Electronic Supplementary Information

for

Synthesis, Characterization, and Physical Properties of Oligo(1-(*N*,*N*-dimethylamino)pyrrole)s and Their Doped Forms, Precursors of Candidates for Molecular Flat-band Ferromagnets

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Contents

1. Materials

Solvents and reagents were used as received unless otherwise noted. [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) ($NiCl_2$(dppp)) was synthesized according to an established procedure.[12] 1-(*N*,*N*-Dimethylamino)pyrrole and tris(4-bromophenyl)aminium hexachloroantimonate were from Aldrich Ltd. Nickel(II) chloride anhydrous and celite were from Wako Pure Chemical Industries, Ltd. n-Butyllithium in hexane and manganese dioxide were from Kanto Chemical Ltd. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical was from Tokyo Chemical Industry Co. Ltd. THF, used as a solvent for reactions, was distilled from sodium and benzophenone under a nitrogen atmosphere. Spectroscopy-grade acetonitrile was from Kanto Chemical Ltd. Common solvents and anhydrous solvents used for syntheses and measurements were from Kanto Chemical Ltd.

2. Synthesis and isolation of 2, 3, 4, and 5 from 1-(*N*,*N*-dimethylamino)pyrrole (1)

To a THF (500 mL) solution of 1-(*N*,*N*-dimethylamino)pyrrole (**1**, 73 mL, 0.60 mol) was added *n*-butyllithium (2.55 M hexane solution, 500 mL, 1.28 mol) at −78 °C under N_2. The solution was refluxed, and a white lithium salt was precipitated. After 5.0 h, the mixture was cooled to room temperature, and transferred through a Teflon cannula at 0 °C to fractured anhydrous $NiCl_2$ (89 g, 0.69 mmol). The solution turned black immediately. After stirring for 36.5 h at room temperature, the reaction was quenched with ethanol (100 mL), and insoluble materials were filtered off through Celite and silica gel. The solvent was evaporated under reduced pressure, and the residual black solid was purified by column chromatography packed with silica gel (eluent: hexane/ethyl acetate = 7/1). The fraction containing **2** was evaporated under reduced pressure, and recrystallized from hexane to give colorless plates (31.38 g, 143.8 mmol, 48%). The fraction containing **3**, **4**, and **5** was evaporated under reduced pressure, and separated by recycling preparative HPLC with a GPC column. Each separated fraction was evaporated, and recrystallized from acetonitrile to give colorless plates (**3**, 5.50 g, 16.9 mmol, 8%; **4**, 2.00 g, 4.5 mmol, 3%; and **5**, 0.80 g, 1.5 mmol, 1%).

2,2′-Bi[1-(*N*,*N*-dimethylamino)pyrrole] (**2**). Mp: 92.0–94.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (t, 2H, *J* = 2.4 Hz, pyrrole), 6.20 (d, 4H, *J* = 2.4 Hz, pyrrole), 2.79 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8 (C_q), 112.9 (CH), 106.4 (CH), 106.3 (CH), 47.8 (CH_3). EI-MS (*m/z*): 218 (M^+). Anal. Calcd. for $C_{12}H_{18}N_4$: C, 66.02; H, 8.31; N, 25.67. Found: C, 66.04; H, 8.16; N, 25.79.

2,2′:5′,2″-Ter[1-(*N*,*N*-dimethylamino)pyrrole] (**3**). Mp: 128.0–132.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, 2H, *J* = 2.5 Hz, pyrrole), 6.23–6.19 (m, 6H, pyrrole), 2.80 (s, 12H, methyl), 2.75 (s, 6H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.3 (C_q), 123.8 (C_q), 112.9 (CH), 108.7 (CH), 108.2 (CH), 106.3 (CH), 48.2 (CH_3), 46.3 (CH_3). EI-MS (*m/z*): 326 (M^+). Anal. Calcd. for $C_{18}H_{26}N_6$: C, 66.23; H, 8.03; N, 25.74. Found: C, 66.49; H, 8.23; N, 25.65.

2,2′:5′,2″:5″,2‴-Quater[1-(*N*,*N*-dimethylamino)pyrrole] (**4**). Mp: 184.5–187.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, 2H, *J* = 2.3 Hz, pyrrole), 6.29–6.17 (m, 8H, pyrrole), 2.79 (s, 12H, methyl), 2.77 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.4 (C_q), 124.3 (C_q), 124.2 (C_q), 112.9 (CH), 110.6 (CH), 108.3 (CH), 107.8 (CH), 106.3 (CH), 48.0 (CH_3), 46.4 (CH_3). EI-MS (*m/z*): 434 (M^+). Anal. Calcd. for $C_{24}H_{34}N_8$: C, 66.33; H, 7.89; N, 25.78. Found: C, 66.16; H, 7.80; N, 25.53.

2,2′:5′,2″:5″,2‴:5‴,2⁗-Quinque[1-(*N*,*N*-dimethylamino)pyrrole] (**5**). Mp: 167.0–168.0 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.04 (dd, 2H, *J* = 2.9, 2.0 Hz, pyrrole), 6.28–6.18 (m, 10H, pyrrole), 2.81 (s, 6H, methyl), 2.79 (s, 12H, methyl), 2.77 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.7 (C_q), 124.32 (C_q), 124.28 (C_q), 124.1 (C_q), 113.0 (CH), 110.3 (CH), 110.2 (CH), 108.7 (CH), 108.1 (CH), 106.4 (CH), 48.0 (CH_3), 46.6 (CH_3), 46.4 (CH_3). EI-MS (*m/z*): 542 (M^+). Anal.; Calcd. for $C_{30}H_{42}N_{10}$: C, 66.39; H, 7.80; N, 25.81. Found: C, 66.36; H, 7.94; N, 25.63.

