

Syntheses, Structures, and Electrochemical Properties of Platinum(II) Complexes Containing Di-*tert*-butylbipyridine and Crown Ether Annelated Dithiolate Ligands

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A series of new platinum(II) complexes containing both 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) and the extended tetrathiafulvalenedithiolate ligands have been prepared and characterized. These complexes include [Pt(dbbpy)-(C₈H₄S₈)] (**1**; C₈H₄S₈²⁻ = 2-{(4,5-ethylenedithio)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate), [Pt(dbbpy)(pdt)] (**2**; pdt = 2-{(4,5-cyclopentodithio)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate), [Pt(dbbpy)(mtdt)] (**3**; mtdt = 2-{(4,5-methylethylenedithio)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate), [Pt(dbbpy)(btdt)] (**4**; btdt = benzotetrathiafulvalenedithiolate), [Pt(dbbpy)(C₈H₆S₈)] (**5**; C₈H₆S₈²⁻ = 2-{4,5-bis(methylthio)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate), [Pt(dbbpy)(3O-C₆S₈)] (**6**; 3O-C₆S₈²⁻ = 2-{4,5-dithia-(3',6',9'-trioxaundecyl)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate), and [Pt(dbbpy)(4O-C₆S₈)] (**7**; 4O-C₆S₈²⁻ = 2-{4,5-dithia-(3',6',9',12'-tetraoxatetradecyl)-1,3-dithiol-2-ylidene}-1,3-dithiol-4,5-dithiolate). The crystal structures of a new ligand precursor (2-[4,5-dithia-(3',6',9',12'-tetraoxatetradecyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole, **IIIc**) and complexes **5–7** have been determined by X-ray crystallography. Complexes **1–7** show intense electronic absorption bands in the UV–vis region due to the intramolecular mixed metal/ligand-to-ligand charge-transfer transition, and they display significant solvatochromic behavior. Redox properties of these compounds have been investigated by cyclic voltammetry, and complex **7** shows a significant response for Na⁺ ions with a large positive shift of ca. 45 mV.

Introduction

Metal complexes with 1,2-dithiolene ligands have been extensively studied for their interesting properties and applications in areas such as conductivity, magnetism, nonlinear materials, and catalysis.^{1–5} Because intermolecular interaction through the S–S interatomic contact is a basic requirement for high conductivity. Metal complexes with more sulfur-rich dithiolate ligands such as those containing extended tetrathiafulvalenedithiolene have been of intense current interest. These complexes usually have a more

extended π -conjugation system, and this is important to improve their electrical conduction properties.^{6–10}

During the past couples of decades, much attention has been paid to the platinum diiminedithiolate complexes because they have interesting physical and spectroscopic properties that have served to stimulate interest in these systems.^{11–16} Planar sulfur-rich dithiolate metal complexes of the [Pt(NN)(SS)] type, with a diimine (NN) as a π -electron

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acceptor and a dithiolate ligand (SS) as an electron donor in the ground state, are known to exhibit intramolecular mixed metal/ligand-to-ligand charge-transfer (CT) bands.^{17–21} The CT excited-state properties of the [Pt(NN)(SS)] complexes have been widely used in multicomponent assemblies for photoinduced charge separation and molecular photochemical devices for light-drive, energy-storing reactions. The utilization of such systems in metal ion sensing is, however, rare.²² In the study of host–guest chemistry, redox-active ligand systems are of critical importance in the area of electrochemically controlled uptake and release of guest metal cations.^{23–25} The incorporation of crown ether units with special organic motifs (such as TTF or their derivatives, where TTF = tetrathiafulvalene) has been used to give sensor materials with high sensitivity and selectivity for metal ion sensing based on electrochemistry or fluorescence signaling.^{26–31} However, only a limited number of dithiolene complexes with crown ether groups have been reported.^{32,33}

In the current work, for the first time, novel crown ether annelated dithiolates are introduced into the [Pt(NN)(SS)] system. Herein we describe the synthesis and properties of

seven new platinum diiminedithiolate complexes **1–7** (Chart 1). Three typical examples of the complexes have been structurally characterized. O₄S₂ crown ether annelated platinum(II) diiminedithiolate complex **7** shows a significant positive shift upon the addition of alkali-metal ions Na⁺, and it has no response to other alkali cations Li⁺ and K⁺.

Experimental Section

General Procedure. All of the commercial reagents used were analytically pure and without further purification. Schlenk techniques were used in carrying out manipulation under a nitrogen atmosphere. The compound (dbbpy)PtCl₂ (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) was prepared by the literature method.³⁴ The proligand compounds, such as C₈H₄S₈(CH₂CH₂CN)₂, ptdt(CH₂CH₂CN)₂, bttdt(CH₂CH₂CN)₂, 5-bis(methylthio)-1,3-dithiole-2-thione (**Ia**), 5,8,11-trioxa-2,14,16,18-tetrathiabicyclo[13.3.0]octadec-1(15)-ene-17-thione (**Ib**), 5,8,11,14-tetraoxa-2,17,19,21-tetrathiabicyclo[16.3.0]heneicos-1(15)-ene-17-thione (**Ic**), and 5-bis(2-cyanoethylthio)-1,3-dithiole-2-one (**II**), were synthesized as described in the literature.^{7,31,35} The compound mtdt(CH₂CH₂CN)₂ was prepared by a method similar to that of C₈H₄S₈(CH₂CH₂CN)₂.

