Electrochemical, Photophysical, and Anion-Binding Properties of a Luminescent Rhenium(I) Polypyridine Anthraquinone Complex with a Thiourea Receptor

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We report the synthesis, characterization, and electrochemical and photophysical properties of a new luminescent rhenium(I) polypyridine-thiourea-anthraquinone complex, [Re(Me$_4$-phen)(CO)$_3$(Py-An)](CF$_3$SO$_3$) (**1**), and its anthraquinone-free analogue [Re(Me$_4$-phen)(CO)$_3$-(Py-Ph)](CF$_3$SO$_3$) (**2**) (Me$_4$-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Py-An = *N*-(1-anthraquinonyl)-*N'*-(4-pyridinylmethyl)thiourea; Py-Ph = *N*-(1-phenyl)-*N'*-(4-pyridinylmethyl)-thiourea)). The crystal structure of complex **2** has been studied by X-ray crystallography. Upon irradiation, both complexes **1** and **2** show intense and long-lived green luminescence in fluid solutions at 298 K and in alcohol glass at 77 K. The emission is assigned to an excited state of triplet metal-to-ligand charge-transfer ^{3}MLCT (dπ(Re) → π*(Me$_4$-phen)) character. In low-temperature glass, biexponential decays are observed for both complexes **1** and **2**, and the longer- and shorter-lived components are assigned to ^{3}IL ($\pi \rightarrow \pi^*$)(Me$_4$-phen) and ^{3}MLCT (dπ(Re) → π*(Me$_4$-phen)) excited states, respectively. The binding of anions to complexes **1** and **2** has been investigated by electronic absorption and emission titrations. Of the six anions we have studied (fluoride, acetate, dihydrogen phosphate, iodide, hydrogen sulfate, and nitrate), complexes **1** and **2** can recognize F$^-$, OAc$^-$, and H$_2$PO$_4$$^-$, with log K_s values ranging from ca. 3.53 to 4.94. While the anion-binding properties of complex **2** can only be reflected by its emission spectral changes, both the absorption and emission spectra of complex **1** display significant changes upon binding of anions, as a result of the additional anthraquinone unit.

Introduction

The photophysics and photochemistry of luminescent rhenium(I) polypyridine complexes have been extensively studied.[1−14] Increasing attention has been paid to the exploitation of luminescent rhenium(I) polypyridine complexes in different analytical applications: for example, these complexes have been employed as ion

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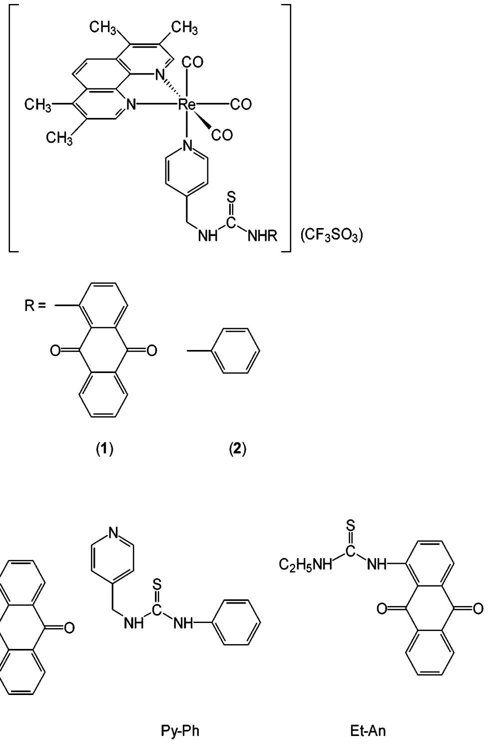
sensors,[7d,13a,15] intercalators and photocleavage agents for nucleic acid,[6,13b,c] reporters of rigidity,[7b] anisotropic probes for proteins,[12] and luminescent labeling reagents and probes for biological molecules.[14]

Recognition of common anions is of paramount importance due to the important roles of anions in industrial and biological processes. The development of anion sensors using various luminescent and redox-active systems has been investigated extensively.[7d,15,16] While the amide group has been most commonly used to recognize anionic species,[7d,15,16a−c] there is increasing interest in exploring other functional groups that show strong binding interaction with common anions. The thiourea moiety is one of the promising candidates. This unit has been attached to organic chromophores and fluorophores such as indoaniline,[17] naphthalene,[18] anthracene,[19] and pyrene[20] to produce effective anion sensors. Recently, a colorimetric anion sensor constructed from the conjugation of thiourea to a strongly absorbing anthraquinone unit has been reported.[21] A remarkable color change of the solution from orange to brown was observed upon addition of fluoride ion. We anticipate that an interesting anion sensory system could be achieved by the incorporation of an ion-responsive chromophore into a luminophore with emission at an energy region where the absorption of the chromophore would change upon anion binding. Thus, the anion uptake could change the absorption spectrum of the chromophore and hence affect the luminescence properties of the luminophore. Here, we report the synthesis, characterization, and electrochemical, photophysical, and anion-binding properties of a new luminescent rhenium(I) polypyridine complex equipped with a thiourea-anthraquinone moiety, [Re(Me$_4$-phen)(CO)$_3$(Py-An)](CF$_3$SO$_3$) (**1**) (Me$_4$-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Py-An = *N*-(1-anthraquinonyl)-*N*′-(4-pyridinylmethyl)thiourea). The properties of this complex have been compared to those of the control compounds, [Re(Me$_4$-phen)(CO)$_3$(Py-Ph)](CF$_3$SO$_3$) (**2**) (Py-Ph = *N*-(1-phenyl)-*N*′-(4-pyridinylmethyl)thiourea) and *N*-(1-anthraquinonyl)-*N*′-ethylthiourea (Et-An), in which the anthraquinone unit and the rhenium(I) diimine luminophore are absent, respectively. The structures of complexes **1** and **2**, Py-An, Py-Ph, and Et-An are shown in Chart 1.

Chart 1. Structures of Complexes 1 and 2, Py-An, Py-Ph, and Et-An



Experimental Section

Materials and Reagents. All solvents were of analytical grade and were purified according to published procedures.[22] 1-Aminoanthraquinone (Acros), thiophosgene (Aldrich), calcium carbonate (BDH), ethylamine (70 wt % solution in water) (Aldrich), Re(CO)$_5$Cl (Strem), AgCF$_3$SO$_3$ (Acros), Me$_4$-phen (Acros), 4-aminomethylpyridine (Aldrich), aniline (Aldrich), *n*-Bu$_4$NF (Acros), *n*-Bu$_4$NOAc (Aldrich), *n*-Bu$_4$NH$_2$PO$_4$ (Aldrich), *n*-Bu$_4$NI (Acros), *n*-Bu$_4$NHSO$_4$ (Acros), and *n*-Bu$_4$NNO$_3$ (Acros) were used as received. The supporting electrolyte *n*-Bu$_4$NPF$_6$ was recrystallized twice from hot absolute ethanol and then dried in vacuo for 12 h at 110 °C before use.