3. Synthesis and isolation of 4, 6, 8, and 10 from 2

To a THF (300 mL) solution of **2** (34.89 g, 159.8 mmol) was added *n*-butyllithium (1.52 M hexane solution, 224 mL, 340 mmol) at −78 °C under N_2. The reaction mixture was refluxed for 7 h, before being cooled to room temperature, and transferred through a Teflon cannula at 0 °C to fractured anhydrous $NiCl_2$ (25 g, 190 mmol). The solution turned black immediately. After stirring for 40 h at room temperature, the reaction was quenched with ethanol (100 mL), and insoluble materials were filtered off through Celite and silica gel. The solvent was evaporated under reduced pressure, and **2** was removed by column chromatography packed with silica gel (eluent: hexane/ethyl acetate = 12/1). Evaporation of the solvent gave **2** as a yellow solid (9.59 g, 43.9 mmol, 28%). The fraction containing **4**, **6**, **8**, and **10** was evaporated under reduced pressure, and separated by recycling preparative HPLC with a GPC column. Each separated fraction was evaporated, and recrystallized from acetonitrile to give colorless plates for **4** and **6** and white solids for **8** and **10** (**4**, 5.35 g, 12.3 mmol, 15%; **6**, 3.81 g, 5.85 mmol, 11%; **8**, 2.58 g, 2.98 mmol, 8%; and **10**, 1.62 g, 1.49 mmol, 5%).

2,2′:5′,2″:5″,2‴:5‴,2″″:5″″,2‴″-Sexi[1-(*N*,*N*-dimethylamino)pyrrole] (**6**). Mp: 184.5–186.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (dd, 2H, *J* = 2.9, 2.0 Hz, pyrrole), 6.28–6.18 (m, 12H, pyrrole), 2.81 (s, 12H, methyl), 2.79 (s, 12H, methyl), 2.77 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.7 (C_q), 124.6 (C_q), 124.3 (C_q, ×2), 124.1 (C_q), 112.9 (CH), 110.2 (CH), 110.1 (CH), 109.9 (CH), 108.5 (CH), 108.0 (CH), 106.3 (CH), 48.0 (CH_3), 46.5 (CH_3), 46.3 (CH_3). ESI-MS (*m/z*): 650.44 (M^+). Anal.; Calcd. for $C_{36}H_{50}N_{12}$: C, 66.43; H, 7.74; N, 25.82. Found: C, 66.24; H, 7.65; N, 25.64.

2,2′:5′,2″:5″,2‴:5‴,2″″:5″″,2‴″:5‴″,2‴‴:5‴‴,2‴‴′-Octi[1-(*N*,*N*-dimethylamino)pyrrole] (**8**). Mp: 193.5–195.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (dd, 2H, *J* = 2.9, 2.0 Hz, pyrrole), 6.29–6.19 (m, 16H, pyrrole), 2.81 (s, 12H, methyl), 2.80 (s, 12H, methyl), 2.79 (s, 12H, methyl), 2.78 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.84 (C_q), 124.81 (C_q), 124.71 (C_q), 124.69 (C_q), 124.34 (C_q), 124.28 (C_q), 124.2 (C_q), 113.0 (CH), 110.3 (CH), 110.2 (CH), 110.0 (CH), 109.87 (CH), 109.86 (CH), 108.4 (CH), 108.0 (CH), 106.4 (CH), 48.0 (CH_3), 46.5 (CH_3, ×2), 46.4 (CH_3). ESI-MS (*m/z*); 866.57 (M^+). Anal.; Calcd. for $C_{48}H_{66}N_{16}$: C, 66.48; H, 7.67; N, 25.84. Found: C, 66.38; H, 7.68; N, 25.76.

2,2′:5′,2″:5″,2‴:5‴,2″″:5″″,2‴″:5‴″,2‴‴:5‴‴,2‴‴′:5‴‴′,2‴‴″:5‴‴″,2‴‴‴-Deci[1-(*N*,*N*-dimethylamino)pyrrole] (**10**). Mp: 209.5–212.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, 2H, *J* = 2.4 Hz, pyrrole), 6.29–6.19 (m, 20H, pyrrole), 2.81 (s, 24H, methyl), 2.80 (s, 12H, methyl), 2.79 (s, 12H, methyl), 2.78 (s, 12H, methyl). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.9 (C_q, ×2), 124.80 (C_q), 124.76 (C_q), 124.7 (C_q, ×2), 124.4 (C_q), 124.28 (C_q), 124.26 (C_q), 113.0 (CH), 110.3 (CH), 110.2 (CH), 110.0 (CH, ×2), 109.9 (CH), 109.82 (CH), 109.78 (CH), 108.3 (CH), 107.9 (CH), 106.3 (CH), 48.0 (CH_3), 46.5 (CH_3, ×3), 46.3 (CH_3). ESI-MS (*m/z*): 1082.76 (M^+). Anal. Calcd. for $C_{60}H_{82}N_{20}$: C, 66.51; H, 7.63; N, 25.86. Found: C, 66.73; H, 7.87; N, 25.88.

