

Luminescent Iridium Phenanthroline Crown Ether Complex for the Detection of Silver(I) Ions in Aqueous Media

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The crown ether-linked iridium(III) complex $[\text{Ir}(\text{ppy})_2(\text{di-aza-phen})]^+$ (**1**) {ppy = 2-phenylpyridine and di-aza-phen = 4,7-di(1,4-dioxo-7,13-dithia-10-azacyclopenta-dec-10-yl)-1,10-phenanthroline (**7**)} has been prepared. Compound **1** exhibits a notable luminescence enhancement in the presence of Ag^+ in aqueous media. The analogous ruthenium(II) complex $[\text{Ru}(\text{phen})_2(\text{di-aza-phen})]^{2+}$ (**4**) {phen = 1,10-phenanthroline}, although equally exhibiting a luminescence enhancement in the presence of Ag^+ , is a far inferior sensor for Ag^+ than **1**. The 10 times higher luminescence enhancement $(I - I_0)/I_0$ of **1** was attributed to a dominance of the emission involving the di-aza-phen ligand that is responsible for binding to the metal ion. In contrast, the $^3\text{MLCT}$ emission of **4** does not involve the di-aza-phen ligand but does involve the phen ligand, thus only allowing for a remote effect upon addition of Ag^+ ions. While **1** is a highly selective chemosensor for Ag^+ in the presence of many metal ions, there is a strong interference of Hg^{2+} that may restrict its practical use.

Introduction

Selective and sensitive detection as well as quantification of heavy and transition metal ions play a crucial role in biological, chemical, clinical, and environmental applications. Although considerable efforts have been devoted to the elaboration of luminescence sensors for various metal ions in the last two decades,¹ there are only a handful of reports on Ag^+ ion sensing² and even less on Ag^+ in aqueous solution monitored by emission enhancement.^{2f} Because of the flourishing demand of silver compounds in miscellaneous commercial sectors and their augmented industrial sludge,³ severe contamination of the environment by Ag^+ is rising. Likewise, the interaction of Ag^+ ions with essential nutrients has further raised the awareness of its potential toxicity.³ Obviously, very reliable luminescence sensors for Ag^+ are

still required that show emission enhancement and ratiometric shift in aqueous solution even in presence of other frequently found metal ions.

Although ruthenium(II) complexes have been widely applied as probes for metal cations, inorganic anions, and biological analytes,⁴ iridium(III) complexes, to the best of our knowledge, have received little attention in chemosensor applications,⁵ particularly for metal cations.^{5e} This is astounding in light of the enticing photophysical and photochemical properties of iridium complexes.⁶ Herein, we present the design and synthesis of the crown ether appended iridium(III) complex **1**, which behaves as a sensitive and selective luminescent chemosensor for Ag^+ . The idea for the design was ignited by the fact that the LUMO of **1** should

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mainly be localized on the azacrown ether-substituted 1,10-phenanthroline ligand **7**.⁷ As a consequence, binding of metal ions at the two azacrown ether receptor sites of **7** should strongly change the LUMO energy, leading to a substantial alteration of the absorption and emission properties of **1**. For a close investigation of the role of the aza-dioxa-dithia crown ether in **1**, iridium complexes **2** and **3** and the analogous ruthenium complex **4** were prepared as well. The study of these complexes in the absence and in the presence of metal ions provided an insightful view on the special performance of **1** for metal ions sensing properties.

Experimental Section

General Information and Materials. ¹H and ¹³C NMR spectra were recorded in CD₂Cl₂ or CDCl₃ on a Bruker Avance 400 (400 MHz). Chemical shifts are reported in parts per million (ppm). Electrospray ionization (ESI) spectra were recorded on a LCQ Deca ThermoQuest instrument. Microanalyses were performed on an Euro elemental analyzer from EuroVector.

All reagents and chemicals were received from commercial sources and used without further purification. 2-Phenylpyridine was obtained from Aldrich; IrCl₃·xH₂O was obtained from ChemPur, and bis(2-methoxyethyl)amine was obtained from Merck.

The synthesis of 4,7-dichloro-1,10-phenanthroline (**5**),⁸ 1,4-dioxa-7,13-dithia-10-azacyclopentadecane (**6**),⁹ [(ppy)₂IrCl]₂ (ppy = 2-phenylpyridine),¹⁰ and the parent iridium complex **3**⁷ was accomplished according to known literature procedures. All manipulations related to Ir(III) and ruthenium(II) complexes, although

they have been proven to be air stable, were carried out under a nitrogen blanket. ¹H NMR, ¹³C NMR, ESI-MS, and elemental analyses were used to evaluate the purity of all compounds.