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were taken on a Vector22 Bruker spectrophotometer (400–4000 cm⁻¹) with KBr pellets. UV–vis spectra were recorded on a UV-3100 spectrophotometer. NMR spectra were measured on a Bruker AM 500 spectrometer. Chemical shifts were measured as δ units (ppm) relative to tetramethylsilane. Melting points were determined with a X-4 digital micro melting point apparatus and were uncorrected. Mass spectra were recorded on a Bruker Autoflex II TOF/TOF spectrometer or on a Varian MAT 311A instrument. Cyclic voltammetry (CV) experiments were performed on a CHI660b electrochemistry workstation with a three-electrode system. A platinum electrode, a platinum wire, and Ag/AgNO₃/acetonitrile were used as the working, auxiliary, and reference electrodes, respectively. CV measurements were made in a CH₂Cl₂/CH₃CN (1:1, v/v) solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

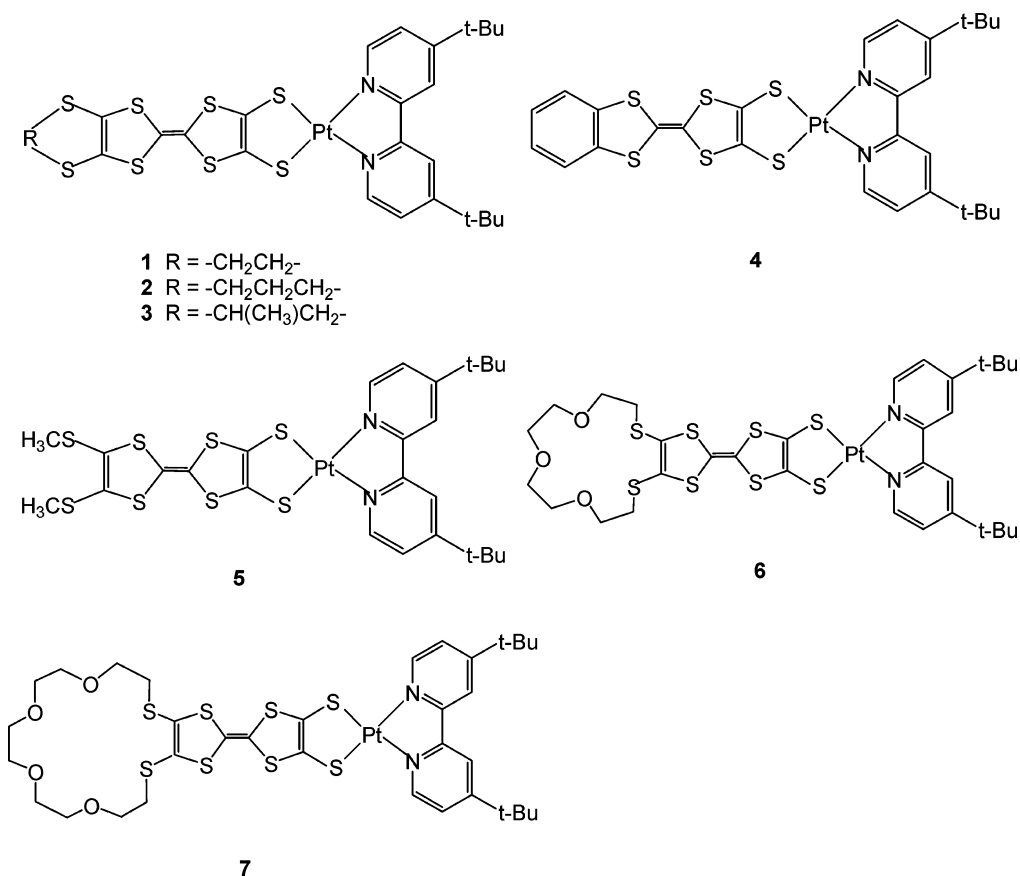
Synthesis. 2-[4,5-Bis(2-methylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (IIIa). Following the procedure of Becher et al.,³¹ the coupling reaction of compounds **Ia** and **II** was conducted in neat P(OEt)₃ and the mixture was heated to 110 °C. After 1.5 h, the red solution was cooled to room temperature. A crude precipitate was obtained at –20 °C, and it was dissolved in dichloromethane. Pure bis(protected) compound **IIIa** was isolated as an orange solid after separation by silica gel column chromatography. Yield: 53%. IR (KBr, ν_{max}, cm⁻¹): 1410 (C–S), 1634 (C=C), 2249 (C≡N). ¹H NMR (500 MHz, CDCl₃, δ): 2.49 (6H, s), 2.77 (4H, t), 3.12 (4H, t). MS (MALDI-TOF, *m/z*): 465.7 (M⁺). Anal. Calcd for C₁₄H₁₄N₂S₈: C, 36.02; H, 3.02; N, 6.00. Found: C, 36.18; H, 2.99; N, 6.08.

2-[4,5-Dithia-(3',6',9'-trioxaundecyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (IIIb). A procedure similar to that in the preparation of **IIIa** was used. Mixing of compounds **Ib** and **II** in neat P(OEt)₃ and refluxing of the mixture gave the crude product. After isolation by silica gel column chromatography,

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Chart 1



IIIb was obtained as an orange-red solid. Yield: 38%. IR (KBr, ν_{\max} , cm⁻¹): 1120 (C–O), 1410 (C–S), 1636 (C=C), 2247 (C≡N). ¹H NMR (500 MHz, CDCl₃, δ): 2.81 (4H, t), 3.06 (4H, t), 3.14 (4H, t), 3.71 (8H, m), 3.83 (4H, t). MS (MALDI-TOF, m/z): 595.8 (M⁺). Anal. Calcd for C₂₀H₂₄N₂O₃S₈: C, 40.27; H, 4.03; N, 4.70. Found: C, 40.15; H, 4.09; N, 4.76.

2-[4,5-Dithia-(3',6',9',12'-tetraoxatetradecyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (IIIc). A procedure similar to that in the preparation of **IIIa** was used. Mixing of compounds **Ic** and **II** in neat P(OEt)₃ and refluxing of the mixture gave the crude product. After isolation by silica gel column chromatography, **IIIc** was obtained as an orange-red solid. Yield: 34%. IR (KBr, ν_{\max} , cm⁻¹): 1126 (C–O), 1417 (C–S), 1638 (C=C), 2246 (C≡N). ¹H NMR (500 MHz, CDCl₃, δ): 2.78 (4H, t), 3.07 (4H, t), 3.12 (4H, t), 3.71 (12H, m), 3.77 (4H, t). MS (MALDI-TOF, m/z): 639.7 (M⁺). Anal. Calcd for C₂₂H₂₈N₂O₄S₈: C, 41.28; H, 4.39; N, 4.38. Found: C, 41.35; H, 4.51; N, 4.47.