4. Synthesis and isolation of 8 and 12 from 4

To a THF (300 mL) solution of **4** (2.89 g, 6.66 mmol) and potassium *tert*-butoxide (1.13 g, 10.0 mmol) was added *n*-butyllithium (1.52 M hexane solution, 8.0 mL, 12 mmol) at −78 °C under N_2. After stirring for 6.0 h, the mixture was warmed to room temperature, and transferred through a Teflon cannula at 0 °C to anhydrous $NiCl_2$(dppp) (5.74 g, 10.6 mmol). The solution turned black immediately. After stirring for 18.0 h at room temperature, the reaction was quenched with ethanol (50 mL), and insoluble materials were filtered off through Celite. The solvent was evaporated under reduced pressure, the residual black solid was dissolved in dichloromethane, and the organic layer was washed with water three times. The solution was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residual black solid was separated by recycling preparative

HPLC with a GPC column. Evaporation of each separated fraction gave white solids for **4** and **8** and a brown solid for **12** (**4**, 1.05 g, 2.42 mmol, 36%; **8**, 0.65 g, 0.75 mmol, 23%; **12**, 0.29 g, 0.22 mmol, 10%). Other oligomers such as **9**, **10**, **11**, and the higher oligomers were also obtained but could not be isolated.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″:5⁗″,2⁗‴:5⁗‴,2⁗⁗:5⁗⁗,2⁗⁗′:5⁗⁗′,2⁗⁗″:5⁗⁗″,2⁗⁗‴-Duodeci[1-(*N*,*N*-dimethylamino)pyrrole] (**12**). Mp: 218.0–222.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (t, 2H, *J* = 2.4 Hz, pyrrole), 6.30–6.18 (m, 24H, pyrrole), 2.81 (s, 36H, methyl), 2.80 (s, 12H, methyl), 2.78 (s, 12H, methyl), 2.77 (s, 12H, methyl). ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.87 (C_q), 124.81 (C_q ×5), 124.76 (C_q), 124.74 (C_q), 124.37 (C_q), 124.32 (C_q), 124.27 (C_q), 113.0 (CH), 110.4 (CH), 110.3 (CH), 110.1 (CH ×6), 110.0 (CH), 108.5 (CH), 108.0 (CH), 106.4 (CH), 48.0 (CH_3), 46.5 (CH_3 ×4), 46.4 (CH_3); HRMS (ESI): Exact mass calcd. for $C_{72}H_{98}N_{24}$, 1298.8406. Found: *m/z* = 1298.8433 (M^+).

5. Synthesis of $\mathbf{4^{2+}(SbCl_6^-)_2}$, $\mathbf{6^{2+}(SbCl_6^-)_2}$, and $\mathbf{8^{2+}(SbCl_6^-)_2}$

Tris(4-bromophenyl)aminium hexachloroanitimonate (201 mg, 0.25 mmol) was added to a THF (10 mL) solution of **1** (55 mg, 0.13 mmol) under N_2. The solution turned from colorless to dark red immediately and was stirred for 10 min at room temperature. The black precipitate was filtered, washed with THF and then with dichloromethane to give $\mathbf{4}^{2+}(SbCl_6^-)_2$ (57 mg, 42%). In a similar fashion, $\mathbf{6}^{2+}(SbCl_6^-)_2$ and $\mathbf{8}^{2+}(SbCl_6^-)_2$ were obtained in 70% and 61% yield, respectively.

6. Synthesis of $\mathbf{10^{4+}(SbCl_6^-)_4}$ for EPR and SQUID measurements

To a solution of **10** (15 mg, 0.014 mmol) in THF (4 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (45 mg, 0.056 mmol) at room temperature under nitrogen. The solution immediately turned dark green, and it was stirred for 10 min. The black precipitate was filtered, and washed with THF and dichloromethane to give $\mathbf{10}^{4+}(SbCl_6^-)_4$ (6 mg, 19%).

7. X-ray structure analysis

Crystal data for **2**: $C_{12}H_{18}N_4$, M = 218.3 $gmol^{-1}$, monoclinic, space group P21/n, a = 7.770(3) Å, b = 7.311(2) Å, c = 11.141(4) Å, β = 109.425(4)°, V = 596.8(1) Å^3, Z = 2, ρ = 1.21 gcm^{-3}, μ = 0.076 mm^{-1}, F(000) = 236.0, crystal size = 0.40 × 0.40 × 0.10 mm^3. Crystals of **2** were removed from the mother liquor, and cooled to 103 K on a Rigaku Saturn 724 CCD area detector system