Synthesis of Complex 1. A mixture of [(ppy)₂IrCl]₂ (45.0 mg, 42.0 μmol) and ligand **7** (62.0 mg, 91.6 μmol) in CH₂Cl₂ (10 mL) was heated to reflux for 6 h, followed by the addition of excess of NH₄PF₆ (100 mg). Stirring was continued for another 1 h. The yellow reaction solution was washed with H₂O and dried with anhydrous MgSO₄. After removal of the solvent, the crude product was purified by column chromatography (neutral Al₂O₃, 1% MeOH in CH₂Cl₂ as eluent) to yield a yellow powder as pure product (35.0 mg, 34%).

¹H NMR (400 MHz, CD₂Cl₂): δ 8.01 (s, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 6.0 Hz, 2H), 7.70–7.75 (m, 4H), 7.49 (dd, *J* = 6.0, 0.7 Hz, 2H), 7.06 (dt, *J* = 7.4, 1.2 Hz, 2H), 6.92–6.96 (m, 4H), 6.88 (ddd, *J* = 7.4, 6.0, 1.2 Hz, 2H), 6.39 (dd, *J* = 7.4, 0.7 Hz, 2H), 3.84–3.88 (m, 8H), 3.77–3.79 (m, 8H), 3.67 (s, 8H), 3.00–3.04 (m, 8H), 2.74–2.76 (m, 8H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 168.5, 156.3, 151.9, 149.9, 149.2, 148.9, 144.4, 138.0, 132.2, 130.8, 125.1, 124.8, 123.2, 122.6 (2C), 119.9, 112.7, 74.3, 71.1, 54.0, 32.6, 30.5. ESI-MS for [C₅₄H₆₂IrN₆O₄S₄]⁴⁺: calcd *m/z* = 1179.3; found *m/z* = 1179.4. Anal. Calcd for C₅₄H₆₂IrN₆O₄S₄PF₆: C, 48.97; H, 4.72; N, 6.34. Found: C, 48.81; H, 4.62; N, 5.95.

Synthesis of Complex 2. Preparation of **2** followed the same procedure as that for **1** except that ligand **8** was used instead of **7**. Yield = 78%.

¹H NMR (400 MHz, CD₂Cl₂): δ 8.23 (s, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 6.2 Hz, 2H), 7.70–7.76 (m, 4H), 7.50 (ddd, *J* = 5.9, 1.4, 0.6 Hz, 2H), 7.05–7.09 (m, 4H), 6.94 (td, *J* = 7.4, 1.3 Hz, 2H), 6.87 (ddd, *J* = 7.4, 5.9, 1.4 Hz, 2H), 6.41 (dd, *J* = 7.4, 0.9 Hz, 2H), 3.76–3.85 (m, 8H), 3.67 (t, ³*J* = 5.6 Hz, 8H), 3.29 (s, 12H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 168.5, 157.7, 152.1, 149.7, 149.2, 148.9, 144.4, 137.9, 132.2, 130.7, 125.0, 124.7, 123.1, 122.7, 122.4, 119.8, 113.1, 70.0, 59.1, 52.6. ESI-MS for [C₄₆H₅₀IrN₆O₄]⁴⁺: calcd *m/z* = 943.4; found *m/z* = 943.3. Anal. Calcd for C₄₆H₅₀IrN₆O₄P: C, 50.78; H, 4.63; N, 7.72. Found: C, 50.85; H, 4.38; N, 7.66.

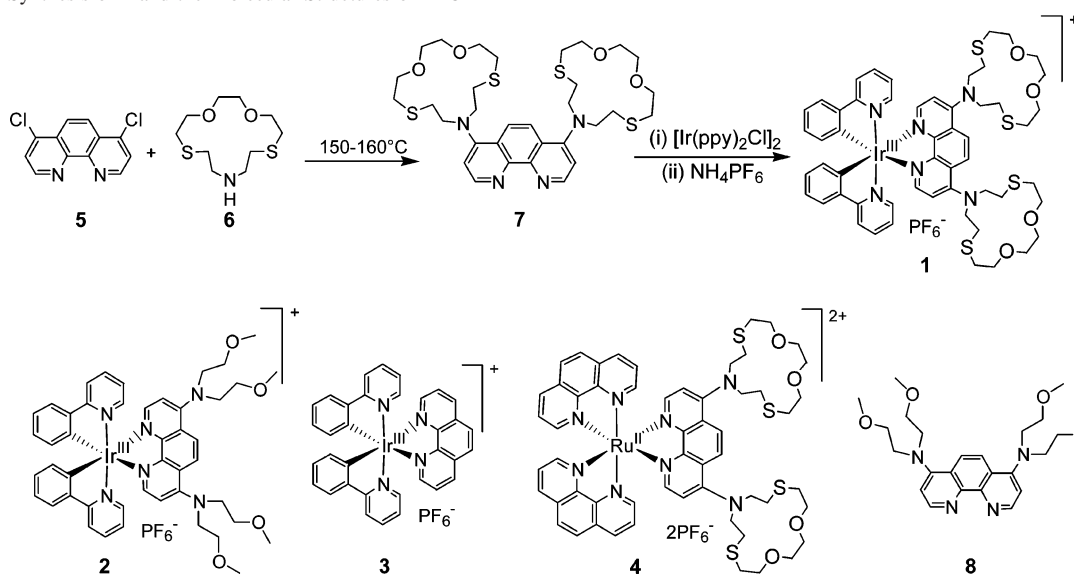
Synthesis of Complex 4. Complex **4** was prepared according to the literature procedure described earlier.¹¹ Accordingly, a mixture of *cis*-(phen)₂RuCl₂ (53.0 mg, 99.5 μmol) and ligand **7** (68.0 mg, 100 μmol) was heated to reflux in ethanol for 24 h, followed by anion exchange with NH₄PF₆. The crude product was purified by column chromatography (neutral Al₂O₃, 1% MeOH in CH₂Cl₂ as elutant) providing a pure red solid (98.0 mg) in 69% yield.