[Pt(dbbpy)(C₈H₄S₈)] (1). Under a nitrogen atmosphere, compound C₈H₄S₈(CH₂CH₂CN)₂ (138 mg, 0.3 mmol) was added to 20 mL of an ethanol solution of NaOEt (68 mg, 1 mmol) at 20 °C. The reaction mixture was left stirring for 1 h and changed to dark red. A suspension of (dbbpy)PtCl₂ (160 mg, 0.3 mmol) in 25 mL of dimethyl sulfoxide (DMSO) was added, the resulting dark-blue product was collected by filtration after 30 min and washed with water, methanol, and ether. The yield was 140 mg (58%). IR (KBr, ν_{\max} , cm⁻¹): 3426(s), 2964(m), 1615(m), 1416(m), 1128(w), 1029(s), 874(m), 835(w), 769(m), 597(m). ¹H NMR (500 MHz, DMSO-*d*₆, 50 °C, δ): 1.42 (18H, s, ^tBu), 3.39 (4H, s, SCH₂), 7.75 (2H, d, *J*_{HH} = 5.5 Hz, Hdbbpy), 8.60 (2H, s, Hdbbpy), 8.74 (2H, d, *J*_{HH} = 5 Hz, Hdbbpy). ESI-MS (m/z): 819.7 (M⁺). Anal. Calcd for PtC₂₆H₂₈N₂S₈: C, 38.08; H, 3.44; N, 3.42. Found: C, 38.22; H, 3.50; N, 3.47.

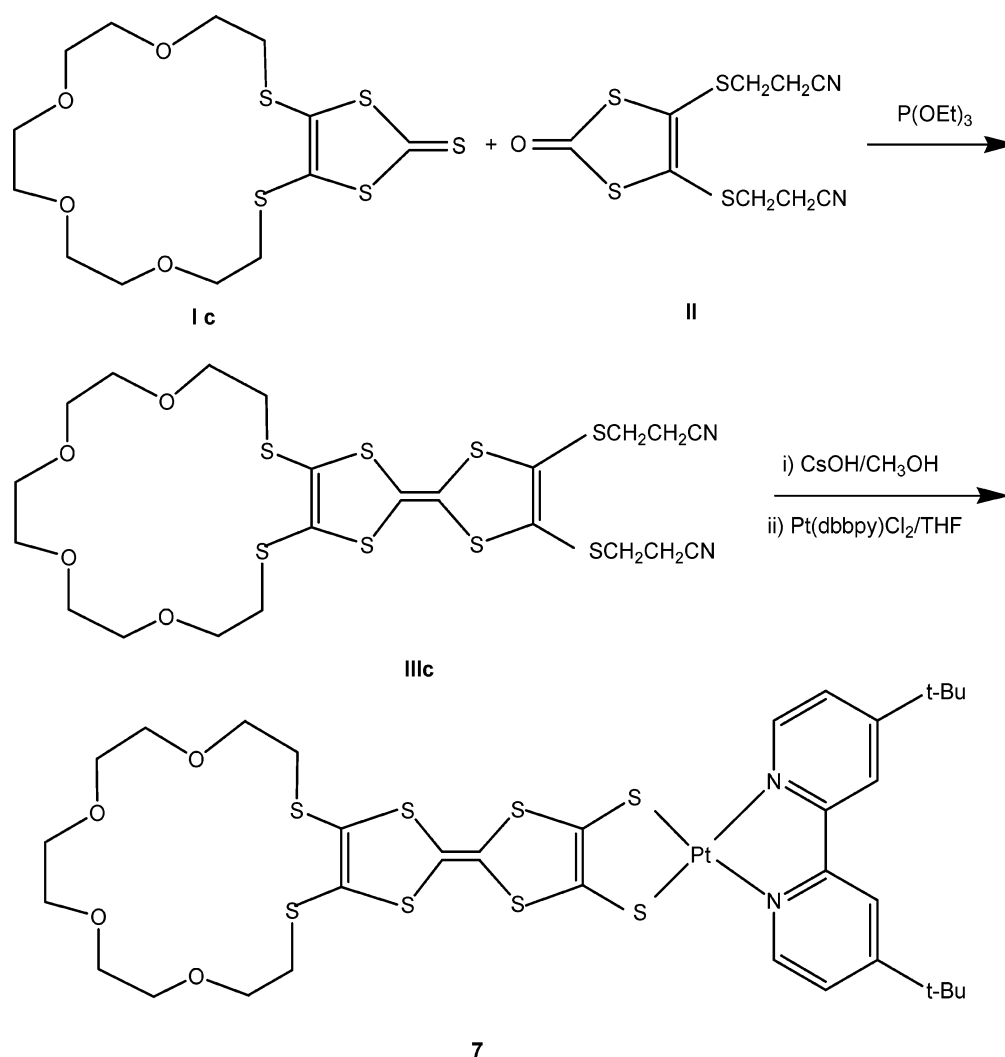
[Pt(dbbpy)(ptdt)] (2). Compound **2** was obtained by a method similar to the preparation of **1** using ptdt(CH₂CH₂CN)₂ instead of C₈H₄S₈(CH₂CH₂CN)₂. Yield: 52%. IR (KBr, ν_{\max} , cm⁻¹): 3443(s), 2959(s), 1615(m), 1449(s), 1368(m), 1031(w), 880(m), 835(w), 768(m), 596(m). ¹H NMR (500 MHz, DMSO-*d*₆, 50 °C, δ): 1.44 (18H, s, ^tBu), 2.04 (2H, m, CH₂), 2.78 (4H, d, SCH₂), 7.75 (2H, d, *J*_{HH} = 5 Hz, Hdbbpy), 8.59 (2H, s, Hdbbpy), 8.75 (2H, d, *J*_{HH} = 6 Hz, Hdbbpy). ESI-MS (m/z): 833.9 (M⁺). Anal. Calcd for PtC₂₇H₃₀N₂S₈: C, 38.89; H, 3.63; N, 3.36. Found: C, 38.82; H, 3.55; N, 3.41.

