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Chemosensing of Chloride Based on a Luminescent Platinum(II) NCN Pincer Complex in Aqueous Media

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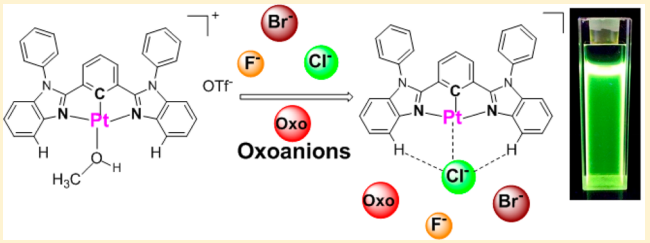
Supporting Information

ABSTRACT: The new luminescent platinum(II) pincer complex [Pt(NCN)(S)]TfO (**I**; NCN = 1,3-bis(2-*N*-phenylbenzimidazolyl)benzene, S = solvent, and TfO^- = triflate anion) was synthesized and studied as a chemosensor for chloride in aqueous media. In 50 vol % aqueous DMF or CH_3CN chloride quenches the fluorescence with association constants of 1.2×10^3 and 81 M^{-1}, respectively. On the other hand, in the micellar medium of cetyltrimethylammonium hydrogensulfate at pH 7.0 additions of inorganic anions to **I** enhance the fluorescence with a pronounced selectivity toward chloride, which shows also much tighter binding to the receptor with association constant 7.9×10^4 M^{-1} in comparison to that in mixed organic solvents. On basis of ^1H NMR titration experiments and the crystal structure of the neutral chloro complex of **I** the binding mode of chloride is proposed involving the coordination of chloride to the Pt(II) atom with simultaneous formation of intramolecular short C−H···Cl−Pt contacts. The combination of the cyclometalated platinum complex **I** with a cationic surfactant allows for the detection of chloride in the micromolar concentration range in samples of bottled mineral water.



INTRODUCTION

Recognition and sensing of biological anions such as chloride remains an active and important area in supramolecular chemistry.[1] Chloride anion recognition has been dominated by the use of synthetic receptors containing arrays of hydrogen bond donors as association sites. However, such receptors are restricted to nonaqueous media,[2,3] which limits their practical applications in water. On the other hand, the optical detection of chloride in water can be achieved with fluorescent dyes, nanoparticle-based fluorescent probes, and luminescent iridium complexes, which undergo a collision-induced quenching process in the presence of chloride.[4−6] Typically, these dyes or sensors show Stern−Volmer quenching constants between 1 and 300 M^{-1}. Consequently, they are suitable to sense chloride in the millimolar concentration range, but not significantly below. Furthermore, these probes are not particularly selective, and interference from other halides, pseudohalides, heavy-atom-containing molecules, and oxygen can be a problem.[4,6] In principle, it should be possible to overcome these limitations by using an optical chemosensor with a specific, high-affinity binding site for chloride. However, the creation of a potent and selective receptor for chloride in pure water is an ongoing challenge. The difficulty in making receptors for chloride recognition in water is due to the high solvation energy of chloride ($\Delta G° = -340$ kJ mol^{-1}).[7] Water is thus an efficient competitor for any chloride-binding molecule. Reports in the context of medicinal inorganic chemistry have shown that the organometallic aqua complexes $[(arene)Ru(en)(OH_2)]^{2+}$ are able to bind chloride in water with association constants between 100 and 200 M^{-1}.[8] Recently a series of Rh^{III} aqua complexes of general formula $[Cp^*Rh(N-N\text{-chelate})(OH_2)]^{2+}$ showed higher values of up to 660 M^{-1}.[9] This work is based on the idea that the capture of chloride in water is possible with a transition-metal-based receptor with a high affinity for this halide. In this context, Pt^{II} complexes containing one available coordination site occupied by a solvent molecule or a noncoordinating anion are potential receptors and sensors for chloride. The results obtained for a green luminescent platinum pincer complex, including synthesis, X-ray crystal structures, and spectroscopic studies, are summarized below.