1-Anthraquinonyl Isothiocyanate (AnNCS). A mixture of 1-aminoanthraquinone (409 mg, 1.83 mmol), calcium carbonate (550 mg, 5.50 mmol), and thiophosgene (210 μL, 2.75 mmol) in acetone (70 mL) was stirred overnight at room temperature under an inert atmosphere of nitrogen. The mixture was filtered, and the filtrate was evaporated to dryness to give an orange-red solid. The solid was then dissolved in CH$_2$Cl$_2$ and loaded onto a chromatographic column (silica). The desired product appeared as a yellow band on the column, and it was eluted with CH$_2$Cl$_2$. The solution was collected and evaporated to dryness to give a yellow solid. Yield = 408 mg (84%). ^{1}H NMR (300 MHz, acetone-d_6, 298 K, relative to TMS): δ 8.33−8.26 (m, 3H, H$_2$, H$_3$, and H$_4$ of anthraquinone), 8.02−7.91 (m, 4H, H$_5$, H$_6$, H$_7$, and H$_8$ of anthraquinone). IR (KBr) ν/cm^{-1}: 2146 (s, NCS), 1676 (s, C=O).

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***N*-(1-Anthraquinonyl)-*N′*-(4-pyridinylmethyl)thiourea (Py-An).** A mixture of AnNCS (103 mg, 0.39 mmol) and 4-aminomethylpyridine (42 mg, 0.39 mmol) in acetone (30 mL) was refluxed overnight under an inert atmosphere of nitrogen. The solution was evaporated to dryness to give a yellow solid. The solid was washed with diethyl ether and recrystallized from acetone/diethyl ether to afford yellow crystals. Yield = 94 mg (65%). ^{1}H NMR (300 MHz, acetone-d_6, 298 K, relative to TMS): δ 12.21 (s, 1H, An-N*H*), 9.26 (s, 1H, H_2 of anthraquinone), 9.12 (s, 1H, CH_2NH), 8.53 (d, 2H, J = 4.4 Hz; H_2 and H_6 of pyridine ring), 8.30−8.22 (m, 2H, H_5 and H_8 of anthraquinone), 8.01 (d, 1H, J = 7.6 Hz; H_4 of anthraquinone), 7.94−7.91 (m, 2H, H_6 and H_7 of anthraquinone), 7.83 (t, 1H, J = 8.1 Hz; H_3 of anthraquinone), 7.41 (d, 2H, J = 5.0 Hz; H_3 and H_5 of pyridine ring), 5.02 (d, 2H, J = 5.0 Hz; CH_2). IR (KBr) ν/cm^{-1}: 3217 (m, NH), 1572 (s, C═O), 1268 (s, C═S). Positive-ion ESI-MS ion cluster at *m*/*z* 374 {M}$^+$. Anal. Calcd for $C_{21}H_{15}N_3O_2S\cdot 1^1/_2H_2O$: C, 62.99; H, 4.53; N, 10.49. Found: C, 63.27; H, 4.72; N, 10.36. UV/vis [λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: CH_3CN, 250 (36 180), 264 sh (27 260), 280 sh (17 010), 306 (9745), 438 (4755); CH_2Cl_2, 244 sh (27 240), 252 (32 170), 271 sh (23 715), 281 sh (16 650), 308 (9955), 440 (4990).

***N*-Phenyl-*N′*-(4-pyridinylmethyl)thiourea (Py-Ph).** A mixture of PhNCS (391 mg, 2.89 mmol)[23] and 4-aminomethylpyridine (313 mg, 2.90 mmol) in acetone (25 mL) was refluxed overnight under an inert atmosphere of nitrogen. The solution was evaporated to dryness to give a light brown solid. The solid was then washed with diethyl ether and recrystallized from acetone/diethyl ether to afford light brown crystals. Yield = 560 mg (80%). ^{1}H NMR (300 MHz, acetone-d_6, 298 K, relative to TMS): δ 9.26 (s, 1H, CH_2NH), 8.50 (d, 2H, J = 4.4 Hz; H_2 and H_6 of pyridine ring), 7.88 (s, 1H, Ph-N*H*), 7.51−7.48 (m, 2H, H_2 and H_6 of phenyl ring), 7.40−7.35 (m, 4H, H_3 and H_5 of phenyl ring, and H_3 and H_5 of pyridine ring), 7.19 (t, 1H, J = 7.3 Hz; H_4 of phenyl ring), 4.95 (d, 1H, J = 4.4 Hz; CH_2). IR (KBr) ν/cm^{-1}: 3158 (m, NH), 2995, 2918 (m, CH), 1538 (s, C═O), 1245 (s, C═S). Positive-ion ESI-MS ion cluster at *m*/*z* 244 {M}$^+$. Anal. Calcd for $C_{13}H_{13}N_3S\cdot {}^1/_4H_2O$: C, 63.00; H, 5.49; N, 16.95. Found: C, 63.05; H, 5.43; N, 17.09. UV/vis [λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: CH_3CN, 245 sh (11 805), 263 (12 925); CH_2Cl_2, 244 sh (10 620), 264 (15 540).

***N*-(1-Anthraquinonyl)-*N′*-ethylthiourea (Et-An).** A mixture of AnNCS (110 mg, 0.42 mmol) and ethylamine (70 wt % solution in water) (27 μL, 0.42 mmol) in acetone (80 mL) was stirred overnight at room temperature under an inert atmosphere of nitrogen. The solution was then evaporated to dryness to give an orange solid. The crude product was recrystallized from acetone/diethyl ether to afford orange crystals. Yield = 96 mg (74%). ^{1}H NMR (300 MHz, acetone-d_6, 298 K, relative to TMS): δ 11.62 (s, 1H, An-N*H*), 9.46 (s, 1H, C_2H_5NH), 8.97 (d, 1H, J = 8.5 Hz; H_2 of anthraquinone), 8.28−8.21 (m, 2H, H_3 and H_4 of anthraquinone), 8.00−7.83 (m, 4H, H_5, H_6, H_7, and H_8 of anthraquinone), 3.64−3.62 (m, 2H, CH_2), 1.29−1.24 (m, 3H, CH_3). IR (KBr) ν/cm^{-1}: 3226 (m, NH), 3075, 2985 (m, aliphatic CH), 1545 (s, C═O), 1278 (s, C═S). Positive-ion ESI-MS ion cluster at *m*/*z* 393 {M}$^+$. Anal. Calcd for $C_{17}H_{14}N_2O_2S\cdot {}^1/_4H_2O$: C, 64.85; H, 4.64; N, 8.90. Found: C, 65.02; H, 4.57; N, 8.67. UV/vis [λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: CH_3CN, 249 (12 370), 271 (8680), 307 (4110), 440 (2240); CH_2Cl_2, 252 (16 730), 269 (12 500), 307 (5400), 440 (2840).