¹H NMR (400 MHz, CD₂Cl₂): δ 8.52 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.47 (dd, *J* = 8.3, 1.2 Hz, 2H), 8.15–8.20 (m, 6H), 8.04 (s, 2H), 7.99 (dd, *J* = 5.3, 1.2 Hz, 2H), 7.75 (dd, *J* = 8.3, 5.3 Hz, 2H), 7.64 (dd, *J* = 8.3, 5.3 Hz, 2H), 7.45 (d, *J* = 6.4 Hz, 2H), 6.84 (d, *J* = 6.4 Hz, 2H), 3.81–3.85 (m, 8H), 3.75–3.78 (m, 8H), 3.65 (s, 8H), 2.97–3.02 (m, 8H), 2.72–2.75 (m, 8H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 155.5, 152.6, 150.4, 149.8, 148.5, 148.4, 136.5, 131.2 (2C), 128.5, 128.4, 126.4, 126.2, 124.5, 122.5, 112.8, 74.1, 71.0, 54.0, 32.4, 30.3. ESI-MS for [C₅₆H₆₂N₈O₄RuS₄]²⁺: calcd *m/z* = 570.1; found *m/z* = 570.2. ESI-MS for [C₅₆H₆₂N₈O₄RuS₄PF₆]⁺: calcd *m/z* = 1285.2; found *m/z* = 1285.3. Anal. Calcd for C₅₆H₆₂N₈O₄RuS₄P₂F₁₂·1/2H₂O: C, 46.73; H, 4.41; N, 7.78. Found: C, 46.85; H, 4.53; N, 7.53.

Synthesis of Ligand 7. A mixture of 4,7-dichloro-1,10-phenanthroline (**5**) (314 mg, 1.26 mmol) and 1,4-dioxa-7,13-dithia-10-

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Scheme 1. Synthesis of **1** and the Molecular Structures of **2–8**

azacyclopentadecane (**6**) (700 mg, 2.78 mmol) was heated at 150–160 °C for 2 h. The crude product was dissolved in CH_2Cl_2 (20 mL) and washed with 20% KOH solution. After it was dried with anhydrous MgSO_4 and the solvent was removed, column chromatography (silica gel, 5% MeOH in CH_2Cl_2) was used to purify the crude product. A yellow oil (540 mg) was obtained as pure product in 67% yield.

^1H NMR (400 MHz, CDCl_3): δ 8.92 (d, $J = 5.2$ Hz, 2H), 7.99 (s, 2H), 7.09 (d, $J = 5.2$ Hz, 2H), 3.82 (t, $J = 5.2$ Hz, 8H), 3.73 (s, 8H), 3.65–3.69 (m, 8H), 2.94–2.98 (m, 8H), 2.77 (t, $J = 5.2$ Hz, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.1, 149.9, 148.5, 123.6, 121.0, 112.5, 73.9, 70.9, 53.3, 32.0, 30.0. ESI-MS for $[\text{C}_{32}\text{H}_{46}\text{N}_4\text{O}_4\text{S}_4 + \text{H}]^+$: calcd $m/z = 679.2$; found $m/z = 679.2$.

Synthesis of Ligand 8. The preparation of ligand **8** was similar to that of ligand **7** except that bis(2-methoxyethyl)amine (670 mg, 5.03 mmol) was used instead of 1,4-dioxo-7,13-dithia-10-azacyclopentadecane (575 mg, 65%).

^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, $J = 5.2$ Hz, 2H), 8.06 (s, 2H), 7.19 (d, $J = 5.2$ Hz, 2H), 3.65 (t, $J = 6.0$ Hz, 8H), 3.55 (t, $J = 6.0$ Hz, 8H), 3.29 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.6, 149.7, 148.2, 123.9, 121.1, 113.3, 70.3, 58.9, 53.0. ESI-MS for $[\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_4 + \text{H}]^+$: calcd $m/z = 443.3$; found $m/z = 443.3$.