[λ(Mo$K\alpha$) = 0.7107 Å] with a graphite monochromator, which was used to record 720 frames with an ω scan width of 0.50°, for 10 s each, using a crystal–detector distance of 45 mm and a 0.8 mm collimator. A total of 4382 reflections ($3.9 < \theta < 27.5$) were collected, of which 1344 reflections were unique (R_{int} = 0.0205). An empirical absorption correction using equivalent reflections and Lorentzian polarization were performed with the program Crystal Clear 1.3.6. T_{max} and T_{min} were 0.992 and 0.970, respectively. The structure was solved with the program SIR-92 and refined against F2 using SHELXL-97 to R = 0.0372 and wR_2 = 0.1017 for 1183 reflections with $I > 2\sigma(I)$, GoF = 1.19, and R = 0.041 for all reflections with 73 parameters; max/min residual electron density was 0.225 and −0.198 eÅ^3, respectively. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were added geometrically. CCDC 1027851 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **3**: $C_{18}H_{26}N_6$, M = 326.45 gmol^{-1}, monoclinic, space group P21/c, a = 14.8107(13) Å, b = 7.9825(5) Å, c = 15.3064(11) Å, β = 91.463(1)°, V = 1809.0(2) Å^3, Z = 4, ρ = 1.199 gcm^{-3}, μ = 0.075 mm^{-1}, F(000) = 704.0, crystal size = 0.40 × 0.30 × 0.20 mm^3. Crystals of **3** were removed from the mother liquor, and cooled to 103 K on a Rigaku Saturn 724 CCD area detector system [λ(Mo$K\alpha$) = 0.7107 Å] with a graphite monochromator, which was used to record 720 frames with an ω scan width of 0.50°, each for 15 s, using a crystal–detector distance of 45 mm and a 0.5 mm collimator. A total of 13892 reflections ($3.0 < \theta < 27.5$) were collected, of which 4139 were unique (R_{int} = 0.0267). An empirical absorption correction using equivalent reflections and Lorentzian polarization was performed with the program Crystal Clear 1.3.6. T_{max} and T_{min} were 0.985 and 0.973, respectively. The structure was solved with the program SIR-92, and refined against F2 using SHELXL-97 to R = 0.047 and wR_2 = 0.12 for 3410 reflections with $I > 2\sigma(I)$, GoF = 1.165, R = 0.0576 for all reflections with 217 parameters; max/min residual electron density was 0.221 and −0.277 eÅ^3, respectively. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added geometrically. CCDC 1027852 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **4**: $C_{24}H_{34}N_8$, M = 434.59 gmol^{-1}, monoclinic, space group C2/c, a = 23.414(12) Å, b = 7.947(3) Å, c = 15.216(8) Å, β = 126.073(2)°, V = 2288.3(19) Å^3, Z = 4, ρ = 1.261 gcm^{-3}, μ = 0.079 mm^{-1}, F(000) = 936.0, crystal size = 0.50 × 0.50 × 0.05 mm^3. Crystals of **4** were removed from the mother liquor, and cooled to 103 K on a Rigaku Saturn 724 CCD area detector system [λ(Mo$K\alpha$) = 0.7107 Å] with a graphite monochromator, which was used to record 720 frames with an ω scan width of 0.50°, each for 15 s, with a crystal–detector distance of 45 mm and 0.8 mm collimator. A total of 8732 reflections ($3.3 < \theta < 27.5$) were collected, and 2609 reflections were unique (R_{int} = 0.0207). An empirical absorption correction using equivalent reflections and Lorentzian polarization was performed with the program Crystal Clear 1.3.6. T_{max} and T_{min} were 0.996 and 0.961, respectively. The structure was solved with the program SIR-92, and refined against F2 using SHELXL-97 to R = 0.0388 and wR_2 = 0.1018 for 2299 reflections with $I > 2\sigma(I)$, GoF = 1.045, R = 0.0445 for all reflections with 145 parameters; max/min residual electron density was 0.258 and –0.2 eÅ^3, respectively. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added geometrically. CCDC 1027853 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **5**: $C_{30}H_{42}N_{10}$, M = 542.74 gmol^{-1}, triclinic, space group P $\bar{1}$, a = 8.347(5) Å, b = 13.899(9) Å, c = 14.2043(9) Å, α = 106.524(6)°, β = 95.771(6)°, γ = 105.689(6)°, V = 1492.6(16) Å^3, Z = 2, ρ = 1.208 gcm^{-3}, μ = 0.076 mm^{-1}, F(000) = 584.0, crystal size = 0.60 × 0.50 × 0.20 mm^3. Crystals of **5** were removed from the mother liquor, and cooled to 103 K on a Rigaku Saturn 724 CCD area detector system [λ(Mo$K\alpha$) = 0.7107 Å] with a graphite monochromator, which was used to record 720 frames with an ω scan width of 0.50°, each for 15 s, with a crystal–detector distance 45 mm and a 0.8 mm collimator. A total of 11917 reflections ($3.0 < \theta < 27.5$) were collected, of which 6569 were unique (R_{int} = 0.0250). An empirical absorption correction using equivalent reflections and Lorentzian polarization was performed with the program Crystal Clear 1.3.6. T_{max} and T_{min} were 0.985 and 0.955, respectively. The structure was solved with the program SIR-92, and refined against F2 using SHELXL-97 to R = 0.0479 and wR_2 = 0.1336 for 4952 reflections with $I > 2\sigma(I)$, GoF = 1.173, R = 0.0627 for all reflections with 361 parameters; max/min residual electron density was 0.515 and −0.38 eÅ^3, respectively. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added geometrically. CCDC 1027854 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **6**: $C_{36}H_{50}N_{12}$, M = 650.88 gmol^{-1}, triclinic, space group P $\bar{1}$, a = 7.659(5) Å, b = 13.191(5) Å, c = 18.976(5) Å, α = 77.128(5) °, β = 83.248(5)°, γ = 79.800(5)°, V = 1833.3(15) Å^3, Z = 2, ρ = 1.179 gcm^{-3}, μ = 0.074 mm^{-1}, F(000) = 700.0, crystal size = 0.40 × 0.30 × 0.10 mm^3. Crystals of **6** were removed from the mother liquor, and cooled to 103 K on a Rigaku Saturn 724 CCD area detector system [λ(Mo$K\alpha$) = 0.7107 Å] with a graphite monochromator, which was used to record 720 frames with an ω scan width of 0.50°, each for 15 s, using a crystal–detector distance of 45 mm and a 0.5 mm collimator. A total of 14764 reflections ($3.0 < \theta < 27.5$) were collected, of which 8016 were unique (R_{int} = 0.0522). An empirical absorption correction using equivalent reflections and Lorentzian polarization was performed with the program Crystal Clear 1.3.6. T_{max} and T_{min} were 0.993 and 0.974, respectively. The structure was solved with the program SIR-92, and refined against F2 using SHELXL-97 to R = 0.0726 and wR_2 = 0.2305 for 4320 reflections with $I > 2\sigma(I)$, GoF = 1.014, R = 0.1188 for all reflections with 433 parameters; max/min residual electron density was 0.397 and −0.279 $eÅ^3$, respectively. All non-hydrogen atoms were added geometrically. CCDC 1027855 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

8. UV–vis–NIR spectroscopy

UV–vis–NIR spectra were recorded in solution with a JASCO V-570 spectrometer at 295 K. Quartz cells (optical path: 1.0 cm) were used for the measurement. Cryogenic temperature UV–vis–NIR spectra in solutions at 240 K were recorded with a spectrometer equipped with a UNISOKU temperature-variable unit.