[Re(Me$_4$-phen)(CO)$_3$(Py-An)](CF$_3$SO$_3$) (1). A mixture of [Re(Me$_4$-phen)(CO)$_3$(CH$_3$CN)](CF$_3$SO$_3$) (102 mg, 0.15 mmol)[1c] and Py-An (55 mg, 0.15 mmol) in THF (20 mL) was refluxed overnight under an inert atmosphere of nitrogen. The solution was evaporated to dryness to give a brownish-yellow solid. The solid was then washed with diethyl ether. Subsequent recrystallization from acetone/diethyl ether afforded complex **1** as brownish-yellow crystals. Yield = 154 mg (52%). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, relative to TMS): δ 11.67 (s, 1H, An-N*H*), 9.70 (s, 1H, CH_2NH), 9.49 (s, 2H, H_2 and H_9 of Me$_4$-phen), 8.81 (d, 1H, J = 8.5 Hz; H_2 of anthraquinone), 8.53 (d, 2H, J = 6.2 Hz; H_2 and H_6 of pyridine ring), 8.35 (s, 2H, H_5 and H_6 of Me$_4$-phen), 8.15 (d, 2H, J = 6.2 Hz; H_5 and H_8 of anthraquinone), 7.96−7.89 (m, 3H, H_4, H_6, and H_7 of anthraquinone), 7.76 (t, 1H, J = 7.9 Hz; H_3 of anthraquinone), 7.24 (d, 2H, J = 5.9 Hz; H_2 and H_5 of pyridine ring), 4.70 (s, 2H, CH_2), 2.79 (s, 6H, CH_3 at C4 and C7 of Me$_4$-phen), 2.68 (s, 6H, CH_3 at C3 and C8 of Me$_4$-phen). IR (KBr) ν/cm^{-1}: 3254 (m, NH), 2030, 1912 (s, C═O), 1268 (s, C═S). Positive-ion ESI-MS ion cluster at *m*/*z* 880 {M}$^+$. Anal. Calcd for $C_{40}H_{29}N_5O_8S_2F_3Re\cdot H_2O$: C, 46.51; H, 3.02; N, 6.78. Found: C, 46.63; H, 3.25; N, 6.73.

[Re(Me$_4$-phen)(CO)$_3$(Py-Ph)](CF$_3$SO$_3$) (2). A mixture of [Re(Me$_4$-phen)(CO)$_3$(CH$_3$CN)](CF$_3$SO$_3$) (152 mg, 0.218 mmol)[1c] and Py-Ph (53 mg, 0.218 mmol) in THF (20 mL) was refluxed overnight under an inert atmosphere of nitrogen. The mixture was filtered, and the filtrate was evaporated to dryness to give an orange solid. The solid was then purified by column purification, and recrystallization from dichloromethane/diethyl ether afforded complex **2** as yellow crystals. Yield = 80 mg (41%). ^{1}H NMR (300 MHz, acetone-d_6, 298 K, relative to TMS): δ 9.64 (s, 2H, H_2 and H_9 of Me$_4$-phen), 9.20 (s, 1H, CH_2NH), 8.53 (d, 2H, J = 4.7 Hz; H_2 and H_6 of pyridine ring), 8.45 (s, 2H, H_5 and H_6 of Me$_4$-phen), 7.80 (s, 1H, Ph-N*H*), 7.43−7.40 (m, 2H, H_2 and H_6 of phenyl ring), 7.33−7.24 (m, 4H, H_3 and H_5 of phenyl ring, and H_3 and H_5 of pyridine ring), 7.15 (t, 1H, J = 7.2 Hz; H_4 of phenyl ring), 4.79 (d, 1H, J = 4.7 Hz; CH_2), 2.92 (s, 6H, CH_3 at C4 and C7 of Me$_4$-phen), 2.78 (s, 6H, CH_3 at C3 and C8 of Me$_4$-phen). IR (KBr) ν/cm^{-1}: 3315 (m, NH), 2030, 1918 (s, C═O), 1276 (m, C═S). Positive-ion ESI-MS ion cluster at *m*/*z* 752 {M}$^+$. Anal. Calcd for $C_{33}H_{29}N_5O_6S_2F_3Re\cdot {}^3/_4CH_2Cl_2$: C, 42.11; H, 3.19; N, 7.27. Found: C, 42.04; H, 3.20; N, 7.07.

Instrumentals and Methods. ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer at 298 K. ESI mass spectra were measured on a Perkin-Elmer Sciex API 365 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario EL elemental analyzer or a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. The electrochemical experiments were carried out at 298 K with a two-compartment glass cell with a working volume of 500 μL. A platinum gauze counter electrode was accommodated in the working electrode compartment. The working electrode was a glassy carbon electrode, and the reference electrode was a silver/silver nitrate electrode. The reference electrode compartment was connected to the working electrode compartment via a Luggin capillary. All potentials were referred to SCE. Electronic absorption and steady-state emission spectra were recorded on an Agilent 8453 diode array spectrophotometer and a Fluoromax-3 fluorescence spectrophotometer, respectively. Unless specified otherwise, all solutions for photophysical studies were degassed with no fewer than four successive freeze−pump−thaw cycles and stored in a 10 cm^3 round-bottomed flask equipped with a sidearm 1 cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Luminescence quantum yields were measured by the optical dilute method[24] using an aerated aqueous solution of [Ru(bpy)$_3$]Cl$_2$ (Φ = 0.028)[25] as the standard solution. The excitation source for emission lifetime measurement was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals from a Hamamatsu R928 photomultiplier tube were converted to

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potential changes by a 50 Ω load resistor and then recorded on a Tektronix model TDS 620A digital oscilloscope. For the electronic absorption and steady-state emission spectral titrations for binding constant determination, the supporting electrolyte (0.1 mol dm^{-3} n-Bu$_4$NPF$_6$) was present to maintain a constant ionic strength of the sample solution during the titration. The binding constant, K_s, for the 1:1 complexation that controls the equilibrium between an anion A, the receptor Re, and their adduct Re−A, was obtained by a nonlinear least-squares fit of the absorbance or emission intensity (X_a) versus the concentration of the anion (C_a) in the mixture according to eq 1:[26]

$$\mathrm{Re} + \mathrm{A} \overset{K_s}{\rightleftharpoons} \mathrm{Re{-}A}$$

$$X_a = X_o + \left(\frac{X_{lim} - X_o}{2C_o}\right) \times \left[C_o + C_a + \frac{1}{K_s} - \sqrt{\left(C_o + C_a + \frac{1}{K_s}\right)^2 - 4C_oC_a}\right] \quad (1)$$

where C_o is the initial concentration of the receptor, and X_o and X_{lim} are the absorbance or emission intensity of the receptor in the free and anion-bound states, respectively.