Luminescence and UV–vis. Luminescence and UV–vis measurements were carried out with a solution containing complexes **1–4** (10 μM) in MeCN. The luminescence titration experiments were performed with 5.0 μM solution (MeCN/ $\text{H}_2\text{O} = 1:1$) of **1** and **4**. UV–vis spectra were measured on a Varian Cary 100 Bio UV–vis spectrophotometer, and emission spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer with excitation and emission slit widths at 5 nm. All emission spectra were corrected. Equivalents of metal ions (as perchlorate salts) are always denoted according to the iridium or ruthenium complex.

Electroanalytical Investigations. Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) of **1–4** were measured by using a standard three-electrode setup (Pt working and Pt auxiliary electrode, silver wire as reference electrode) connected to a PARSTAT 2273 Advanced electrochemical system. The experiments were carried out on a 1.0 mM solution of **1–4** in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. All potentials are referenced to ferrocene as internal standard, with $E_{1/2}(\text{Fc}^+/\text{Fc}) = 0.39$ V vs SCE (scan rate = 100 mV s^{-1}).

Results and Discussions

Synthesis and Characterization. The preparation of **1** and the chemical structures of **2–8** are shown in Scheme 1. A multistep pathway was needed to prepare the desired iridium complex **1**. The important intermediate, 4,7-di(1,4-dioxo-7,13-dithia-10-azacyclopentadec-10-yl)-1,10-phenanthroline (**7**), was synthesized by a direct reaction of 4,7-dichloro-1,10-phenanthroline (**5**)⁸ and 1,4-dioxo-7,13-dithia-10-azacyclopentadecane (**6**)⁹ heated at 150–160 °C for 2 h. Compound **7** reacted with the chloride bridged dimeric iridium complex $[(\text{ppy})_2\text{IrCl}]_2$ ($\text{ppy} = 2\text{-phenylpyridine}$)¹⁰ in CH_2Cl_2 held at reflux temperature for 6 h, followed by anion exchange with NH_4PF_6 , to yield the desired iridium complex **1**. The same procedure was used to prepare **2** and **3**. Preparation of the analogous ruthenium complex **4** was accomplished according to the procedure that we had described earlier.¹¹

Electronic Absorption Properties. UV–vis absorption data of complexes **1–4** are summarized in Table 1. The absorption spectra (see Supporting Information, Figure S1) of iridium complexes **1–3** in MeCN displayed intense ligand-centered LC ($\pi \rightarrow \pi^*$) absorption bands of ppy at approximately 252–255 nm for **1–3** and of phen at 266 nm for **3** (ϵ on the order of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$). In contrast to parent complex **3**, the 4,7-diamino-substituted phenanthroline iridium complexes **1** and **2** exhibited more intense absorption bands in the lower-energy region of 320–450 nm (ϵ on the order of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (see Table 1 and Figure S1). These intense absorption bands may be assigned to ligand-centered LC ($\pi \rightarrow \pi^*$) transitions of **7** or **8** since the free ligands **7** and **8** also absorb in a similar region (e.g., $\lambda_{\text{max}}(\text{abs}) = 335$ nm for **7**, see Supporting Information, Figure S2). According to previous studies, metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) should also contribute to the visible-region absorption bands.¹² However, no distinct absorption bands above 400 nm were observed for **1** and **2**, suggesting that the MLCT ($d_{\pi}(\text{Ir}) \rightarrow \pi^*$ (**7**, **8** or

Table 1. Summary of Electrochemical and Spectroscopic (UV-vis, Photoluminescence) Data of Complexes **1–4**

	redox data (V _{Fc}) ^a				UV-vis (nm) ^b (log ε)	photoluminescence (nm) ^b (λ _{ex})
	E _{1/2} ^{ox} (1)	E _{1/2} ^{ox} (2)	E _{1/2} ^{red} (1)	E _{1/2} ^{red} (2)		
1	0.74	1.02 ^c	-2.10	-2.62 ^c	255 (4.77), 352 (4.34), 375 (4.35)	527, 559 (375)
2	0.73	1.10 ^c	-2.11	-2.61 ^c	252 (4.77), 348 (4.63), 374 (4.38)	520, 553 (374)
3	0.86		-1.80 ^c	-2.56 ^c	253 (4.69), 266 (4.73), 372 (3.82), 409 (3.54), 467 (2.79)	596 (372)
4	0.59	1.20 ^c	-1.80 ^c	-1.95 ^c	265 (5.00), 318 (4.21), 431 (4.40), 462 (sh) (4.33)	667 (431)

^a Electroanalytical experiments were carried out in MeCN (0.1 mM solution) with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as electrolyte. Ferrocene was used as internal standard. All potentials are reported with respect to the Fc/Fc⁺ couple. ^b UV-vis and photoluminescence spectra were recorded in 10 μM MeCN solutions. The values in the parentheses of the photoluminescence emission experiments are the excitation wavelengths. ^c Irreversible waves.

ppy)) transition bands in **1** and **2** are either too weak or merged together with the LC ($\pi \rightarrow \pi^*$) transition bands.