9. Electrochemical measurements

Electrochemical experiments were performed with a CHI 750A electrochemical analyzer. The working electrode was a glassy carbon rod (3 mm ø) embedded in Pyrex glass; the counter electrode was a Pt wire, and reference electrode was Ag/Ag^+. Cyclic voltammetry was carried out at room temperature. All potentials are calibrated against Fc/Fc^+ redox couple (0.35 V vs Ag/AgCl).

10. ESR studies.

ESR spectra were recorded on a JEOL continuous wave X-band spectrometer (JES-RE2X) in the range 6.6–300 K. The sample was sealed in a quartz tube under vacuum. The magnetic field and *g* value were calibrated by the signals of a Mn^{2+} marker at $g = 2.034$ and 1.981. Spin concentration was calculated from the double integration value by comparison with a solid sample of 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 1 spin/molecule).

11. Magnetic measurement using SQUID magnetometer

The magnetization of $\mathbf{10}^{4+}$ was measured with a VHF SQUID Amplifier Model 2000. The powder product $\mathbf{10}^{4+}$ was quickly transferred to the capsule of the SQIUD magnetometer and measured at 2 K.

12. Other measurements and apparatus

^{1}H NMR spectra were recorded with a JEOL AL-400 or a Bruker DRX-500 spectrometer. Recycling preparative HPLC with a GPC column was performed by LC-908 (Japan Analytical Industry Co., Ltd., eluent: chloroform). ESI-TOF-MS spectra were recorded with a Micromass LCT time-of-flight mass spectrometer. Oxidant reagents were handled in a glove box filled with argon.

13. Cyclic voltammograms of **1**, **2**, and **3**

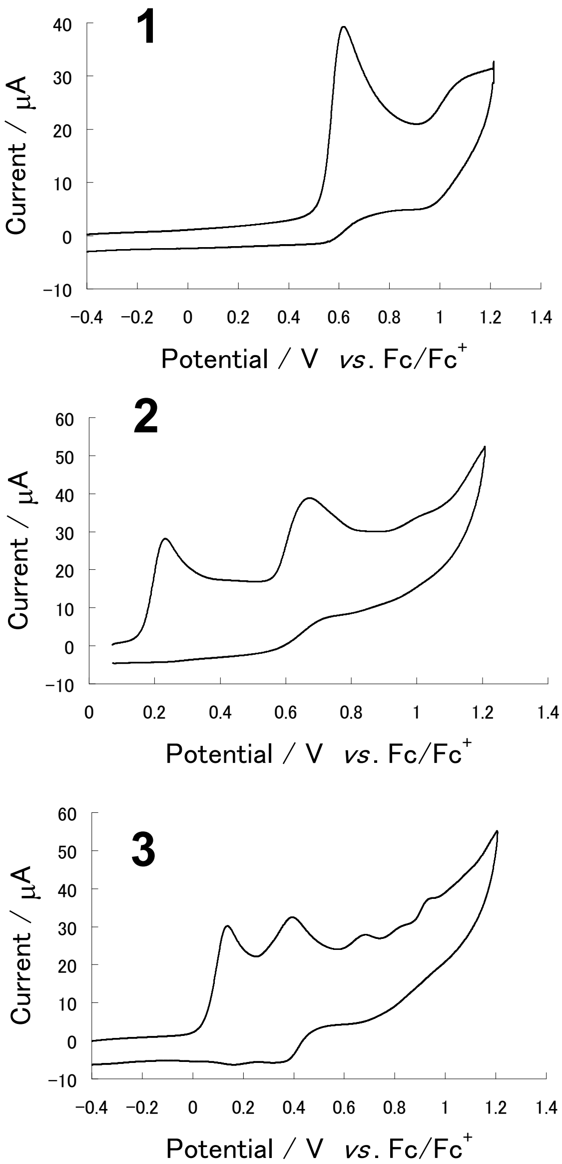

Figure S1. Cyclic voltammograms of **1**, **2**, and **3**.