RESULTS AND DISCUSSION

Platinum pincer complexes of the general formula Pt(NCN)Cl (NCN = N,C,N-chelating ligand) are often highly luminescent, and these have been used in catalysis, as biomarkers for proteins, as probes for DNA, and as phosphorescent compounds for new materials.[10,12b,c,13,14] However, anion recognition still remains largely unexplored. The chloride ligand in these complexes can be abstracted efficiently with silver salts (e.g., AgOTf).[12a] The resulting cationic complexes $[Pt(NCN)(S)]^+$ (S = solvent) display a strong affinity for chloride.[11] The aqua complex $[Pt\{C_6H_3(CH_2NMe_2)_2\}(OH_2)]^+$, for example, was shown to bind chloride in water with an association constant of $K_a \approx 280$ M^{-1}.[11] An interesting platinum aqua complex with a bis(imidazolinyl)phenyl ligand,

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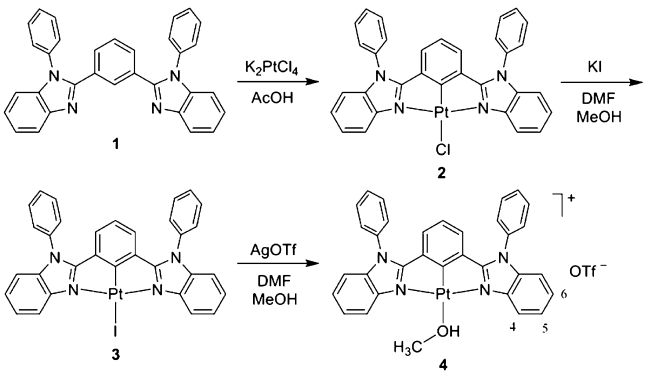
on the other hand, was reported to abstract chloride from CH_2Cl_2 in the crystallization process.[12a] These findings suggested that $[Pt(NCN)(S)]^+X^-$ (X = noncoordinating anion) complexes could be used as receptor units for chloride sensors. It therefore appears possible to obtain a luminescent platinum(II) complex with interesting properties, to sense chloride without the need for an additional signaling unit. For these investigations, the ionic complex **4** was successfully obtained following the procedure described in Scheme 1, which

Scheme 1



is similar to that reported by Song.[12a] Complex **4** is structurally close to cyclometalated complexes reported by Yam.[12b] The synthesis of **4** was accomplished by metalation of 1,3-bis(2-*N*-phenylbenzimidazolyl)benzene (**1**) with K_2PtCl_4 in acetic acid to give the neutral chloro complex **2**. Halide exchange with KI gave the iodo complex **3**, which was converted to **4** by reaction with AgOTf in DMF/CH_3OH (1/9 v/v).[12d−f] Complex **4** was isolated in good yield as a light brown crystalline powder, pure according to ^1H NMR in CD_2Cl_2 (Figure S9, Supporting Information). Direct abstraction of the chloride ligand from complex **2** using AgOTf did not produce the pure complex **4**. Complexes **2** and **3** are insoluble in CH_3OH; in contrast, the complex **4** is moderately soluble at room temperature. The mass spectrum of **4** by positive electrospray ionization showed essentially two peaks that can be assigned to the cationic complex $[\mathbf{4}]^+$ (656.16 *m*/*z*) and the methanolic complex $[\mathbf{4}(CH_3OH)]^+$ (697.17 *m*/*z*). Elemental analysis (C, N, H) was rather consistent with the methanolic adduct. The ^{19}F NMR spectrum of **4** showed one signal at −80.0 ppm (Figure S10, Supporting Information), which can be assigned to a noncoordinated triflate anion by comparison with the spectrum of NaOTf.

Single crystals of **2** and **3** were obtained by slow evaporation from CH_2Cl_2 solutions. Crystallographic analysis showed that both complexes display a distorted-square-planar geometry (Figure 1). The platinum−halide bond distances Pt−Cl = 2.4213(19) and 2.4150(19) Å (two independent molecules in the unit cell) and Pt−I = 2.6911(4) Å are significantly longer than what was found for Pt−terpyridine complexes such as $[Pt(terpy)Cl]OTf$ (2.307(1) Å),[14] $[Pt(terpy)Cl]ClO_4$ (2.301(6) and 2.302(7) Å),[15] or $[Pt(terpy)I][AuI_2]$ (2.5930(5) Å)[16] (Table 1). This difference can be ascribed to the strong trans influence of the phenyl ligand opposite the halide.[17] Both complexes feature intramolecular short CH···X−Pt contacts between hydrogen atoms of the benzimidazole groups and the halide ligands (1-CH···Cl−Pt = 2.744(4) and 4-CH···Cl−Pt = 2.752(4) Å; 1-CH···I−Pt = 2.863(4) and 4-CH···I−Pt = 2.891(5) Å). In the case of **2**, the lengths of the