Electrochemical Properties. The electrochemical properties of **1–4** were determined by cyclic voltammetry (CV) and differential pulsed voltammetry (DPV), see Table 1. The first reversible oxidation waves E_{1/2} at 0.74 V_{Fc} for **1**, 0.73 V_{Fc} for **2**, and 0.86 V_{Fc} for **3** were assigned to the Ir^{3+/4+} redox process, whereas the second irreversible oxidation waves at 1.02–1.10 V_{Fc} in **1** and **2** should correspond to the oxidation of ligands **7** and **8**.¹¹ Because of the electron-donating character of the amino nitrogens in ligands **7** and **8**, the Ir^{3+/4+} oxidation potentials of **1** and **2** are situated at less anodic potential than that of **3**. The oxidation potential of **4** at 0.59 V_{Fc} was attributed to the Ru^{2+/3+} transition, equally shifted cathodically in comparison with its parent complex.¹¹ Reversible reduction waves at ~ -2.10 V_{Fc} for **1** and **2** and irreversible reduction waves at approximately -1.80 V_{Fc} for **3** and **4** may be assigned to the reduction of the phenanthroline ligands **7** and **8** in **1** and **2** and to phen in **3** and **4**, respectively.¹¹ The second, more cathodically shifted irreversible reduction waves at approximately -2.56 to -2.62 V_{Fc} in **1–3** are attributed to the reduction of the ppy ligand, being consistent with earlier result.⁷ The $\pi \rightarrow \pi^*$ energy gaps of ligands **7** and **8** in **1** and **2** were calculated from the electrochemical data to be 3.12 eV for **1** and 3.21 eV for **2**, respectively. According to electronic absorption data, the lower-energy absorption bands correspond to ~3.54 (at λ_{max} = ~350 nm) and 3.32 eV (at λ_{max} = ~374 nm) for **1** and **2**, respectively. This is comparable with results obtained from electrochemical data. Thus, we can tentatively assign the intense absorption bands of **1** and **2** at 320–450

nm mainly to ligand-centered (**7** or **8**) LC ($\pi \rightarrow \pi^*$) transitions.

Luminescence Properties. The photoluminescence (PL) study revealed the similarities between **1** and **2** but also the differences with **3** (see Supporting Information, Figure S1). The emissions of **1** and **2** were found at higher-energy regions than **3** featuring two emission maxima (λ_{max} = 527 and 559 nm for **1** and λ_{max} = 520 and 553 nm for **2**, respectively). Because a careful characterization of **1** and **2** confirmed their purity and furthermore excitation spectra at the two emission wavelengths were almost identical, we had to conclude that the two emission maxima are not caused by the presence of impurities (see Supporting Information, Figure S3). For cationic iridium(III) complexes containing diimine ligands, emission commonly comes from a mixed excited-state containing ³LC and ³MLCT transitions.^{6b,c,13} Hence, emission spectra featuring multiple emission maxima (or shoulders) are often observed in iridium(III) diimine complexes depending on the different contributions of the two components.^{5b,d,13d,e} According to previous studies, PL spectra from ligand-centered ³LC($\pi \rightarrow \pi^*$) states often display vibronic progressions and small dependence on solvent polarity and temperature, while those from CT states are broad, featureless, and sensitive to solvent polarity and temperature.^{13c,14} The present study on **1** and **2** showed that their emission was independent of solvent polarity (see Supporting Information, Figure S4) and temperature. When the temperature was lowered from 298 to 10 K, however, a better resolution of the vibronic substructure and a slight blue-shift was noticed (see Supporting Information, Figure S12). Thus, it can be concluded that the emission of **1** and **2** is caused by excited states with dominant ligand-centered (on ligands **7** and **8**) character (³-LC). In agreement with this designation, recent experimental and theoretical insight into cationic iridium complexes, including [Ir(2-phenylpyridine)₂(4,4'-dimethylamino-2,2'-bipyridine)](PF₆),¹⁵ furthermore allows us to refine the assignment by suggesting that the two maxima in the emission of **1** and **2** result from mixing MLCT and LC phen($\pi \rightarrow \pi^*$) transitions, with the latter ones dominating. In contrast, the solvent polarity dependence of the PL emission of **3** is in accordance with its dominating ³MLCT emission at room temperature^{5b,d,13c} (see Supporting Information, Figure S4). Absorption and emission characteristics of **4** were as expected and resembled those of its parent complex and other type of azacrown ether appended phenanthroline ruthenium complexes.¹¹