X-ray Structural Analysis of Complex 2. A crystal of dimensions 0.15 × 0.15 × 0.07 mm mounted in a glass capillary was used for data collection at −20 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data collection was made with a 2° oscillation step of φ, 15 min exposure time, and scanner distance at 120 mm; 100 images were collected. The images were interpreted and intensities integrated using the program DENZO.[27] The structure was solved by direct methods employing the SIR-97 program[28] on a PC. Rhenium, sulfurs, and many non-hydrogen atoms were located according to the direct methods and successive least-squares Fourier cycles. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using the program SHELXL-97[29] on a PC. The anion $CF_3SO_3^-$ and an acetone solvent molecule were located. Two hydrogen atoms on nitrogen atoms were added according to the difference Fourier map and refined isotropically. Both hydrogens participated in hydrogen bonding with the oxygen atoms of the anion. One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by SHELXL-97.[29] The positions of the hydrogen atoms were calculated on the basis of a riding mode with thermal parameters equal to 1.2 times that of the associated carbon atoms, and participated in the calculation of final R-indices. Crystal data and a summary of data collection and refinement details are given in Table 1.

Table 1. Crystal Data and Summary of Data Collection and Refinement for Complex 2

formula	$C_{36}H_{35}F_3N_5O_7ReS_2$
fw	957.01
cryst size (mm)	0.15 × 0.15 × 0.07
T (K)	253
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	10.688(2)
b (Å)	23.535(5)
c (Å)	15.620(3)
β (deg)	104.31(3)
V (Å^3)	3807.2(13)
Z	4
ρ_{calcd} (g cm^{-3})	1.670
μ (mm^{-1})	3.370
F(000)	1904
θ range (deg)	1.60−25.51
oscillation (deg)	2
no. of images collected	100
distance (mm)	120
exposure time (min)	15
index ranges	$-12 \le h \le 12$; $-28 \le k \le 27$; $-18 \le l \le 18$
no. of data collected	22 278
R_{int}[a]	0.0590
no. of unique data/restraints/ params	6990/0/501
GOF on F^2 [b]	0.961
R_1, wR_2 ($I > 2\sigma(I)$)[c]	0.0365, 0.0920
R_1, wR_2 (all data)	0.0526, 0.0972
largest diff peak/hole (e Å^{-3})	0.665, −0.912

[a] $R_{int} = \sum|F_o^2 - F_o^2(\mathrm{mean})|/\sum[F_o^2]$. [b] GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_o^2 + \max(F_o^2,0)]/3$, $a = 0.0479$, and $b = 0$. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

Synthesis. Thiourea derivatives can be conveniently synthesized from the facile reaction of an isothiocyanate with an amine in a basic medium.[30] In this work, the thiourea-containing pyridine ligands Py-An and Py-Ph are synthesized from the reactions of 4-aminomethylpyridine with AnNCS and PhNCS, respectively. Similarly, Et-An is obtained from the reaction of ethylamine with AnNCS. Complexes **1** and **2** are prepared from the reactions of the precursor complex [Re(Me$_4$-phen)(CO)$_3$(CH$_3$CN)](CF$_3$SO$_3$) with Py-An and Py-Ph, respectively, in refluxing THF. All the new compounds are characterized by ^{1}H NMR, positive-ion ESI-MS, and IR, and they give satisfactory elemental analysis. The thiourea moieties of all the compounds display an ν(C═S) absorption peak at ca. 1245−1278 cm^{-1} in the IR spectra. The crystal structure of complex **2** is also studied by X-ray crystallography.

Crystal Structure. Single crystals of complex **2** are obtained by layering a concentrated acetone solution of the complex with a mixture of diethyl ether and petroleum ether. The perspective drawing of the cation of complex **2** with the atomic numbering scheme is depicted in Figure 1. Selected bond distances and angles are summarized in Table 2. The rhenium(I) center adopts a distorted octahedral coordination geometry, and the carbonyl groups are arranged in a *facial* orientation. The bond lengths and angles associated with the rhenium center are normal and similar to those observed in related systems.[2a,13b,c,14a,b] It is interesting to note the phenyl ring is almost coplanar with the Me$_4$-phen ligand, with a dihedral angle of ca. 4.5°. The thiourea plane exhibits dihedral angles of ca. 9.0° and 78.0° with the phenyl and the pyridine rings, respectively.

Electrochemical Properties. The electrochemical properties of complexes **1** and **2** and Et-An have been

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[26] Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.

[27] DENZO: Otwinowski, Z.; Minor, W. *Methods in Enzymology*; Academic Press: San Diego, 1997; Vol. 276, p 307.

[28] SIR-97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna. R. *J. Appl. Crystallogr.* **1998**, *32*, 115.

[29] SHELXL-97: Sheldrick, G. M. *Programs for Crystal Structure Analysis (Release 97-2)*; University of Götingen: Germany, 1998.

[30] Jobbagy, A.; Kiraly, K. *Biochim. Biophys. Acta* **1966**, *124*, 166.

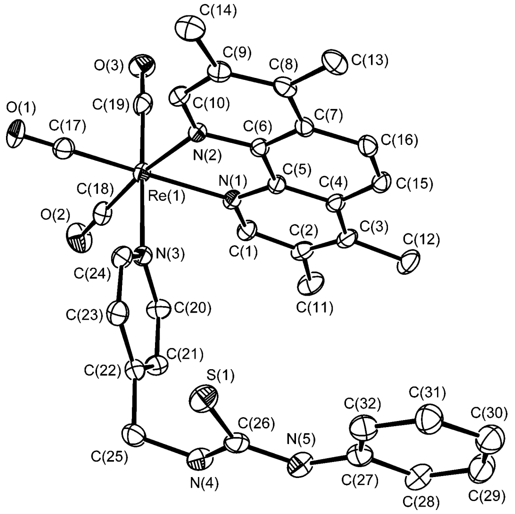

Figure 1. Perspective drawing of the cation of complex **2** with the atomic numbering scheme. Thermal ellipsoids are shown at the 20% probability level.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of Complex 2

Re(1)−N(1)	2.178(4)	Re(1)−N(2)	2.171(4)
Re(1)−N(3)	2.220(4)	Re(1)−C(17)	1.919(6)
Re(1)−C(18)	1.924(6)	Re(1)−C(19)	1.937(6)
N(4)−C(26)	1.366(7)	N(5)−C(26)	1.358(7)
C(26)−S(1)	1.666(6)		

N(1)−Re(1)−N(2)	75.6(14)	N(1)−Re(1)−N(3)	83.9(15)
N(1)−Re(1)−C(17)	171.8(19)	N(1)−Re(1)−C(18)	98.6(19)
N(1)−Re(1)−C(19)	95.0(19)	N(2)−Re(1)−N(3)	84.2(14)
N(2)−Re(1)−C(17)	97.2(18)	N(2)−Re(1)−C(18)	173.2(18)
N(2)−Re(1)−C(19)	95.9(19)	N(3)−Re(1)−C(17)	91.5(2)
N(3)−Re(1)−C(18)	91.8(2)	N(3)−Re(1)−C(19)	178.7(19)
C(17)−Re(1)−C(18)	88.4(2)	C(17)−Re(1)−C(19)	89.7(2)
C(18)−Re(1)−C(19)	88.0(2)	C(22)−C(25)−N(4)	111.3(4)
C(25)−N(4)−C(26)	121.9(5)	N(4)−C(26)−S(1)	121.7(5)
N(4)−C(26)−N(5)	111.7(5)	S(1)−C(26)−N(5)	126.7(5)
C(26)−N(5)−C(27)	131.9(6)		