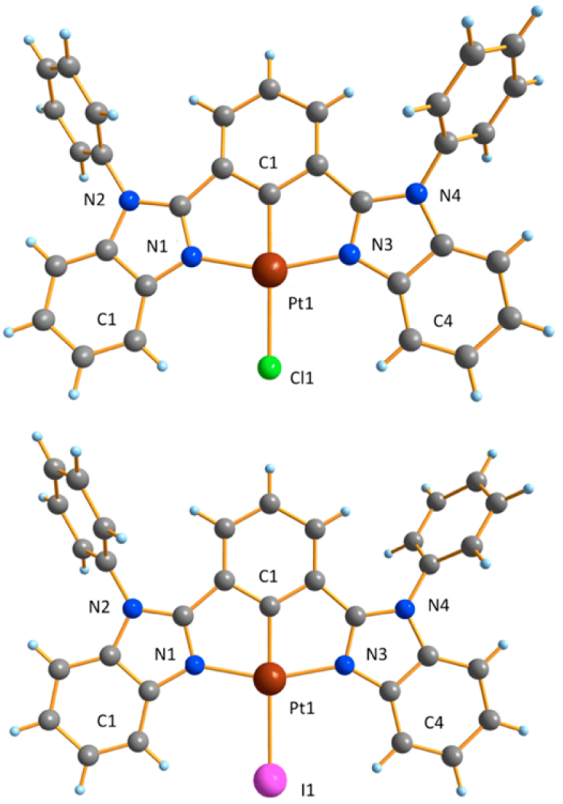


Figure 1. Ball and stick models of the molecular structures of complex **2** (top) and **3** (bottom) in the crystal. Solvent molecules are omitted for clarity. For complex **2**, two independent molecules are found in the unit cell, only one of which is shown.

CH···Cl−Pt interaction are longer than a typical hydrogen bonding interaction such as $Cl_3C-H\cdots Cl^-$ (2.39(3) Å).[19] This difference of 0.35 Å is possibly a result of the low flexibility of the NCN pincer ligand and the chloride ligand in the complex. Despite this, in the ^1H NMR spectra of **2** and **3**, these CH atoms are characterized by a pronounced downfield shift (δ 9.05 ppm for **2** and 9.58 ppm for **3** in CD_2Cl_2; see the Supporting Information). Similar short CH···Cl−Pt contacts and ^1H NMR spectroscopic features were observed for a Pt(NCN)Cl complex with a pinene-derived pincer ligand.[18]

Attempts to get suitable crystals of **4** in CH_3OH were not successful; however, the crystallization of **4** in CH_3CN/CH_2Cl_2 (1/1 v/v) at room temperature generated suitable yellow single crystals. X-ray diffraction showed a cocrystal of general formula $[Pt(NCN)CH_3CN]OTf\cdot[Pt(NCN)Cl]$ (**5**; NCN = ligand **1**) (Figure S11, Supporting Information), where two different platinum complexes are inside the same unit cell: one cationic adduct with one molecule of CH_3CN in a trans position with respect to the carbon atom and a second complex which is the neutral chloro complex **2**. This finding is interesting because it shows that complex **4** can abstract chloride from CH_2Cl_2, which illustrates the high affinity of the platinum atom for this anion.

Anion Binding Studies. The first evidence for the high affinity of complex **4** for chloride was obtained by NMR measurements. Solutions of **4** in a mixture of CD_2Cl_2 and CD_3OD (1/1 v/v) were stable over a prolonged period of time. In pure CD_2Cl_2, however, the formation of the neutral chloro complex **2** was observed after several hours (Figure S12, Supporting Information). A new and modest ^1H NMR signal gradually appeared (δ 9.05 ppm). This new signal is consistent