Metal Ion Binding Studies. The ability of complex **1** to bind metal ions was studied by electronic absorption and

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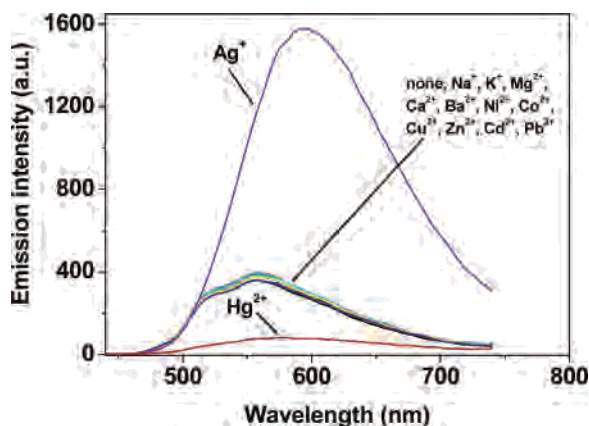


Figure 1. Effects on the emission of **1** (5.0 μM in $\text{MeCN}/\text{H}_2\text{O} = 1:1$) upon addition of different metal ions (100 equiv). The excitation wavelength was set to 375 nm.

PL measurements in aqueous media. The responses of **1** (5.0 μM in $\text{MeCN}/\text{H}_2\text{O} = 1:1$, v/v) were interrogated in the presence of a wide range of metal ions as their perchlorate salts, that is, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} (100 equiv) (see Figure 1 and Figure S5 in Supporting Information). The UV–vis absorption investigations showed that for a large variety of metal ions the absorption was only significantly changed upon addition of Ag^+ and Hg^{2+} , both leading to a decrease of the intensity of the low-energy absorption band (320–450 nm). A survey of the emission response of **1** in the presence of the same array of metal ions showed similar results. Again, only pronounced changes were detected for Ag^+ and Hg^{2+} ions, while all other metal ions led to relatively insignificant variations. Upon addition of excess of Ag^+ (100 equiv), the emission intensity ($I - I_0$)/ I_0 of **1** was enhanced ~ 3.4 -fold (with I and I_0 referring to the maximum emission intensity of **1** in the presence and absence of Ag^+ , respectively) and was accompanied by a pronounced red shift of $\lambda_{\text{max}}(\text{em})$ to 595 nm. In contrast, the addition of Hg^{2+} quenched the emission of **1** (quenching efficiency = $\sim 80\%$ with 100 equiv of Hg^{2+}), equally showing a $\lambda_{\text{max}}(\text{em})$ red shift. The selectivity with regard to different metal ions can be evaluated by using the ratio $I_{(595)}/I_{0(595)}$ of **1**, where $I_{(595)}$ and $I_{0(595)}$ refer to the emission intensity of **1** at 595 nm in the presence and absence of metal ions, respectively. The ratio $I_{(595)}/I_{0(595)}$ was found to be 5.7 for Ag^+ and 0.28 for Hg^{2+} , respectively. All other metal ions revealed constant values of $I_{(595)}/I_{0(595)} = 1.0$ – 1.1 . Control experiments with **2** and **3** were performed in presence of the above-mentioned set of metal ions (100 equiv) resulting in no obvious intensity changes in both UV–vis and emission. These results indicated that the UV–vis absorption and luminescent emission responses of **1** in the presence of Ag^+ or Hg^{2+} can be attributed to their complexation with the aza-dioxa-dithia crown ethers of **1**, being consistent with the well-known strong thiophilic properties of Ag^+ and Hg^{2+} .

For comparison, the UV–vis and emission responses of the analogous ruthenium complex **4** were studied with the same set of metal ions. We observed similar results as with **1**, that is, minor alterations in the $^1\text{MLCT}$ absorption bands

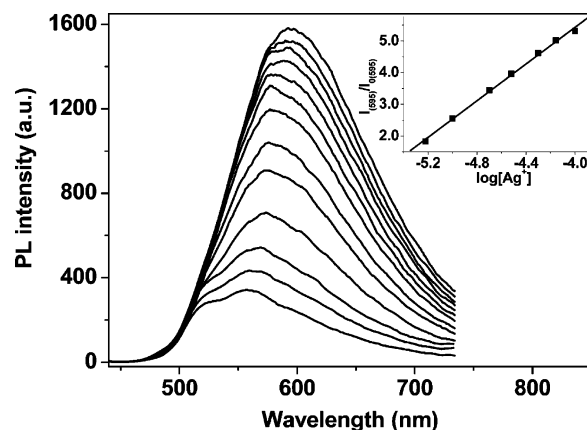


Figure 2. Emission intensity responses of **1** (5.0 μM in $\text{MeCN}/\text{H}_2\text{O} = 1:1$) upon addition of 3.0, 6.0, 10, 20, 30, 50, 70, 100, 150, 200, 300, and 500 μM Ag^+ ions. Inset: The correlation between emission intensity of **1** at 595 nm and $\log[\text{Ag}^+]$. The excitation wavelength was 375 nm.