Table 3. Electrochemical Data of Complexes 1 and 2 and Et-An in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) at 298 K (glassy carbon working electrode, sweep rate = 100 mV s^{-1}, all potentials versus SCE)

compound	oxidation, $E_{1/2}$ or E_a/V	reduction, $E_{1/2}$ or E_c/V
1	+1.36,[a] +1.67[b]	−0.74, −1.00, −1.40,[b] −1.58,[b] −1.78,[b] −1.92[b]
2	+1.29,[a] +1.43,[a] +1.65[b]	−1.39,[b] −1.57,[b] −1.80,[b] −1.94[b]
Et-An	+0.85,[a] +1.27,[a] +1.83[a]	−0.77, −1.06

[a] Irreversible waves. [b] Quasi-reversible couples.

Table 4. Electronic Absorption Spectral Data of Complexes 1 and 2 at 298 K

complex	medium	λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})
1	CH_3CN	249 (56 465), 272 sh (45 720), 278 (47 305), 299 sh (26 575), 362 sh (5670), 435 (4720)
	CH_2Cl_2	252 (49 250), 272 (42 740), 281 (44 645), 306 sh (23 415), 367 sh (6390), 437 (5200)
2	CH_3CN	248 (39 900), 279 (42 200), 362 sh (3710)
	CH_2Cl_2	248 (40 910), 281 (45 380), 362 sh (4585)

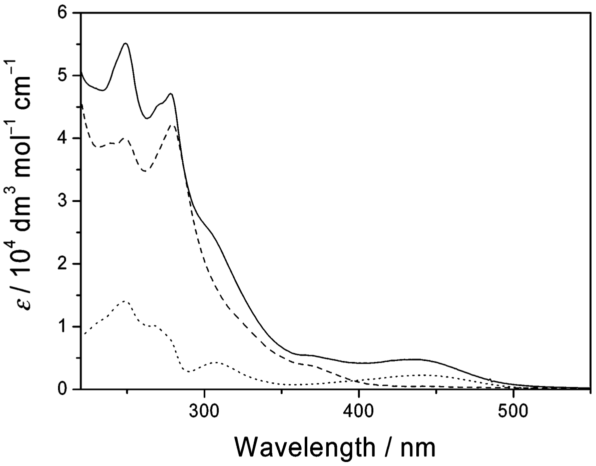

Figure 2. Electronic absorption spectra of complexes **1** (—) and **2** (- - -) and Et-An (···) in CH_3CN at 298 K.

studied by cyclic voltammetry. The electrochemical data are listed in Table 3. Complexes **1** and **2** exhibit quasi-reversible Re(II/I) oxidation couples at ca. +1.7 V versus SCE.[2a,3a,4b,c,d,7c,8a,9,10b,11b,31] Additional irreversible waves are also observed at ca. +1.4 V for **1** and +1.3 and +1.4 V for **2**. These features are attributable to the oxidation of the thiourea groups because similar irreversible waves are also observed for Et-An at ca. +0.9 and +1.3 V and other thiourea-containing compounds.[32] The quasi-reversible couples at ca. −1.4 V for complexes **1** and **2** are assigned to the reduction of the Me_4-phen ligand. More quasi-reversible couples are also observed for both complexes at lower potential, and they are tentatively assigned to reduction of the diimine ligand and Re(I/0) reduction. It is important to note that complex **1** displays two additional reversible couples at ca. −0.7 and −1.0 V, which are absent for complex **2**. We assign these redox couples to reduction of the anthraquinone moiety since similar reversible couples are also observed for Et-An at ca. −0.8 and −1.1 V and other anthraquinone derivatives.[33,34]

Electronic Absorption and Photophysical Properties. The electronic absorption spectral data of complexes **1** and **2** are summarized in Table 4. The absorption spectra of complexes **1** and **2** and Et-An are shown in Figure 2. For complex **1** in CH_3CN, the intense absorption bands at ca. 249−299 nm with extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1} are assigned to ligand-centered transitions involving the Me_4-phen and Py-An ligands. With reference to previous spectroscopic studies of related rhenium(I) diimine systems,[1−14] the less intense absorption shoulder at ca. 362 nm is assigned to spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) ($d\pi(Re) \rightarrow \pi^*(Me_4\text{-phen})$) transition. However, since the ligand Py-An also absorbs fairly strongly in this region (ϵ on the order of 10^3 dm^3 mol^{-1} cm^{-1}), it is likely that this absorption transition also possesses some intraligand (^{1}IL) character associated with the anthraquinone moiety. Additionally, the absorption spectrum of complex **1** also displays a low-energy absorption band at ca. 435 nm (Figure 2), which is absent in the anthraquinone-free analogue **2** and common rhenium(I) phenanthroline complexes. In view of the fact that an absorption band at a similar wavelength is observed for the anthraquinone-containing compounds Py-An and Et-An, we assign this low-

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[31] Ruiz, G. T.; Juliarena, M. P.; Lezna, R. O.; Wolcan, E.; Feliz, M. R.; Ferraudi, G. *Helv. Chim. Acta* **2002**, *85*, 1261.

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[34] Moteki, S.; Sykes, A. G. *J. Electroanal. Chem.* **1998**, *447*, 91.

Table 5. Photophysical Data of Complexes 1 and 2[a] and Me$_4$-phen

compound	medium (T/K)	λ_{em}/nm	τ_o/μs	Φ
1	CH_3CN (298)	520	4.36	0.019
	CH_2Cl_2 (298)	515	3.11	0.029
	glass[b] (77)	468, 500, 533 sh	64.00 (36%), 12.79 (64%)	
2	CH_3CN (298)	520	9.77	0.61
	CH_2Cl_2 (298)	515	11.46	0.88
	glass[b] (77)	467, 500, 535 sh	88.35 (31%), 19.20 (69%)	
Me$_4$-phen[c]	glass[b] (77)	464, 501, 540, 584, 640	1.938×10^6 [d]	

[a] [Re] = 100 μM. [b] EtOH/MeOH (4:1 v/v). [c] From refs 3a and 3c. [d] In glycerol at 77 K.

energy band to an ^{1}IL (n → π*)(Py-An) transition.[35] For complex **2** in CH_3CN, the intense absorption bands at ca. 248–279 nm and the absorption shoulder at ca. 362 nm are assigned to ^{1}IL (π → π*)(Me$_4$-phen and Py-Ph) and ^{1}MLCT (dπ(Re) → π*(Me$_4$-phen)) transitions, respectively. In fact, a close examination of the electronic absorption spectrum of complex **1** (Figure 2) reveals that its features are essentially a combination of those of complex **2** and Et-An. The absence of new absorption characteristics in the spectrum of complex **1** suggests the lack of electronic communication between the rhenium(I) diimine unit and the thiourea-anthraquinone moiety.