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 2 and 3

2				3	
Pt1−C1	1.933(8)	Pt2−C33	1.927(7)	Pt1−C1	1.947(3)
Pt1−N3	2.039(6)	Pt2−N5	2.037(6)	Pt1−N1	2.047(3)
Pt1−N1	2.042(6)	Pt2−N7	2.042(6)	Pt1−N3	2.050(3)
Pt1−Cl1	2.4213(19)	Pt2−Cl2	2.4150(19)	P1−I1	2.6911(4)
C1−Pt1−N3	79.8(3)	C33−Pt2−N5	79.6(3)	C1−Pt1−N1	79.72(11)
C1−Pt1−N1	79.9(3)	C33−Pt2−N7	80.0(3)	C1−Pt1−N3	79.67(11)
N3−Pt1−Cl1	100.36(18)	N5−Pt2−Cl2	101.10(18)	N1−Pt1−I1	100.04(7)
N1−Pt1−Cl1	99.84(19)	N7−Pt2−Cl2	99.31(18)	N3−Pt1−I1	100.57(7)

with that of chloro complex **2**. On the other hand, the addition of NaCl (1.0 equiv) to a solution of **4** (2.0 mM) induces a notable downfield shift ($\Delta\delta$ = 1.20 ppm at saturation) of the 1-CH proton (see Figure 1 for the numbering of the structure) and small upfield changes for protons 5-CH and 6-CH, as shown in Figure 2. The ^{1}H NMR spectrum of **4**-triflate + NaCl

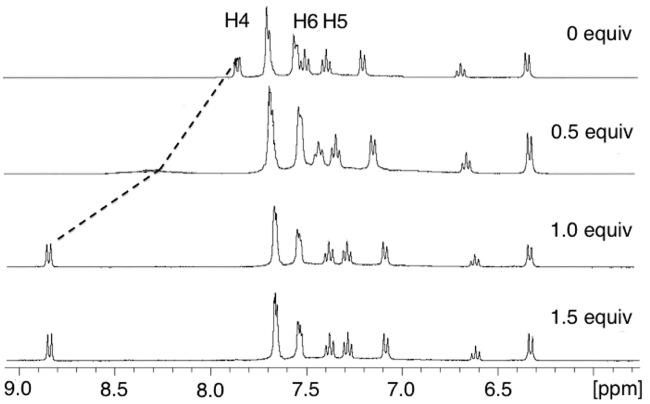

Figure 2. ^{1}H NMR spectral changes observed of **4** (2.0 mM) in CD_2Cl_2/CD_3OD (1/1 v/v) during the addition of up 1.5 equiv of NaCl.

(1.0 equiv), corresponds to the chloro complex **2**. In this context, the NMR changes support the formation of the Pt−Cl bond and the involvement of the intramolecular C−H···Cl−Pt interaction, which was observed in the crystal structure of **2** (Figure 1).

Complex **4**-triflate displays poor solubility in pure water. However, it can be dissolved in aqueous solutions containing 50 vol % DMF or CH_3CN, and those mixtures were used for further studies. When excited at 360 nm, solutions of complex **4** in DMF/water are luminescent with emission maxima at 500 and 537 nm. Similar results are obtained in acetonitrile/water. The quantum yields of **4** in these solvent mixtures are Φ = 0.054 (CH_3CN/H_2O) and Φ = 0.15 (DMF/H_2O). The lifetimes calculated upon excitation at λ 360 nm were 2.0 and 2.2 μs, respectively. These values are close to those of other NCN and NCCN platinum(II) complexes.[13b,c] In the context of chemosensing, luminescent sensors which display long-lived emission in the microsecond range are of interest in the analysis of bioactive ions or molecules in solution, since their emission may be discriminated readily from scattered light and shorter-lived background fluorescence normally present in biological and clinical samples.[20]

The addition of NaCl (0−3.5 mM) to a buffered aqueous solution of complex **4**-triflate (20 μM) in DMF/H_2O (40 mM MOPS, pH 7.0) induced a quenching at the maxima and a red shift for both emission bands ($\Delta\lambda$ = 7−9 nm; Figure 3, top). These spectral changes are in line with the (partial) conversion