were only induced by addition of Ag^+ and Hg^{2+} . Moreover, Ag^+ was the only metal ion that triggered an emission enhancement, while Hg^{2+} quenched the emission (see Supporting Information, Figure S6). Comparison of **1** and **4** exhibited that the iridium complex **1** was >10 times more efficient as apparent from the emission enhancement factors ($(I - I_0)/I_0$) for Ag^+ sensing, which amounted to 3.4 for **1** and only 0.3 for **4**. The smaller PL enhancement of ruthenium complex **4** as compared to iridium complex **1**, after Ag^+ addition can now easily be rationalized. According to the discussion above, we assign the dominant emission of **1** to a ^3LC (di-aza-phen, **7**) excited state. In contrast, the emission of ruthenium complex **4** is mainly attributed to the well-known $^3\text{MLCT}$ excited-state arising from the parent phen ligand. Thus, binding of Ag^+ to the aza-dioxa-dithia crown ether sites of ligand **7** should induce much more intense influence on iridium complex **1** than on ruthenium complex **4**.

To further interrogate the binding properties of **1** to Ag^+ ions, titration experiments were carried out (Figure 2). A gradual emission enhancement and a red shift of $\lambda_{\text{max}}(\text{em})$ were observed upon Ag^+ addition. Moreover, a linear correlation between the emission intensity of **1** at 595 nm and $\log[\text{Ag}^+]$ was received (Figure 2, inset) that allowed the determination of parts per million levels of Ag^+ ion in aqueous solution. The luminescence enhancement of **1** can be rationalized by a weakening of the electron donating ability of the nitrogen of the aza-dioxa-dithio crown ether moiety in **1** upon complexation with Ag^+ thus altering the photophysical properties of **1**.^{5e,16} The red shift of $\lambda_{\text{max}}(\text{em})$ and lower energy emission can be explained by a lowering of the LUMO energy level upon Ag^+ binding because the energy gap was decreased. Interestingly, the titration also revealed that the two emission maxima of **1** gradually merged into one single maximum at $\lambda_{\text{max}}(\text{em}) = 595$ nm. A titration of **1** was also performed against Hg^{2+} under the same conditions (Figure S7, Supporting Information). The titration

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showed that the emission intensity of **1** first slightly enhanced (<2.0 equiv); however, with larger amounts of Hg²⁺ added, the emission of **1** subsequently was quenched (>2.5 equiv). Again, the merging of two emission maxima into one was observed along with a red shift of the emission. The complex emission intensity behavior of **1** upon Hg²⁺ addition may be explained by a competition between emission-enhancing effects (decrease of the nitrogen electron donating ability upon Hg²⁺ binding) and well-known electron- or energy-transfer quenching effects of unbound Hg²⁺ ions.¹⁷ The merging of the two emission maxima into one upon addition of Ag⁺ or Hg²⁺ is assumed to arise from a change of the dominating ³LC emission in the metal-free form of **1** to a dominating ³MLCT emission in the metal-loaded form.¹⁸ The emission titration data also allowed us to evaluate and determine the special binding modes and association constants between **1** and Ag⁺ or Hg²⁺ by using the computer program SPECFIT.¹⁹ One-step association to **1**·(Ag⁺)₂ and **1**·(Hg²⁺)₂ was found, showing best fitting results with log β^{Ag(I)} = 8.6 ± 0.1 and log β^{Hg(II)} = 9.0 ± 0.1.²⁰ To confirm the binding modes and association constants of **1** with Ag⁺ and Hg²⁺, ¹H NMR titration and ESI-MS experiments were performed. ¹H NMR titration results showed that ~2.0 equiv of Ag⁺ or Hg²⁺ were required to reach the maximum chemical shift change (see Supporting Information, Figure S11), thus supporting the 2:1 (metal ion/**1**) binding model. With the program WinEQNMR,²¹ the titration data of **1** against Ag⁺ suggested a one-step formation of **1**·(Ag⁺)₂ with log β^{Ag(I)} = 8.2, being comparable with the result from the emission titration data. In contrast, NMR titration of **1** with Hg²⁺ did not allow proper fitting because of a broadening of signals. ESI-MS measurements of **1** in the presence of excess amounts of Ag⁺ and Hg²⁺ showed both **1**·(Mⁿ⁺) and **1**·(Mⁿ⁺)₂ (see Supporting Information, Figures S9 and S10). Although the ESI-MS results cannot be used to determine the complexation constant, they help to identify the binding site of the metal ions.

