-1** and **Poly-3** show a reduction peak at approximately  $-2.2$  V. Various poly(aryleneethynylene)-type polymers undergo electrochemical reduction (or n-doping) near  $-2$  V vs  $\text{Ag}^+/\text{Ag}$ ,<sup>6,19</sup> and the observed reduction peaks of **Poly-1** and **Poly-3** are also assigned to the reduction of the  $\pi$ -conjugated polymer main chain. However, the reduction peak may contain contribution from the reduction of the salophen unit.<sup>20</sup> The films turn from yellow to black (**Poly-1**) and red (**Poly-3**) upon reduction.

**Poly-1-Ni** gives two reduction peaks at  $-1.7$  and  $-2.1$  V vs  $\text{Ag}^+/\text{Ag}$ . The former peak is considered to contain a contribution from the one-electron reduction of the  $\text{Ni}(\text{II})$ -salophen complex. Isee et al.<sup>21</sup> and Gosden et al.<sup>22</sup> reported the generation of radical anion species  $[\text{Ni}(\text{II})\text{L}]^{\bullet-}$ ,  $\text{L}$  = salophen) of the  $\text{Ni}(\text{II})$ -salophen complex by electrochemical reduction at  $-1.4$  V vs SCE (or  $-1.74$  V vs  $\text{Ag}^+/\text{Ag}$ ). Isee et al. also revealed that the sequential reduction of  $[\text{Ni}(\text{II})\text{L}]^{\bullet-}$  gives  $\text{Ni}(\text{I})$  species  $[\text{Ni}(\text{I})\text{L}]^{2-}$  at  $-1.9$  V vs SCE (or  $-2.24$  V vs  $\text{Ag}^+/\text{Ag}$ ). These data support the idea that the peak at  $-2.1$  V vs  $\text{Ag}^+/\text{Ag}$  in Figure 8(c) includes contribution from the reduction of  $\pi$ -conjugated polymer main chain and that from the  $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{I})$  reduction.

In the oxidation region, **Poly-1** shows a peak at  $1.33$  vs  $\text{Ag}^+/\text{Ag}$ , whereas **Poly-3** gives rise to two oxidation peaks at  $0.72$  and  $1.20$  vs  $\text{Ag}^+/\text{Ag}$ . Poly(aryleneethynylene) undergoes electrochemical oxidation (or p-doping)<sup>23</sup> and the oxidation peak is assigned to oxidation of  $\pi$ -conjugated polymer main chain. The positive charge formed in the polymer main chain by the oxidation is thought to be delocalized along the polymer main chain; however, the positive charge seems to exist mainly at the aromatic units because of electron-accepting nature of the  $-\text{C}\equiv\text{C}-$  group. Appearance of the two oxidation peaks for **Poly-3** may be due to the presence of two kinds of aromatic units and oxidizable<sup>24a</sup> phenolic group in the polymer. For **Poly-1**, another oxidation peak may be hidden under the somewhat broad peak at  $1.33$  vs  $\text{Ag}^+/\text{Ag}$ . **Poly-1-Ni** also shows two oxidation peaks





**Figure 9.** Changes of UV-vis spectra with applied potential (vs  $\text{Ag}^+/\text{Ag}$ ) for (a) **Poly-1**, (b) **Poly-3**, (c) **Poly-1-Ni**. Polymer films cast on ITO (indium-tin-oxide) glass electrodes were used. In a  $\text{CH}_3\text{CN}$  solution of 0.1 M  $[\text{Bu}_4\text{N}]\text{PF}_6$ . The inset in part b shows a differential spectrum obtained from curves i and a. Noise from the measuring system is observed at about 360 nm.

at 0.75 and 1.4 V vs  $\text{Ag}^+/\text{Ag}$ . The potential of the former peak corresponds to the oxidation potential of the Ni(II)-salophen unit,<sup>24b,c</sup> and the latter larger peak is assigned to the oxidation of the polymer main chain.

The potential difference between the onset of the oxidation peak of **Poly-1** (approximately 0.7 V vs  $\text{Ag}^+/\text{Ag}$ ) and that of the reduction peak of **Poly-1** (approximately -1.8 V vs  $\text{Ag}^+/\text{Ag}$ ) is estimated to be approximately 2.5 V. This potential difference may be compared with the above-described optical band gap of  $E_g(\text{opt}) = 2.3$  eV of **Poly-1**, if the oxidation and reduction of the salophen unit cause changes of the electronic state of whole **Poly-1** molecule. From the onset potential of the oxidation peak,<sup>25</sup> HOMO level of **Poly-1** is estimated at approximately -5.5 eV.

**Spectro-Electrochemical Data.** Figure 9 shows results of spectro-electrochemical measurements of the polymers in the oxidation region. Myrick reported weakening of original UV-vis peaks of a poly(aryleneethynylene)-type polymer by electrochemical oxidation,<sup>26</sup> and similar phenomena are observed with **Poly-1**, **Poly-3**, and **Poly-1-Ni**.

The oxidation leads to an increase of the absorption in the 550–800 nm region, suggesting the formation of polaronic and bipolaronic states reported by Myrick.<sup>26</sup> For **Poly-3**, the differential spectrum depicted in the inset of Figure 9b show a peak at approximately 570 nm, suggesting the formation of the polaronic and/or bipolaronic states; however the peak is not so clear as that previously reported.<sup>26,27</sup> Detailed differential spectroscopic data of the **Poly-3** film depending on the applied potential are shown in Figure S1 in Supporting Information. The reason for smaller spectroscopic changes of **Poly-1-Ni** than those of **Poly-1** is not clear. Oxidized **Poly-1-Ni** may have new electronic transition(s) corresponding to the absorption in the 350–550 nm region. In the reduction region, the polymer films did not attached to the ITO electrode well and spectro-electrochemical response was not followed well.

## Conclusion and Scope

New  $\pi$ -conjugated poly(aryleneethynylene)s polymers consisting of salophen (**Poly-1–Poly-3**) and Ni-salophen (**Poly-1-Ni**) units were obtained in high yields by Pd-catalyzed polycondensation. Model compounds of the polymers were also prepared and  $^1\text{H}$  NMR and UV-vis data of the polymers were discussed using the corresponding data from the model compounds. **Poly-1** responded to  $\text{Ni}^{2+}$  to give a 1:1 Ni complex quantitatively. The polymers were electrochemically active in both the reduction and oxidation regions.  $\pi$ -Conjugated polymers with immobilized salophen-metal complexes will expand the scope of polymer chemistry and coordination chemistry.

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**Supporting Information Available:** Crystallographic information on **Br<sub>2</sub>Salophen-Ni** in CIF format and text giving the X-ray crystallography procedure, tables of crystal data, and a figure showing spectro-electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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