14. Differential pulse voltammograms of 2, 4, 6, 8, 10, and 12

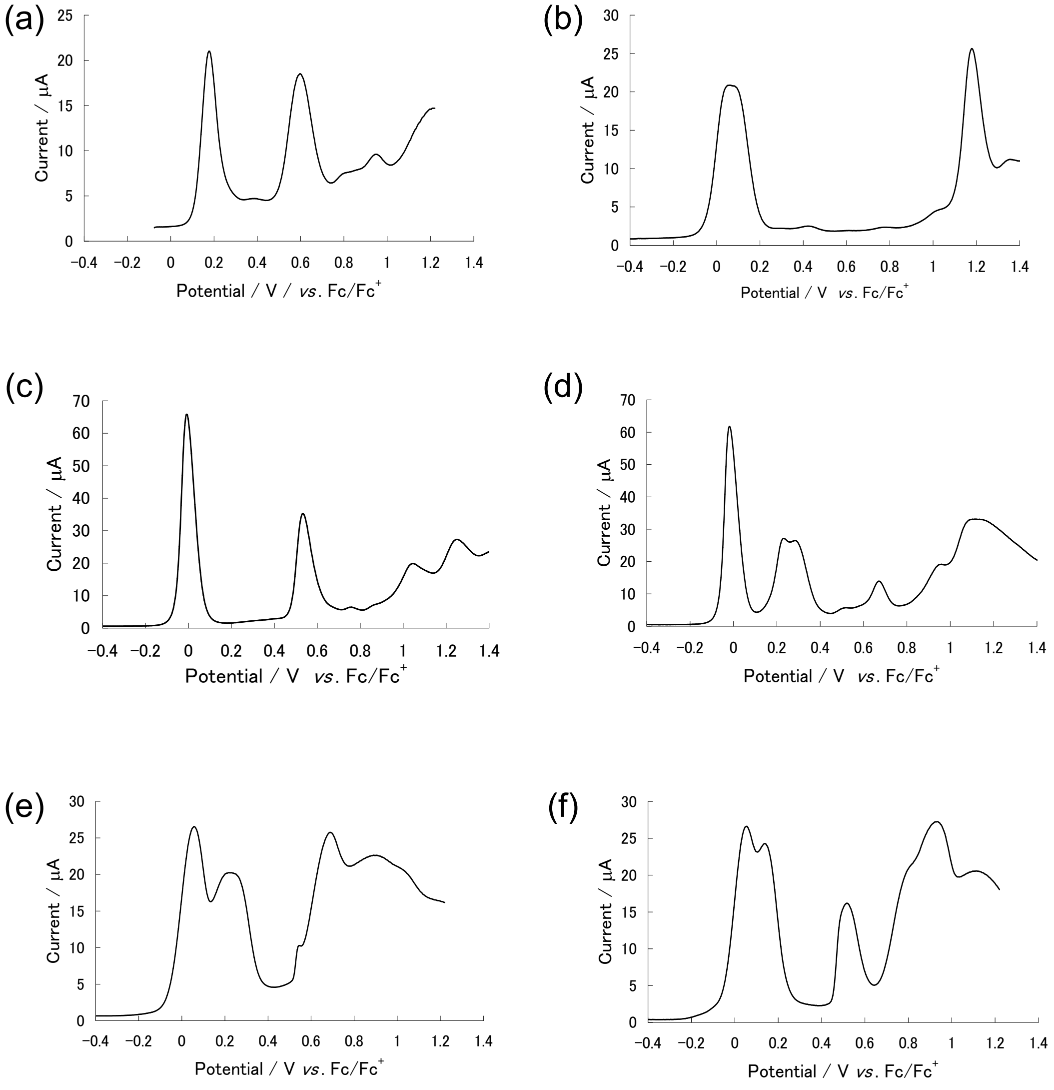

Figure S2. Differential pulse voltammograms of 1 mM **2**, **4**, **6**, **8**, **10**, and **12** in 0.1 M TBAP-CH_3CN.

15. Experimental and simulated cyclic voltammograms of 4, 6, and 8

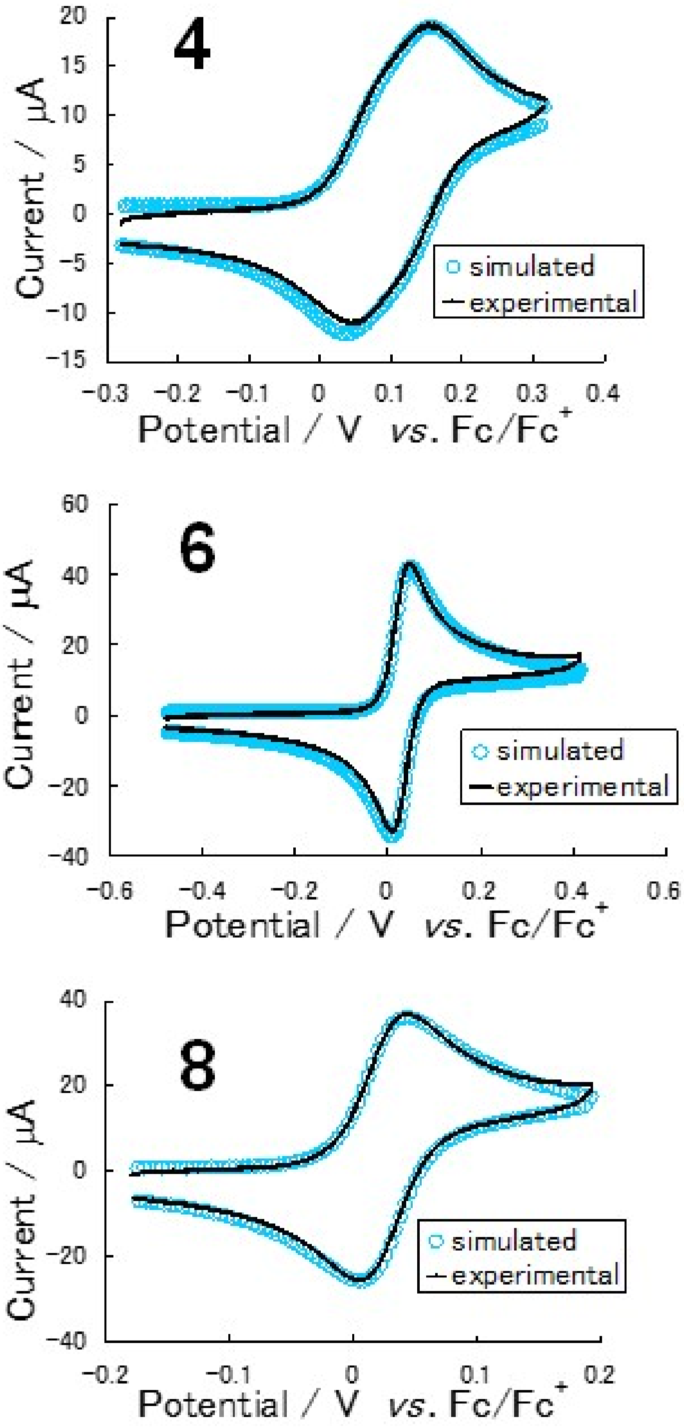

Figure S3. Experimental and simulated cyclic voltammograms of **4**, **6**, and **8**.