[Pt(dbbpy)(mtdt)] (3). Compound **3** was obtained by a method similar to the preparation of **1** using mtdt(CH₂CH₂CN)₂ instead of C₈H₄S₈(CH₂CH₂CN)₂. Yield: 55%. IR (KBr, ν_{\max} , cm⁻¹): 3441(s), 2960(s), 1617(m), 1449(s), 1368(m), 1029(s), 880(m), 835(w), 768(m), 597(m). ¹H NMR (500 MHz, DMSO-*d*₆, 50 °C, δ): 1.41 (3H, d, CH₃), 1.44 (18H, s, ^tBu), 3.39 (2H, d, SCH₂), 3.83 (1H, m, SCH), 7.75 (2H, d, *J*_{HH} = 6 Hz, Hdbbpy), 8.61 (2H, s, Hdbbpy), 8.74 (2H, d, *J*_{HH} = 6 Hz, Hdbbpy). ESI-MS (m/z): 833.9 (M⁺). Anal. Calcd for PtC₂₇H₃₀N₂S₈: C, 38.89; H, 3.63; N, 3.36. Found: C, 38.75; H, 3.55; N, 3.44.

[Pt(dbbpy)(btdt)] (4). Compound **4** was obtained by a method similar to the preparation of **1** using btdt(CH₂CH₂CN)₂ instead of C₈H₄S₈(CH₂CH₂CN)₂. Yield: 45%. IR (KBr, ν_{\max} , cm⁻¹): 3449(s), 2962(s), 1615(m), 1445(s), 1416(s), 1252(s), 1120(s), 1029(m), 873(m), 832(s), 770(s), 741(s), 596(m). ¹H NMR (500 MHz, DMSO-*d*₆, 50 °C, δ): 1.44 (18H, s, ^tBu), 7.20 (2H, m, Ph), 7.49 (2H, m, Ph), 7.75 (2H, d, *J*_{HH} = 6.2 Hz, Hdbbpy), 8.61 (2H, s, Hdbbpy), 8.76 (2H, d, *J*_{HH} = 6 Hz, Hdbbpy). ESI-MS (m/z): 779.0 (M⁺). Anal. Calcd for PtC₂₈H₂₈N₂S₆: C, 43.12; H, 3.62; N, 3.59. Found: C, 43.35; H, 3.66; N, 3.64.

[Pt(dbbpy)(C₈H₆S₈)] (5). Compound **5** was obtained by a method similar to the preparation of **1** using **IIIa** instead of

Scheme 1



$\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$. Yield: 58%. IR (KBr, ν_{max} , cm^{-1}): 3426(s), 2969(m), 1619(m), 1417(m), 1087(w), 1049(s), 879(m), 824(w), 770(m), 594(m). $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 1.46 (18H, s, 'Bu), 2.45 (6H, s, CH_3), 7.45 (2H, d, $J_{\text{HH}} = 6$ Hz, Hdbbpy), 7.92 (2H, s, Hdbbpy), 8.91 (2H, d, $J_{\text{HH}} = 6$ Hz, Hdbbpy). ESI-MS (m/z): 821.9 (M^+). Anal. Calcd for $\text{PtC}_{26}\text{H}_{30}\text{N}_2\text{S}_8 \cdot \text{H}_2\text{O}$: C, 37.17; H, 3.84; N, 3.33. Found: C, 37.32; H, 3.73; N, 3.47.

[Pt(dbbpy)(3O-C₆S₈)] (6). Under a nitrogen atmosphere, compound **IIIb** (59.6 mg, 0.1 mmol) was added to a methanol solution of CsOH (33.6 mg, 0.2 mmol) at 20 °C. After the reaction mixture was stirred for 1 h, a suspension of (dbbpy)PtCl₂ (53.4 mg, 0.1 mmol) in 15 mL of tetrahydrofuran (THF) was added. A dark-blue product was collected by filtration after 30 min of stirring and the solid washed with water, methanol, and ether. The yield was 40 mg (42%). IR (KBr, ν_{max} , cm^{-1}): 3441(s), 2963(s), 1618(s), 1416(m), 1121(s), 1031(w), 881(m), 824(w), 769(m), 597(m). $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 1.47 (18H, s), 2.96 (4H, t), 3.66 (4H, t), 3.71 (4H, t), 3.80 (4H, t), 7.48 (2H, s), 7.95 (2H, s), 8.84 (2H, s). δ_c (CDCl_3/TMS): 30.37, 35.73, 70.13, 70.65, 71.54, 76.77, 77.03, 77.28, 119.57, 124.98, 128.26, 148.28, 155.59, 163.31. ESI-MS (m/z): 951.8 (M^+), 958.8 ($\text{M} + \text{Li}^+$). Anal. Calcd for $\text{PtC}_{32}\text{H}_{40}\text{N}_2\text{O}_3\text{S}_8 \cdot 1.5\text{H}_2\text{O}$: C, 39.25; H, 4.42; N, 2.86. Found: C, 39.37; H, 4.45; N, 2.91.

[Pt(dbbpy)(4O-C₆S₈)] (7). Compound **7** was obtained by a method similar to the preparation of **6** using **IIIc** instead of **IIIb**.

Yield: 52%. IR (KBr, ν_{max} , cm^{-1}): 3423(s), 2962(s), 1617(m), 1416(m), 1116(s), 1029(w), 879(m), 848(w), 769(m), 596(m). $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 1.47 (18H, s), 3.03 (4H, t), 3.65 (4H, s), 3.69 (8H, s), 3.78 (4H, t), 7.47 (2H, s), 7.95 (2H, s), 8.86 (2H, s). δ_c (CDCl_3/TMS): 30.73, 35.79, 36.17, 70.22, 70.71, 71.14, 76.97, 77.40, 77.82, 119.91, 125.76, 148.73, 155.90, 163.37. ESI-MS (m/z): 995.9 (M^+), 1018.7 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{PtC}_{34}\text{H}_{44}\text{N}_2\text{O}_4\text{S}_8$: C, 40.96; H, 4.45; N, 2.81. Found: C, 40.87; H, 4.49; N, 2.87.

X-ray Structure Determination. For compounds **5–7** and **IIIc**, single crystals suitable for the X-ray structure analysis were obtained from dichloromethane/diethyl ether. The data were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation using a ω - 2θ scan mode at 293 K. The highly redundant data sets were reduced using *SAINTE* and corrected for Lorentz and polarization effects. Absorption corrections were applied using *SADABS* supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using *SHELXTL-97*. All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} .