Upon irradiation, complexes **1** and **2** display intense and long-lived green luminescence in fluid solutions at 298 K and in low-temperature glass. The photophysical data are listed in Table 5. With reference to previous photophysical studies on related luminescent rhenium(I) polypyridine systems,[1–14] the emission of the complexes is assigned to a ^{3}MLCT (dπ(Re) → π*(Me$_4$-phen)) excited state. In view of the long emission lifetimes of the complexes in solutions at 298 K (Table 5), it is likely that the excited states of complexes **1** and **2** are mixed with some ^{3}IL (π → π*)(Me$_4$-phen) character.[3] In alcohol glass at 77 K, complexes **1** and **2** show similar intense and long-lived green emission, with structural features in the emission spectra. Biexponential decays are observed for both complexes **1** and **2**, and the longer- and shorter-lived components are assigned to ^{3}IL (π → π*)(Me$_4$-phen) and ^{3}MLCT (dπ(Re) → π*(Me$_4$-phen)) excited states, respectively.[3] Note that the 77 K phosphorescence of the free Me$_4$-phen ligand occurs at similar energy (Table 5).[3a,c] We find that the emission lifetime of complex **1** in fluid solutions at 298 K is dependent on its concentration, and a similar observation is not observed for the anthraquinone-free complex **2**. From a plot of τ^{-1} versus [Re], an intermolecular quenching rate constant of ca. 1.0×10^9 dm^3 mol^{-1} s^{-1} is obtained for complex **1** in CH_3CN at 298 K, and an emission lifetime of ca. 7.78 μs is determined for the "infinitely dilute" solution of the complex. This emission lifetime is shorter than that of complex **2** (ca. 9.77 μs), suggesting that the emission of complex **1** is quenched by the anthraquinone unit. More detailed work is required to fully understand the inter- and intramolecular electron and energy transfer of the system.

Absorption Titration Studies. The anion-binding properties of complexes **1** and **2** and Et-An have been studied by spectrophotometric and luminescence titrations. Of the six anions we studied (F^-, OAc^-, $H_2PO_4^-$, I^-, HSO_4^-, and NO_3^-), complexes **1** and **2** and Et-An do not show any significant changes in the electronic absorption and emission spectra in the presence of HSO_4^- or NO_3^-. These observations suggest the lack of binding of these anions to the thiourea-containing compounds. A similar finding has been observed in related thiourea systems.[21] In contrast, upon addition of F^- ion to an acetonitrile solution of complex **1** at 298 K, the yellow solution turned to purple. In the electronic absorption spectrum, the ^{1}IL (n → π*)(anthraquinone) absorption band at ca. 435 nm exhibits a red shift to ca. 505 nm with a sharp isosbestic point at ca. 372 nm (Figure 3). A similar red shift in the 440 nm absorption band of Et-An is also observed in the presence of F^- (Figure 4). With reference to the spectroscopic studies of a related anthraquinone-thiourea compound,[19] it is likely that the change in the absorption spectra of both complex **1** and Et-An is a consequence of the binding of F^- to the thiourea hydrogen atoms. The binding of an anion is expected to enrich the electron density of the nitrogen atom attached to the anthraquinone unit and thus render the ^{1}IL (n → π*)(anthraquinone) transition to occur at lower energy. We believe that the thiourea group of complex **2** also enables the complex to bind F^- ion. However, the absence of a chromophore (anthraquinone) attached to the thiourea group of this complex means that the binding cannot lead to a significant change in the absorption spectrum and can only be revealed by other means (see below).

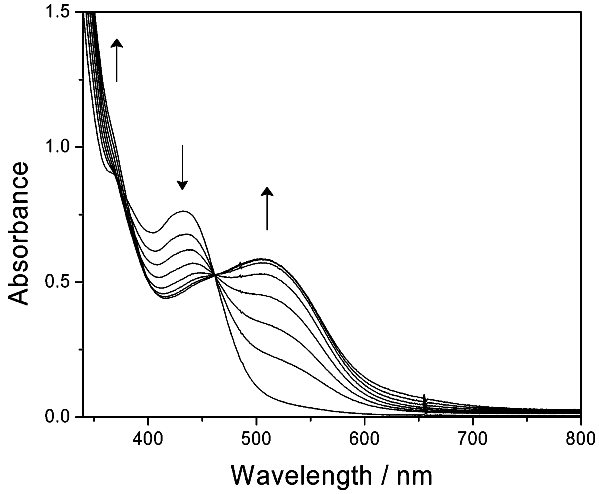

Figure 3. Electronic absorption spectral traces of complex **1** (153 μM) in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) upon addition of n-Bu_4NF at 298 K. The concentrations of fluoride ion are 0, 153, 230, 306, 383, 459, 536, and 612 μM, respectively.

It is noteworthy that the absorption spectrum of complex **1** displays an increase in absorbance and disappearance of the isosbestic point (at 372 nm) upon further addition of fluoride ion (when [F^-]:[**1**] > ca. 10). To illustrate this, the absorption spectra of complex **1**

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[35] Diaz, A. N. *J. Photochem. Photobiol. A* **1990**, *53*, 141.

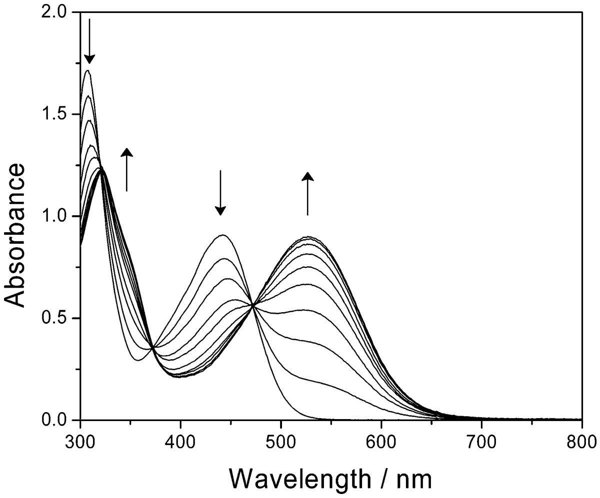

Figure 4. Electronic absorption spectral traces of Et-An (156 μM) in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) upon addition of n-Bu_4NF at 298 K. The concentrations of fluoride ion are 0, 156, 313, 470, 627, 783, 939, 1096, 1263, and 1410 μM, respectively.