16. UV/vis/near-IR spectral changes by addition of $(4\text{-}BrC_6H_4)_3NSbCl_6$

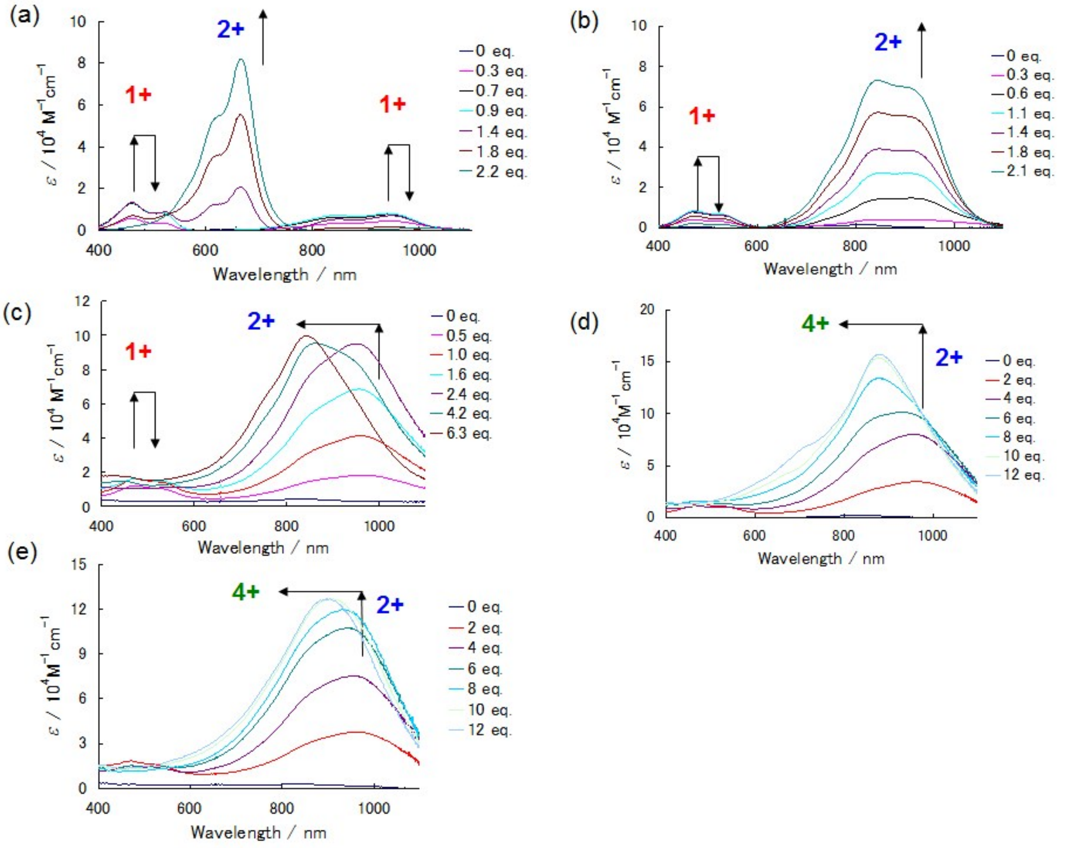

Figure S4. UV/vis/near-IR spectra of oxidized (a) **4**, (b) **6**, (c) **8**, (d) **10**, and (e) **12** by addition of $(4\text{-}BrC_6H_4)_3NSbCl_6$ in CH_3CN.