Table 1. Crystal Data and Structure Refinement for Compounds **IIIc** and **5–7**

	IIIc	5	6	7
empirical formula	C ₂₂ H ₂₈ N ₂ O ₄ S ₈	PtC ₂₆ H ₃₂ N ₂ O ₈ S ₈	Pt ₂ C ₆₄ H ₈₆ N ₄ O ₉ S ₁₆	PtC ₃₄ H ₄₄ N ₂ O ₄ S ₈
fw	640.94	840.11	1958.51	996.28
<i>T</i> , K	293	293	293	293
<i>μ</i> , Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> 21/ <i>c</i>
<i>a</i> , Å	9.6569(19)	22.696(6)	40.239(11)	24.79(4)
<i>b</i> , Å	10.571(2)	10.693(3)	13.491(4)	11.45(2)
<i>c</i> , Å	16.174(3)	14.954(4)	8.126(2)	14.39(3)
α , deg	95.221(4)	90	90	90
β , deg	97.852(4)	100.844(5)	99.236(7)	95.57(4)
γ , deg	116.704(4)	90	90	90
<i>V</i> , Å ³	1439.3(5)	3564.5(17)	4354(2)	4065(13)
<i>Z</i>	2	4	2	4
<i>D</i> , g cm ⁻³	1.479	1.565	1.494	1.629
<i>μ</i> , mm ⁻¹	0.652	4.427	3.641	3.903
<i>F</i> (000)	668	1664	1964	2000
θ range, deg	1.29–26.00	1.83–26.00	1.59–26.00	1.96–26.00
reflns colld	13 125	18 586	11 830	21 402
indep reflns	5644	6964	4471	7923
data/restraints/ param	5644/0/325	6964/0/369	4471/0/233	7923/0/448
GOF on <i>F</i> ²	1.015	1.103	1.084	1.012
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0654, <i>wR</i> 2 = 0.1331	<i>R</i> 1 = 0.0574, <i>wR</i> 2 = 0.1279	<i>R</i> 1 = 0.0494, <i>wR</i> 2 = 0.0855	<i>R</i> 1 = 0.0545, <i>wR</i> 2 = 0.1216
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0992, <i>wR</i> 2 = 0.1432	<i>R</i> 1 = 0.0832, <i>wR</i> 2 = 0.1338	<i>R</i> 1 = 0.0727, <i>wR</i> 2 = 0.0898	<i>R</i> 1 = 0.0818, <i>wR</i> 2 = 0.1297
largest diff peak, hole, e Å ⁻³	0.241, -0.491	0.760, -2.570	1.855, -1.896	0.641, -1.400

Results and Discussions

Synthesis and Characterization. The ligand precursors **Ia–Ic** were synthesized by a previously reported route. The high-dilution method was essential to improve the yields of compounds **Ib** and **Ic**.³¹ The compounds C₈H₄S₈(CH₂CH₂CN)₂, ptdt(CH₂CH₂CN)₂, btdt(CH₂CH₂CN)₂, mtdt(CH₂CH₂CN)₂, and **IIIa–IIIc** were prepared by the standard triethyl phosphite mediated cross-coupling reaction and separated by silica gel column chromatography. They were characterized by melting points, IR, elemental analyses, ¹H NMR, and mass spectrometry. By reaction of their alkali-metal salts with the diimine compounds (dbbpy)PtCl₂, respectively, **1–7** were conveniently prepared in moderate yields (42–58%; Scheme 1).

The introduction of a bulky organic group, such as *tert*-butyl here, into 2,2'-bipyridine usually significantly increases the solubility of the resulting complexes. According to our experience, metal complexes with the extended tetrathiafulvalenedithiolate ligands have lower solubility compared with those of dmit analogues. As expected, the complexes reported here are soluble in most organic solvents but insoluble in ether, alcohol, pentane, and hexane. This makes their characterization possible. Several spectroscopy methods, such as electronic, IR, and ¹H and ¹³C NMR, have been used to characterize these samples. Moreover, single crystals for some typical compounds, **5–7** and **IIIc**, were successfully isolated and structurally characterized. All complexes are air-stable in both solution and solid state at room temperature.

¹H NMR spectra for complexes **6** and **7** show three resonances at δ 7.48/7.47, 7.95, and 8.84/8.86, respectively, of the aromatic protons of the dbbpy ligand. A resonance at

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compounds **5–7** and **IIIc**

bond lengths		bond angles	
Compound IIIc			
C9–C10	1.328(6)	C10–C9–S3	122.4(3)
C9–S3	1.736(5)	C9–C10–S5	123.3(3)
C10–S6	1.766(4)	S3–C9–S4	114.8(3)
C11–C12	1.374(6)	S5–C10–S6	113.5(3)
C7–S3	1.741(4)	C9–S3–C7	96.4(2)
C7–C8	1.368(5)	C11–S6–C10	95.7(2)
Compound 5			
Pt1–N1	2.043(6)	N2–Pt1–N1	78.0(2)
Pt1–N2	2.032(6)	N1–Pt1–S1	96.93(17)
Pt1–S1	2.260(2)	N2–Pt1–S2	95.17(16)
Pt1–S2	2.263(2)	S1–Pt1–S2	90.21(8)
S1–C1	1.682(9)	N2–Pt1–S1	173.33(16)
C3–C4	1.345(11)	N1–Pt1–S2	171.90(14)
Compound 6			
N1–Pt1	2.010(4)	N1–Pt1–N1 ^a	77.5(2)
Pt1–S1	2.2552(14)	N1–Pt1–S1	96.25(13)
C11–C12	1.402(12)	N1–Pt1–S1 ^a	173.80(13)
		C11–C12–S3	122.3(2)
Compound 7			
N1–Pt1	2.058(6)	N2–Pt1–N1	78.4(3)
N2–Pt1	2.014(6)	N1–Pt1–S2	95.98(19)
Pt1–S2	2.253(3)	S2–Pt1–S1	90.18(12)
Pt1–S1	2.272(3)	N2–Pt1–S1	95.5(2)
C1–C2	1.407(11)	N2–Pt1–S2	174.22(19)
C3–C4	1.298(10)	N1–Pt1–S1	173.55(16)

^a Symmetry operation: *x*, -*y* + 1, *z*.