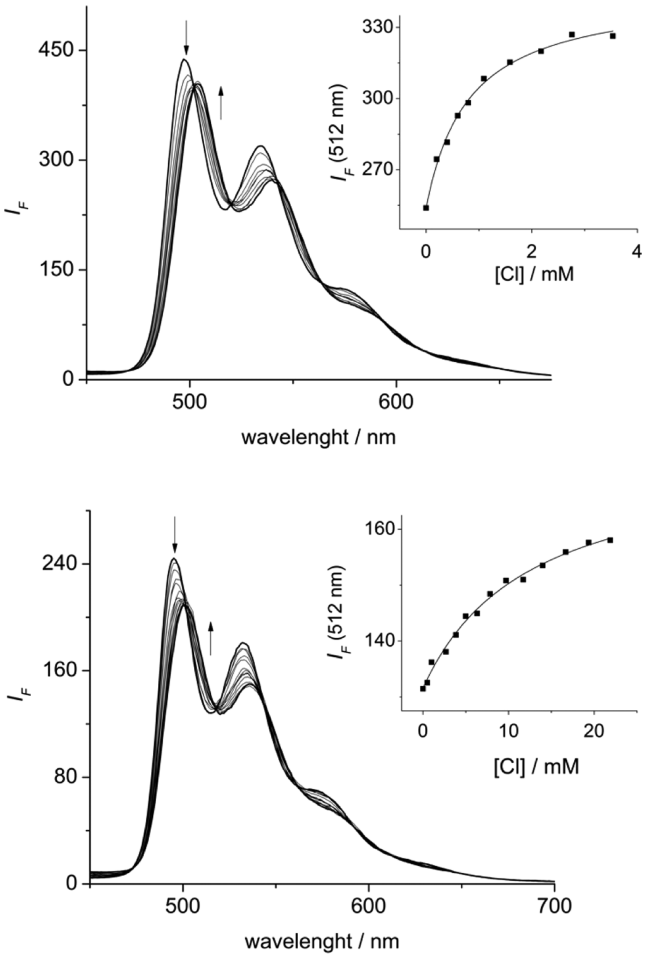

Figure 3. Changes of the emission spectra (λ_{ex} 360 nm) of buffered aqueous solutions (40 mM, MOPS at pH 7.0) of **4** (20 μM) containing 50 vol % DMF (top) or CH_3CN (bottom) upon addition of increasing amounts of NaCl. The insets show the emission intensity at λ 512 nm for different chloride concentrations. The lines were obtained by fitting the data to a 1/1 binding model.

of **4** in the chloro complex **2** (Scheme 2). Due to the strong trans effect of the phenyl ligand,[17] the dynamic equilibrium between **4** and **2** is established quickly and measurements can be performed within minutes. A similar behavior was observed for solutions of complex **4**-triflate in CH_3CN/H_2O (Figure 3, bottom).

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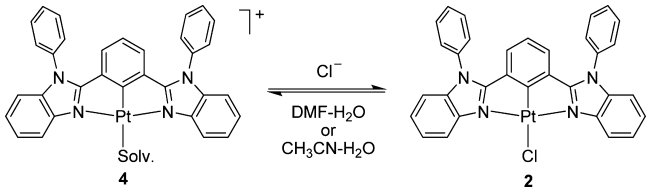
Scheme 2



The variations in emission intensity with increasing NaCl concentration could be well fitted to a 1/1 chemical equilibrium. The resulting association constants are K_a(DMF/H_2O) = (1.2 ± 0.20) × 10^3 M^{-1} and K_a(CH_3CN/H_2O) = 81 M^{-1}. The binding constants were also determined by spectrophotometric titration experiments under the same conditions (40 mM MOPS, pH 7.0), but with more concentrated solutions of **4** (60 μM). Figure 4 illustrates the

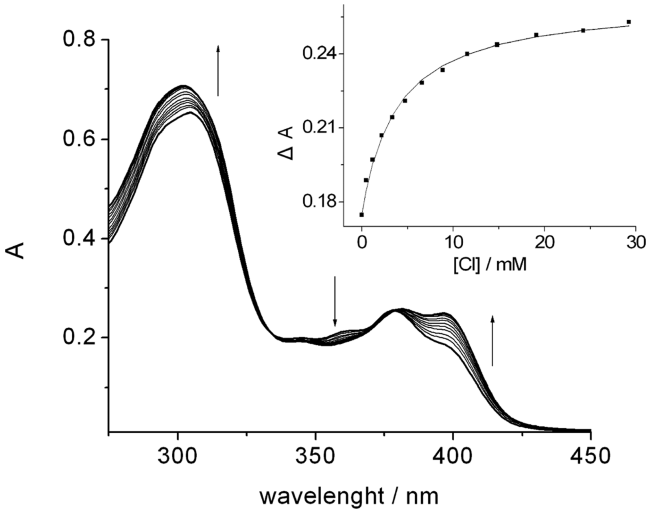


Figure 4. Spectrophotometric titration of buffered aqueous solutions (40 mM MOPS at pH 7.0) of **4** (60 μM) containing 50 vol % CH_3CN. Arrows show the direction of the spectral changes on addition of increasing amounts of NaCl. The insets show the profile of absorbance at 404 nm for different chloride concentrations. The lines were obtained by fitting the data to a 1/1 binding model.