17. UV/vis/near-IR spectral changes at controlled potentials

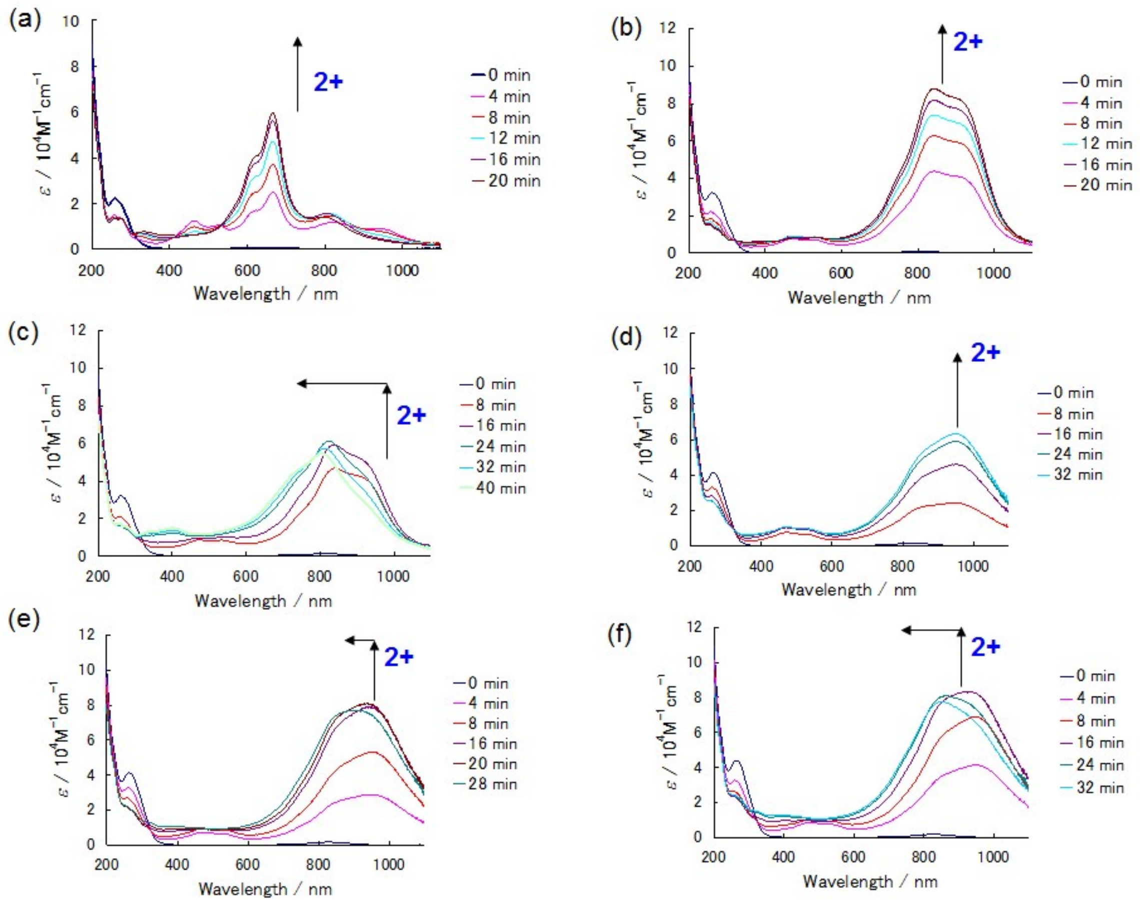

Figure S5. UV/vis/near-IR spectra of electrochemically oxidized (a) **4** at 1.0 V, (b) **6** at 0.6 V, (c) **6** at 1.0 V, (d) **8** at 0.3 V, (e) **8** at 0.75 V, and (f) **8** at 1.0 V.

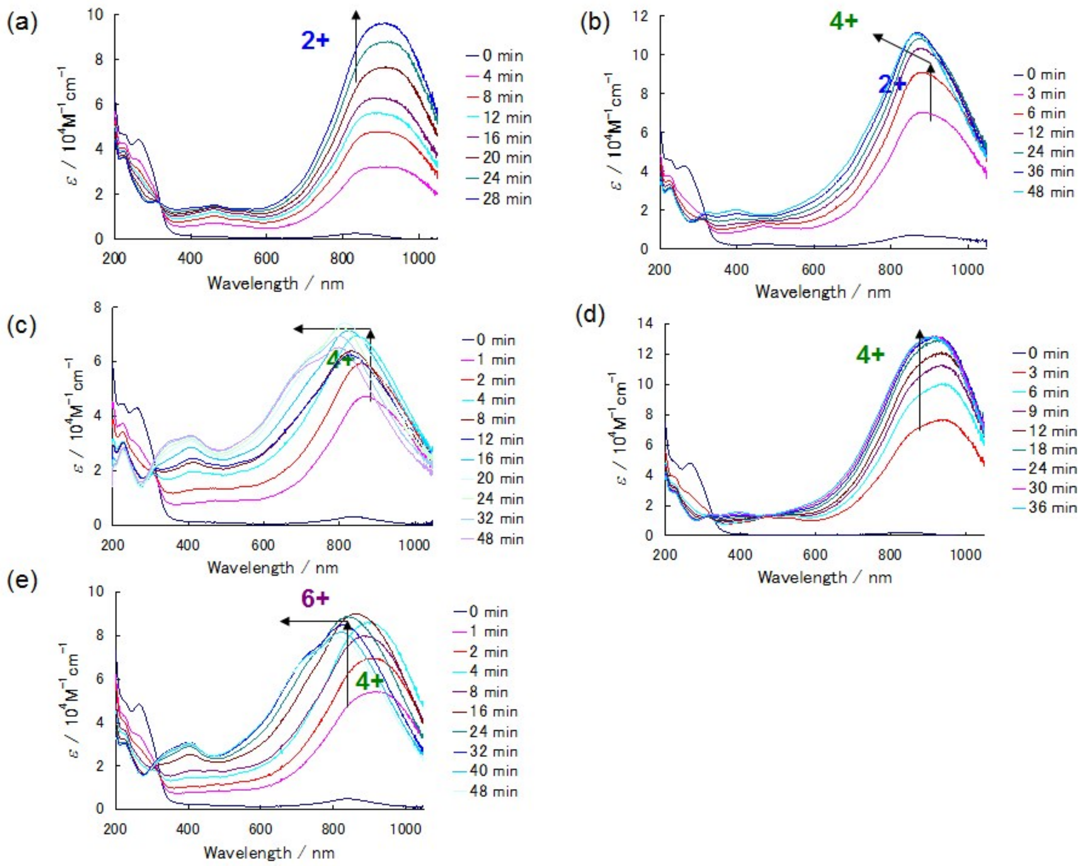

Figure S6. UV/vis/near-IR spectra of electrochemically oxidized (a) **10** at 0.28 V, (b) **10** at 0.6 V, (c) **10** at 1.0 V, (d) **12** at 0.5 V, and (e) **12** at 0.8 V.

18. Stability of $4^{2+}(SbCl_6^-)_2$, $6^{2+}(SbCl_6^-)_2$, and $8^{2+}(SbCl_6^-)_2$

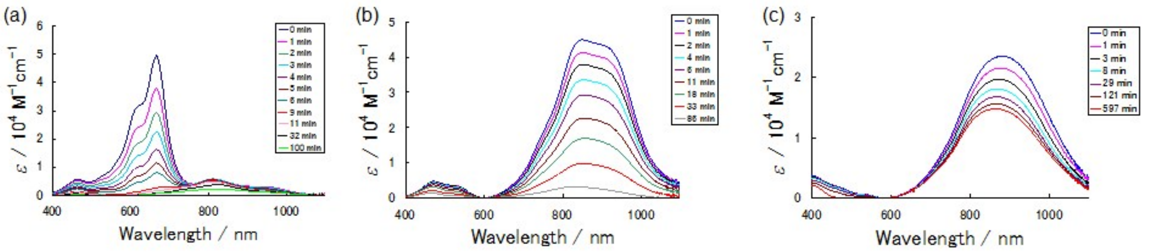

Figure S7. Changes in the UV/vis/near-IR spectra of (a) $\mathbf{4}^{2+}(SbCl_6^-)_2$, (b) $\mathbf{6}^{2+}(SbCl_6^-)_2$, and (c) $\mathbf{8}^{2+}(SbCl_6^-)_2$ with time in CH_3CN.