δ 1.47 is assigned to the dbbpy methyl protons. The resonances of protons in the crown cycles are in good agreement with their structures. The mass spectral data of all compounds are provided in the Experimental Section and agree well with their structures.

Structural Description. The crystallographic and data collection parameters for compounds **IIIc** and **5–7** are given

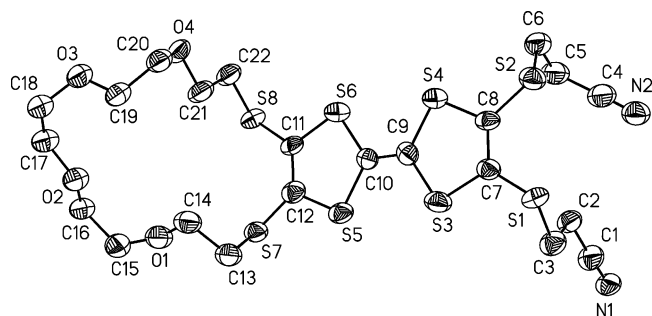


Figure 1. ORTEP view of **IIIc** with an atom-numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

in Table 1. Selected bond lengths and angles are listed in Table 2. Complete lists of refined positional and thermal parameters and bond distances and angles are given in the Supporting Information.

A perspective view of the asymmetric unit with the atom-numbering scheme for the ligand precursor **IIIc** is shown in Figure 1. The macrocycle adopts a crown conformation, which is favored for the metal coordination as some other TTF/monocrown compounds. The S_2O_4 crown ether group is bent toward one side of the TTF unit(s), nearly vertical to the plane of the TTF C_2S_4 core. In the TTF unit, the conjugated π system of this molecule is extended to all of the eight sulfur atoms. The two cyanoethyl groups in compound **IIIc** are greatly deviated from this plane and bent toward the same direction. Along the b axis, the neighboring two molecules form the “dimer” through the shorter intermolecular $S\cdots S$ contacts between $S5\cdots S5'$ [3.694(2) Å; symmetry operator, $1 - x, -y, 2 - z$], which are less than the sum of the van der Waals radii (3.70 Å). The shortest intermolecular $S\cdots S$ interactions between the “dimers” exist between $S1\cdots S6'$ [3.674(2) Å] and $S3\cdots S8'$ [3.635(2) Å; related by the symmetry operators of $1 + x, y, z$; Figure S1 in the Supporting Information], which leads to the one-dimensional chain structure.

The square-planar geometry around platinum in complexes **5–7** was confirmed by single-crystal X-ray diffraction. **6** and **7** represent the first structurally characterized, crown ether annelated sulfur-rich dithiolate systems.

The molecular structures of complexes **5–7** are shown in Figures 2–4, respectively. Each complex consists of a square-planar platinum(II) ion with two chelating ligands: one is dbbpy, and the other is an extended TTF ligand as expected. The average Pt–N distance of 2.028(6) Å in the complexes agrees well with those of other platinum diimine complexes, such as 2.052(3), 2.060(10), and 2.040(5) Å in (dbbpy)Pt(dmtd),²² [Pt(bipy)($C_8H_4S_8$)] $[BF_4]$ (bipy = 2,2'-bipyridine),³⁷ and Pt(dbbpy)($C\equiv CC_6H_4CH_3$)₂,³⁶ respectively. The average Pt–S distance in all of the structures reported here is 2.260(3) Å, and this is in good agreement with the previously reported Pt–S distances of 2.264(1) and 2.269(7) Å for (dbbpy)Pt(dmtd) and [Pt(bipy)($C_8H_4S_8$)] $[BF_4]$, respectively. The deviation from a square-planar geometry

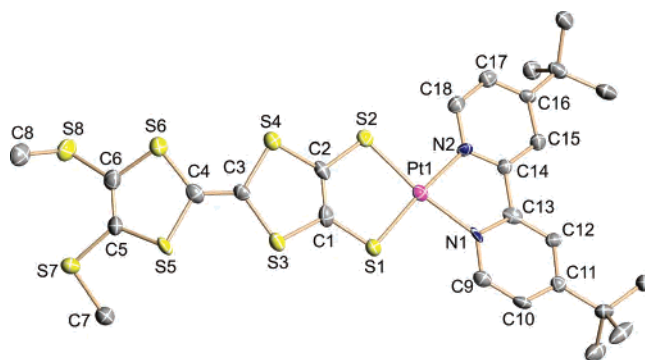


Figure 2. ORTEP view of complex **5** with an atom-numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

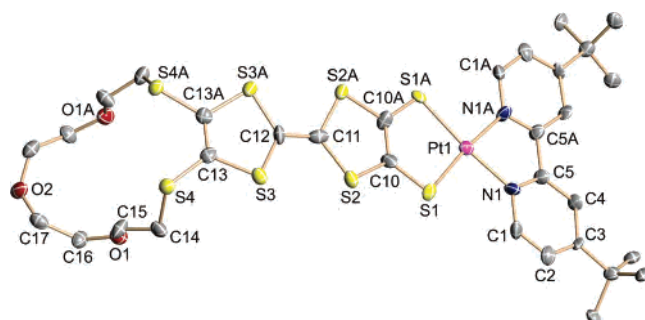


Figure 3. ORTEP view of complex **6** with an atom-numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

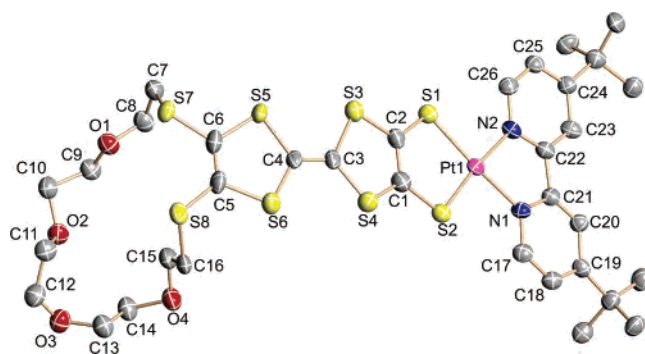


Figure 4. ORTEP view of complex **7** with an atom-numbering scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

for platinum(II) is relatively minor, with a mean S–Pt–S angle of 90.11° and an average N–Pt–N bite angle of 78.0(2)°, the latter resulting from the built-in constraint of the chelated dbbpy ligand.