The results above indicate that complex **1** acts as a sensitive luminescence enhancement chemosensor for Ag⁺ in aqueous solution. The practical benefit of **1** in the detection of Ag⁺ ions was evaluated by the following two tests. First,

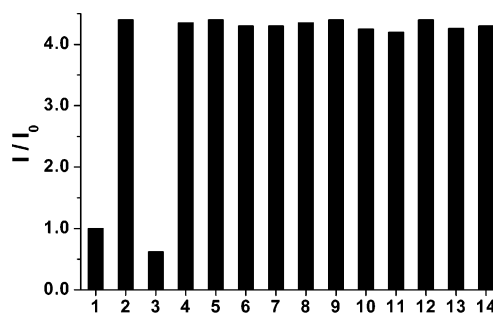


Figure 3. Emission response of **1** in the presence of both Ag⁺ and another competing metal ion (both 100 equiv): (1) **1** only, (2) Ag⁺ only, (3) Ag⁺ and Hg²⁺, (4) Ag⁺ and Na⁺, (5) Ag⁺ and K⁺, (6) Ag⁺ and Mg²⁺, (7) Ag⁺ and Ca²⁺, (8) Ag⁺ and Ba²⁺, (9) Ag⁺ and Co²⁺, (10) Ag⁺ and Ni²⁺, (11) Ag⁺ and Cu²⁺, (12) Ag⁺ and Zn²⁺, (13) Ag⁺ and Cd²⁺, and (14) Ag⁺ and Pb²⁺.

the interference of **1** with other metal ions during the detection of Ag⁺ ions was assessed by test series in which the emission of **1** was monitored in the presence of 100 equiv of both Ag⁺ and other metal ions (Figure 3). Notably, the sensor's luminescence was not influenced to any significant extent, except in presence of Hg²⁺ because of its stronger binding ability with **1**. Second, the selective and sensitive response of **1** to Ag⁺ in a physiological environment ([Na⁺] = 145 mM, [K⁺] = 5 mM, [Mg²⁺] = 2 mM, and [Ca²⁺] = 5 mM)²² was verified. Titration of **1** against Ag⁺ in presence of these physiologically important metal ions resulted in not only a gradual emission enhancement but also a linear correlation between the luminescence intensity of **1** and log [Ag⁺] (Figure S8, see S.I.).

Conclusions

The aza-dithia-dioxa crown-ether-appended iridium(III) and ruthenium(II) complexes **1** and **4** were prepared. Both **1** and **4** exhibited selective binding properties toward Ag⁺ and Hg²⁺ ions in aqueous media by characteristic luminescence responses. Importantly, the iridium complex **1** proved to be a far superior sensor for Ag⁺ than the analogous ruthenium complex **4**. In presence of excess of Ag⁺, the luminescence enhancement factor was more than 10 times higher for **1** than **4**. The larger enhancement of **1** is attributed to the fact that the metal ion binding ligand **7** dominates the emission in **1**. Moreover, larger loadings of metal ions change the character of the emission of **1** from ³LC to ³MLCT because ligand **7** becomes increasingly a better acceptor. Rewardingly, the sensing of Ag⁺ ions with **1** worked accurately in the presence of many competing metal ions, as well as in physiologically relevant samples. This study should therefore provide further impetus to investigate Ir(III)-based chemosensors.

Acknowledgment. We are indebted to the Deutsche Forschungsgemeinschaft (FG 516) and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: UV-vis and emission spectra of **1**–**3**, absorption and emission responses of **4** with various

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- (18) This statement is consistently corroborated by a number of observations and reasonings: (i) We observe identical spectral shape and similar emission energy for the Ag⁺-bound **1** and parent complex **3**. (ii) ³-MLCT emissions are known for their broad and featureless spectrum. (iii) While **1** shows a temperature-independent emission wavelength, the silver-loaded complex displays a strong temperature dependence (see Supporting Information Figures S12 and S13). Apparently, larger loadings of metal ions change the character of the emission of **1** from ³LC to ³MLCT because ligand **7** becomes increasingly a better acceptor.
- (19) (a) Association constants were obtained using the computer program SPECFIT, Global Analysis system, Version 3.0.32. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
- (20) According to the luminescence and NMR titration results, only a one-step model (metal/**1** = 2:1) gave reasonable fitting results. This model suggests that there is no strong interaction between the two bound metal ions (Ag⁺ or Hg²⁺) on one molecule of **1**.
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Iridium Phenanthroline Crown Ether Complex

metal ions addition, luminescence titration of **1** with Hg²⁺ and with Ag⁺ in physiologically relevant samples, ¹H NMR titration of **1** with Ag⁺, ESI-MS of **1** in the presence of excess amounts of Ag⁺ and Hg²⁺, and low-temperature PL emission of **1** and **1**•Ag⁺.

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