family of spectra obtained when a solution of **4** in CH_3CN/H_2O is titrated with NaCl. The presence of two distinct isosbestic points at 335 and 378 nm indicates that only two species are present in the equilibrium (Scheme 2). The inset in Figure 4 shows the increase of absorbance at 404 nm on progressive addition of Cl^- (0–30 mM). The titration profile could be fitted to a 1/1 binding model using a nonlinear least-squares treatment. The calculated association constants are K_a(CH_3CN/H_2O) = 260 ± 16 M^{-1} and K_a(DMF/H_2O) = (2.0 ± 0.2) × 10^3 M^{-1}. The K_a values determined by two spectroscopic techniques are similar, which supports a 1/1 chemical equilibrium. In the case of DMF/H_2O, the addition of NaCl (0–8 mM) increases modestly the absorbance and the course of the titration does not show isosbestic points. However the modest spectral change at 400 nm (ΔA = 0.03) was used to get a fit (Figure S14, Supporting Information). The association constants obtained by spectroscopy make evident that complex **4**-triflate is able to bind chloride in buffered aqueous solutions with high affinity. To obtain a sensitive chemosensor, however, a higher value was required. To address this issue, we decided to explore the behavior of complex **4** in aqueous solutions containing a micelle-forming surfactant. The utilization of micelles for chemosensors is an emerging topic in analytical chemistry.[21] The group of Dalla Cort has shown that a salophen–UO_2 complex is able to bind fluoride in aqueous solutions containing a cationic surfactant,[22a] and Severin has demonstrated that the binding affinity of a Cp*Rh-based receptor for chloride is significantly increased upon addition of cetyltrimethylammonium hydrogensulfate ($CTA^+HSO_4^-$).[9b] Recently, Gabbaï has shown an interesting fluorescent system with high selectivity for fluoride using cetyltrimethylammonium bromide (CTA^+Br^-) and an antimony-based receptor, which is able to sense F^- in the parts per million range using drinking water samples.[22b]

The surfactant $CTA^+HSO_4^-$ was used for the present study. Complex **4**-triflate can be dissolved in buffered aqueous solutions containing $CTA^+HSO_4^-$ ([CTA] = 5.0 mM, 40 mM MOPS, pH 7.0) without the need of an organic cosolvent, which is interesting for our purposes. The aqueous solutions of **4**-triflate with $CTA^+HSO_4^-$ display a modest increase of lifetime 2.9 μs (at λ 360 nm) with emission maxima at 500 and 537 nm. The intensity of the emission increased, which is expected due to the encapsulation of the active species inside the hydrophobic core of the micelle. Interestingly, upon addition of NaCl, a distinct behavior was observed: instead of emission quenching, the intensity of the emission bands increased along with a red shift of the maximum (Figure 5)

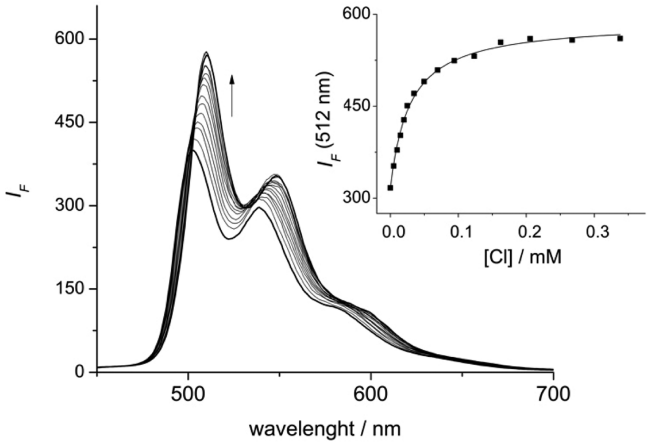


Figure 5. Changes of the emission spectra (λ_{ex} 360 nm) of buffered aqueous solutions (40 mM MOPS buffer at pH 7.0) of **4** (20 μM) containing the surfactant $CTA^+HSO_4^-$ (5.0 mM) upon addition of increasing amounts of NaCl (0–0.35 mM). The inset shows the emission intensity at λ 512 nm for different chloride concentrations. The solid line was obtained by fitting the data profile to a 1/1 binding model.

with quantum yields from Φ = 0.17 for $\mathbf{4}^+OTf^-$ to Φ = 0.25 for chloro complex **2**. Previous work of Gabbaï has demonstrated a fluorescence turn-on response upon anion binding using a micellar system with an anthryltriphenylstibonium-based receptor. This effect may result from the decreased solvation of the neutral complex **2** in comparison to that of the cationic precursor **4**.