In complex **5**, the neighboring molecules are stacked in a head-to-tail arrangement and form the “dimer” structure through the shorter Pt \cdots N contact [3.586 Å; Pt1 \cdots N2'; symmetry operator, $1 - x, 2 - y, -z$; Figure S2 in the Supporting Information]. The shortest Pt \cdots Pt distance is 4.394 Å. In complex **6**, the individual molecules are stacked in a head-to-tail arrangement as shown in Figure S3 in the Supporting Information. The nearest Pt \cdots Pt distance is 3.656 Å, and the nearest Pt \cdots N distance is 3.915. Then the molecules are arranged with an overlap in the same molecular orientation to form a columnar structure along the c axis. No obvious intramolecular Pt \cdots S or S \cdots S interactions were

(37) Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G. *Inorg. Chim. Acta* **2002**, *336*, 120.

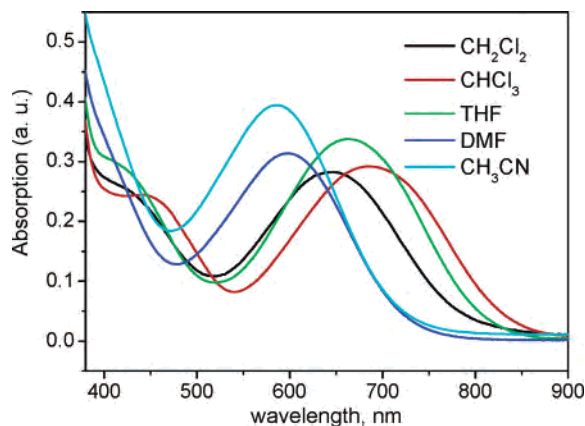


Figure 5. Charge-transfer-to-diimine absorption band for complex **5** in (a) CH_2Cl_2 , (b) CHCl_3 , (c) THF, (d) dimethylformamide (DMF), and (e) CH_3CN .

Table 3. Absorption Bands for Complex **5** as a Function of Different Solvents

solvent	UV-vis λ_{max} , nm	ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$
CH_3CN	586	1.643
	290	13.640
	229	14.008
DMF	598	1.307
	294	11.223
CH_2Cl_2	644	1.569
	297	13.565
	231	13.097
THF	662	1.408
	300	12.166
CHCl_3	683	1.216
	300	11.061
	245	9.009

detected in the structure. For complex **7**, the shortest Pt...Pt distance is 4.129 Å and the nearest Pt...N distance is 3.622 Å. The molecules of complex **7** form no columnar association as complex **5**. In complexes **6** and **7**, the crown ether group is bent toward one side of the TTF unit(s), nearly vertical to the plane of the metal platinum(II) core.

Absorption Spectra. The absorption spectra of all of the complexes **1–7** were measured, and all exhibit continuous UV-vis absorption bands in a fluid solution at room temperature. The CT absorption bands for a typical complex **5** in five solvents with different polarities are shown in Figure 5, and the results are summarized in Table 3. The large solubility of this complex in a variety of organic solvents made it possible to study in detail its solvatochromic behavior. In degassed acetonitrile, the two UV bands at 229 and 290 nm (in acetonitrile) have molar extinction coefficients (ϵ) of 140 080 and 136 400 $\text{M}^{-1} \text{ cm}^{-1}$ and are assigned to ligand-based transitions. The third band is observed in the visible region of the spectrum at 586 nm ($\epsilon = 16 430 \text{ M}^{-1} \text{ cm}^{-1}$). The positions of the lowest-energy absorption maxima for the complexes in the current work were found to depend on the solvent, and their solvatochromic properties are similar. Because the solvatochromic shifts yield information regarding the nature of the excited state, solvatochromic measurements were conducted for each complex. As the solvent polarity decreases, the strong band at 586 nm in MeCN shifts to lower energy, and this

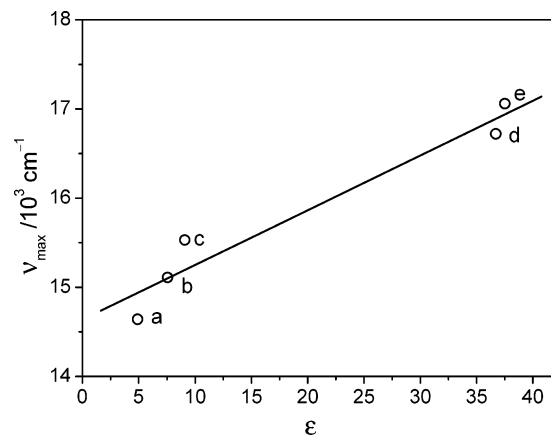


Figure 6. Plots of frequencies of the ligand-to-ligand CT absorption band maxima (ν_{max}) of complex **5** versus dielectric constants (ϵ) of solvents: (a) CHCl_3 ; (b) THF; (c) CH_2Cl_2 ; (d) DMF; (e) CH_3CN .

Table 4. CV Data for Compounds **1–7**, **IIIb**, and **IIIc** (V vs Fc^+/Fc)^a ($\Delta E^{1/2}$ Refers to the Anodic Shift in the First Oxidation Potential after Saturation of the Solution with NaClO_4)

compound	$E^{1/2}$, V	$E^{2/2}$, V	$\Delta E^{1/2}$, mV
1	−0.290	0.202	
2	−0.281	0.197	
3	−0.331	0.176	
4	−0.410		
5	−0.306	0.192	
6	−0.281	0.202	0
7	−0.268	0.192	45
IIIb	0.103	0.322	0
IIIc	0.086	0.292	40

observation is consistent with the presence of a highly polar ground state and a transition in which the polarity of the complex is greatly reduced. The degree of solvatochromism for complex **5** compares well with those of previously reported platinum diiminedithiolate complexes.^{16,20,35} A linear correlation was found between the lowest absorption energies (Table 3) and the Cummings solvent parameter, with a linear correlation coefficient of R^2 of 0.954 (Figure 6). The direction of the observed shift in absorption energy with the solvent polarity is termed “negative” solvatochromism, and it is in accord with the assignment of this transition as a CT from an orbital of mixed metal/dithiolate to a diimine π^* orbital.