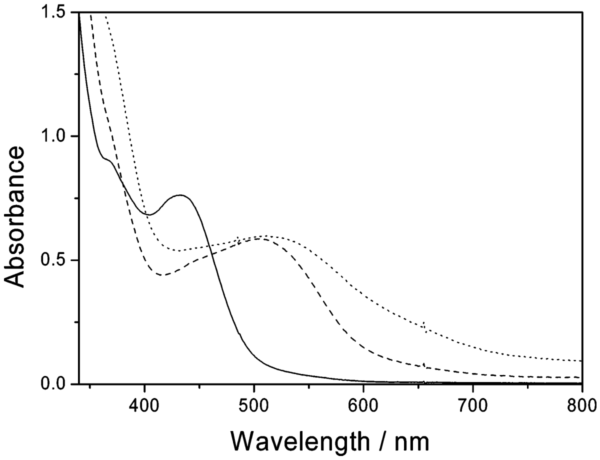

Figure 5. Electronic absorption spectrum of complex **1** (153 μM) in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) in the presence of 0 (—), 4 (- - -), and 20 (···) equiv of n-Bu_4NF at 298 K.

in the presence of 0, 4, and 20 equiv of fluoride ions are shown in Figure 5. Although the baseline of the spectrum rises, the solution remains visually clear and no precipitate is observed. Interestingly, similar increase in absorbance and disappearance of the isosbestic point are also noticed for complex **2** but not for Et-An. The reason for these observations for both complexes is unknown at this stage. However, a plausible explanation is that the excess anion may displace the monodentate pyridine ligands Py-An and Py-Ph from the rhenium(I) centers. Nevertheless, data obtained from the early stage of the electronic absorption titrations (i.e., [F^-]:[**1**] < 10) of complex **1** are used to determine the binding constants. The absorbance change of complex **1** at 435 nm as a function of [F^-] and a theoretical fit of the data using eq 1 are shown in Figure 6. The good agreement between the experimental data and the theoretical fit confirms the 1:1 binding stoichiometry for complex **1** and F^-, and a log K_s value of 3.53 (Table 6) is determined from the fit. Similar 1:1 binding stoichiometry is also observed for Et-An and F^-, and fitting of the absorption titration data gives a log K_s of 3.05 (Table 6). The binding constant of complex **1** and F^- is similar in magnitude to those of other thiourea-based anion receptors such as the indoaniline-thiourea (log K_s = 3.52)[17] and anthracene-thiourea (log K_s = 3.35)[19] conjugates. In this work, the larger binding constant of complex **1** than that of Et-An suggests that the positive charge of the complex plays a role in the fluoride binding.

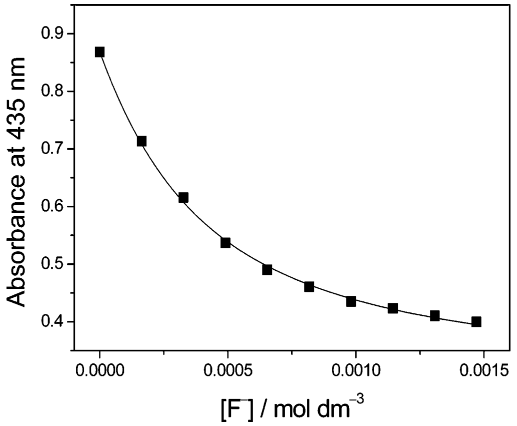

Figure 6. Plot of absorbance of complex **1** (145 μM) versus [F^-] monitored at λ = 435 nm (■) and its theoretical fit (—).

Table 6. Log K_s Values for the Anion-Binding of Complexes 1 and 2 and Et-An in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) at 298 K Determined by Electronic Absorption and Emission Titrations

	1		2		Et-An
anion	absorption	emission	absorption	emission	absorption
F^-	3.53	3.66	*a*	3.60	3.05
OAc^-	4.56	4.61	*a*	4.94	2.65
$H_2PO_4^-$	3.56	3.70	*a*	4.24	1.95

[a] Log K_s values cannot be determined due to the lack of significant changes in the absorption spectra.

In the presence of OAc^- and $H_2PO_4^-$, a similar red shift of the absorption band at ca. 435 nm is observed for complex **1**, and log K_s values of 4.56 and 3.56 are determined form the absorption titration data (Table 6). While the binding constant for OAc^- is larger than those of anthracene-thiourea derivatives (log K_s = 2.5–1.8)[19] and a pyrene-thiourea conjugate (log K_s = 3.85),[20] the affinity of complex **1** to $H_2PO_4^-$ is similar to those of other reported thiourea systems.[17,20] It is worth mentioning that even when excess ions are present (for example, [OAc^-] or [$H_2PO_4^-$]:**1** > 20), the isosbestic points remain sharp and no abnormal increase in absorbance is observed in the spectra. This is in contrast to the case of F^- and reflects that the binding reactions of these two ions are clean, and suggests the absence of additional interactions between these ions and the rhenium(I) complex. A red shift of the absorption band of Et-An is also noticed upon addition of OAc^- and $H_2PO_4^-$. Fitting of the absorption titration data suggests 1:1 binding in both cases and gives log K_s values of 2.65 and 1.95, respectively (Table 6). Note that these values are almost 2 orders of magnitude smaller than those of complex **1**, suggesting that the positive charge of the metal complex is more important in the binding of these two ions compared to the fluoride ion. Similar to the case of fluoride, the absence of significant absorption spectral changes of complex **2** in the presence of OAc^-

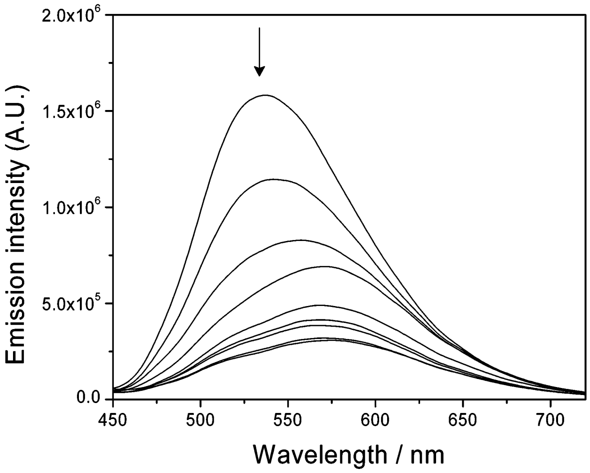

Figure 7. Luminescence spectral traces of complex **1** (145 μM) in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) upon addition of n-Bu_4NF at 298 K. The concentrations of fluoride ion are 0, 145, 289, 434, 723, 868, 1012, 1157, and 1302 μM, respectively.