Complexes **1–4**, **6**, and **7** show absorption bands similar to that of **5** (Tables S1 and S2 and Figures S4–S10 in the Supporting Information). In each case, the lower-energy band exhibits substantial solvatochromism and the high-energy band does not. For complex **6**, the band in DMSO is 586 nm ($\epsilon = 5600 \text{ M}^{-1} \text{ cm}^{-1}$), while in chloroform, it is at 677 nm ($\epsilon = 4180 \text{ M}^{-1} \text{ cm}^{-1}$). For **7**, the bands appear at 583 nm ($\epsilon = 7910 \text{ M}^{-1} \text{ cm}^{-1}$) in DMSO and 665 nm ($\epsilon = 7430 \text{ M}^{-1} \text{ cm}^{-1}$) in chloroform.

Electrochemical Results. The electrochemical behavior of **1–7**, **IIIb**, and **IIIc** was determined by CV, and the results are summarized in Table 4. Complexes **1–3**, **5–7**, **IIIb**, and **IIIc** all exhibit two reversible one-electron redox couples, a typical property of TTFs. For these compounds, the two one-electron oxidation peaks are assigned to m/m^+ and m^+/m^{2+} , respectively. Only one quasi-reversible one-electron redox couple was observed for complex **4**.

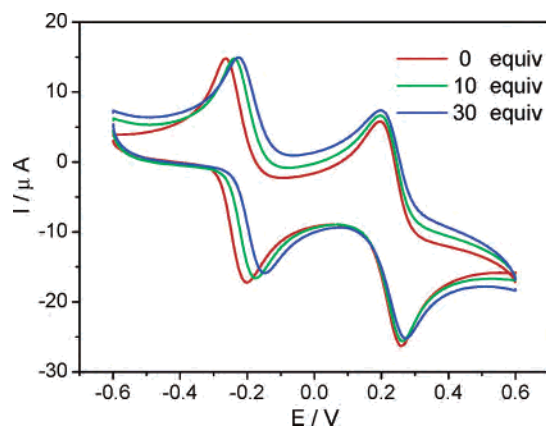


Figure 7. CVs of complex **7** recorded in a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ ($10^{-3} \text{ mol L}^{-1}$) at a scan rate of 100 mV s^{-1} with $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) as the supporting electrolyte in the presence of increasing amounts of Na^+ .

The three compounds **1–3** reported here have similar structures. Compared to **1**, complex **3** has a lower redox potential (about 40 mV) because the weak donor property of the methyl group enriches the electron density of the complex. Apparently, complex **4** shows the lowest redox potential among all complexes, indicating that the introduction of a phenyl group on the TTF molecule framework extends the conjugated system and improves the electron density. As a result, it leads to an increase of orbital overlap and enhances the intermolecular interaction along the stacking direction. Complexes **6** and **7** have lower redox potentials compared to their structural ligand analogues **IIIb** and **IIIc**, respectively. This property makes it easier to get their one-electron-oxidized derivatives in, e.g., reactions with iodine or 7,7,8,8-tetracyanoquinodimethane.

In the presence of 30 equiv of sodium perchlorate, a maximum of a ca. 45 mV shift of $E_{1/2}$ ($\Delta E_{1/2}^{\text{ox}}$) to a more positive (anodic) potential was observed for complex **7** (Figure 7), whereas E^{pa_2} and E^{pc_2} remained unchanged. This may be a result of the electrostatic inductive effect of the metal bound to crown ether that led to the withdrawal of the electron density from the TTF moiety. On the other hand, the dicationic state of the TTF core is reached at a constant $E_{2^{\text{ox}}}$ value, irrespective of the amount of metal cation added. This might be a result of the expulsion of the metal cation from the cavity, owing to the increased repulsive electrostatic interaction with the doubly charged TTF moiety. Under the same conditions, the ligand **IIIc** shows a maximum of a ca. 40 mV shift of $E_{1/2}$ (Figure S11 in the Supporting Information). No CV response was detected in the presence of other

alkali metal, such as Li^+ and K^+ , suggesting the good complexation selectivity of the receptor. Organic TTF and its derivatives are known to have a unique ability to supply electrons efficiently and to be switched reversibly in three redox states through oxidation/reduction. Therefore, crown ether annelated TTFs have been widely studied for ion sensing,^{26–31} and in these systems, the uptake and release of guest metal cations could be electrochemically monitored. Our results demonstrate that metal complexes with crown ether annelated TTFs could be redox-active in Na^+ cation sensors and molecular switches.

Similarly, electrochemical recognition for compounds **5–7**, **IIIb**, and **IIIc** has also been evaluated in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solution in both the absence and presence of metal cations by CV in the same conditions. However, there is no significant response for complexes **6** and **IIIb** under the same conditions. This may be attributed to the unmatched size of the crown cavity or the “binding power” of the alkali-metal ions.³¹

In conclusion, we have reported seven new platinum(II) complexes with both 4,4'-di-*tert*-butyl-2,2'-bipyridine and the extended tetrathiafulvalenedithiolate ligands, two of which are incorporated into the crown ether moieties for the first time. Three complexes were structurally characterized. They show significant solvatochromic behavior due to the intramolecular mixed metal/ligand-to-ligand CT transition. The CV measurements reveal obvious complexation between the crown segment and the guest Na^+ cations for complex **7**. Furthermore, all complexes reported here are soluble in most organic solvents and air-stable. They may also be used as versatile building blocks and redox-active components in new cation sensors, molecular shuttles and switches, and photo-voltaic materials in the future.

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Supporting Information Available: Additional figures and tables and X-ray crystallographic files in CIF format for compounds **5–7** and **IIIc**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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