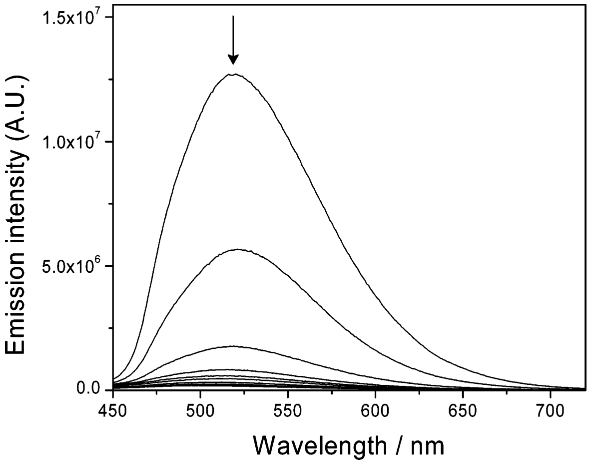

Figure 8. Luminescence spectral traces of complex **2** (272 μM) in CH_3CN (0.1 mol dm^{-3} n-Bu_4NPF_6) upon addition of n-Bu_4NF at 298 K. The concentrations of fluoride ion are 0, 272, 544, 816, 1088, 1360, 1631, 1903, 2175, and 2447 μM, respectively.

and $H_2PO_4^-$ renders it impossible to determine the binding constants.

Emission Titration Studies. We have investigated the anion-binding properties of the luminescent complexes **1** and **2** by monitoring their ^{3}MLCT/^{3}IL luminescence in the presence of various anions. Addition of F^- to an acetonitrile solution of complex **1** decreases the luminescence intensity (Figure 7). A similar decrease is also observed for complex **2** (Figure 8). It is likely that the emission quenching is a consequence of the binding of the anion to the thiourea moieties. A close scrutiny of the emission spectral traces of complex **1** (Figure 7) reveals that the reduction in emission intensity is accompanied by a red shift of the band from ca. 535 to 596 nm. It is important to note that a similar red shift is not observed for complex **2** (Figure 8). It appears that for complex **1** the fluoride-induced red shift of the 435 nm absorption band to 505 nm (a wavelength that is close to the 535 nm emission maximum of the complex) causes the blue-end of the emission band to further lose its intensity due to self-absorption effects. Consequently, the change in the absorption spectrum causes a red shift of the emission band together with the emission intensity reduction upon addition of fluoride ions. A similar red shift is absent in the case of complex **2** because the thiourea of this complex is not attached to an anthraquinone chromophore and thus there is a lack of change in the absorption spectrum.

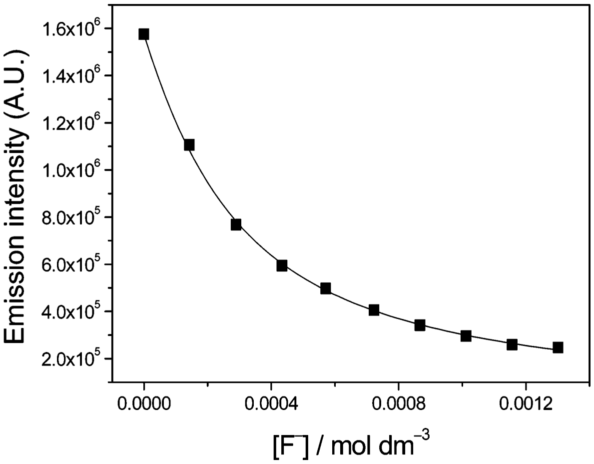

Figure 9. Plot of emission intensity of complex **1** (145 μM) versus [F^-] monitored at $\lambda = 535$ nm (■) and its theoretical fit (—).

The change of emission intensity of complex **1** at 535 nm as a function of [F^-] and the theoretical fit on the basis of a 1:1 binding stoichiometry are shown in Figure 9. A log K_s value of 3.66 is determined, which is in good agreement with that obtained from absorption titrations (Table 6). Similar emission quenching and red shifts in the emission bands are also observed for complex **1** when OAc^- and $H_2PO_4^-$ are present. Treatment of the emission spectral data gives satisfactory fits for a 1:1 binding mode, and log K_s values of 4.61 and 3.70 are determined for OAc^- and $H_2PO_4^-$, respectively. These values are in good agreement with those determined from the absorption titration experiments (Table 6).

Although similar emission quenching is observed for complex **2** in the presence of F^-, OAc^-, and $H_2PO_4^-$, no red shifts in the emission maxima are noticed. These ions bind to complex **2** with a 1:1 stoichiometry, and log K_s values are determined to be ca. 3.60, 4.94, and 4.24, respectively (Table 6). The higher binding affinity of complex **2** to both OAc^- and $H_2PO_4^-$ compared to that of complex **1** may be due to the fact that the absence of an anthraquinone moiety can lower the degree of steric hindrance between the complex and the anions.

Both complexes **1** and **2** show emission quenching in the presence of I^-. However, unlike the cases of F^-, OAc^-, and $H_2PO_4^-$, the emission quenching of complex **1** is not concomitant with a red shift of the emission maxima. This is in line with the observations that no significant changes are found in the absorption spectrum of the complex upon addition of I^-. No absorption spectral changes are observed for complex **2** either. These findings suggest that the emission quenching of both complexes **1** and **2** by I^- is not due to binding of the ion, but the involvement of an excited-state association process. Iodide-induced emission quenching has been reported in related luminescent rhenium(I) diimine systems.[7d]

^{1}H NMR Titration Studies. The anion-binding properties of complexes **1** and **2** have been studied by

^{1}H NMR titration experiments.[36] From the downfield shifts of the thiourea proton of complex **2** at 6.99 ppm, log K_s values of 3.42 and 4.80 are determined for the binding of F^- and OAc^-, respectively, which are comparable to those obtained from the emission titrations (Table 6). The binding of $H_2PO_4^-$ cannot be studied by NMR titrations due to solubility reasons. Unfortunately, under the influence of the anthraquinone unit, the thiourea protons of complex **1** do not show significant downfield shifts in the presence of our target anions, rendering it impossible to determine the binding interactions by NMR methods.

Summary. In this work, we have designed a new luminescent rhenium(I) polypyridine complex containing a thiourea-anthraquinone pendant, [Re(Me$_4$-phen)(CO)$_3$(Py-An)](CF$_3$SO$_3$) (**1**). The electrochemical and photophysical properties of this complex have been studied and compared to those of two control compounds, [Re(Me$_4$-phen)(CO)$_3$(Py-Ph)](CF$_3$SO$_3$) (**2**) and Et-An. The X-ray crystal structure of complex **2** has been studied. Both complexes **1** and **2** exhibit spectral changes upon addition of common anions including F^-, OAc^-, and $H_2PO_4^-$, and the binding stoichiometry and constants have been determined. While the anion-binding properties of complex **2** can only be reflected by its emission spectral changes, both the absorption and emission spectra of complex **1** display significant changes upon binding of anions, as a result of the additional anthraquinone unit. We believe that similar luminophore-receptor-chromophore conjugates can be exploited in the design of efficient receptor molecules for various analytes.

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Supporting Information Available: X-ray data (CIF) of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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