In addition, this effect has been attributed to the disappearance of any intramolecular charge transfer processes in the receptor–anion complex.[22b] The intensity variations at 512 nm were well fitted to a 1/1 binding model to give an

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apparent binding constant of K_a(CTA) = (7.9 ± 0.8) × 10^4 M^{-1}. This value is nearly 2 orders of magnitude higher than that observed in DMF/H_2O. On the other hand, UV−vis titration experiments in this micellar system exhibit a very small spectral change under additions of NaCl (Figure S16, Supporting Information).

Next, the anion selectivity of the micellar system with **4** was analyzed. Sodium salts of simple inorganic anions (halides, AcO^-, NO_3^-, NO_2^-, $H_2PO_4^-$, HCO_3^-, $H_3P_2O_7^-$, and SO_4^{2-}; $[X^-]_{final}$ = 100 μM) were added to a buffered aqueous solution of complex **4** (20 μM) and $CTA^+HSO_4^-$ (5.0 mM), and the emission intensity increase at 512 nm was recorded. All oxoanions and fluoride gave a very low response (Figure 6).

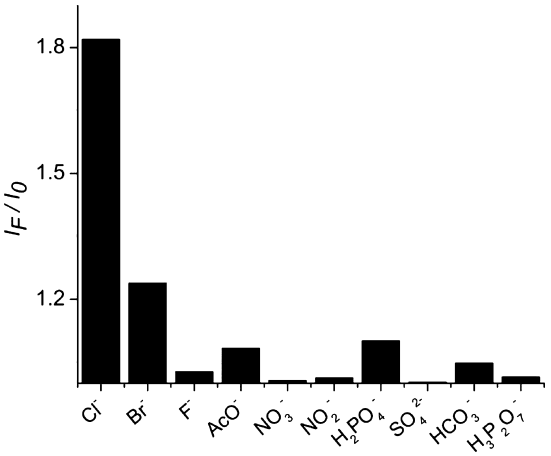

Figure 6. Relative emission intensity at 512 nm (λ_{ex} 360 nm) of buffered aqueous solutions (40 mM MOPS at pH = 7.0) of **4** (20 μM) containing $CTA^+HSO_4^-$ (5.0 mM) upon addition of different anions ($[X^-]$ = 100 μM).

The addition of NaBr resulted in a modest increase in emission intensity, but it was still significantly lower than that observed for NaCl. Addition of NaI resulted in the formation of a precipitate immediately. The interference of the heavier halide anions is not unexpected, especially for bromide. Still, it is remarkable that the sensing ensemble containing $CTA^+HSO_4^-$ with **4** is selective for chloride over bromide because bromide has a lower solvation energy,[7] and because bromide has been shown to form more stable complexes with $[Pt(NCN)(OH_2)]^+$ complexes.[11] The association constant with bromide was calculated under the same conditions as in Figure 5. The resulting value of $K_{a,Br}$(CTA) = (6.3 ± 0.4) × 10^3 M^{-1} is 1 order of magnitude lower than for chloride. The profiles of emission data at 512 nm (λ_{ex} 360 nm) for both anions are shown in Figure 7. The high affinity of **4** for chloride over bromide could be the result of having two directed arene CH groups to the anion-binding site. It expects that these CH groups form stronger hydrogen bonds with a more electronegative halide such as Cl^-. In the case of oxoanions, it is noteworthy that complex **4** has a higher affinity for chloride than for more basic anions such as acetate and pyrophosphate.

In order to probe the utility of this platinum-based sensor, we have determined the chloride concentration in commercial mineral water as described below. A portion of degassed mineral water (700 μL) was added to 1.4 mL of a buffered aqueous solution of complex **4** and CTA (final concentrations: [**4**], 20 μM; $[CTA^+HSO_4^-]$, 5.0 mM; [MOPS], 20 mM; pH 7.0), and the emission intensity of the solution was recorded.

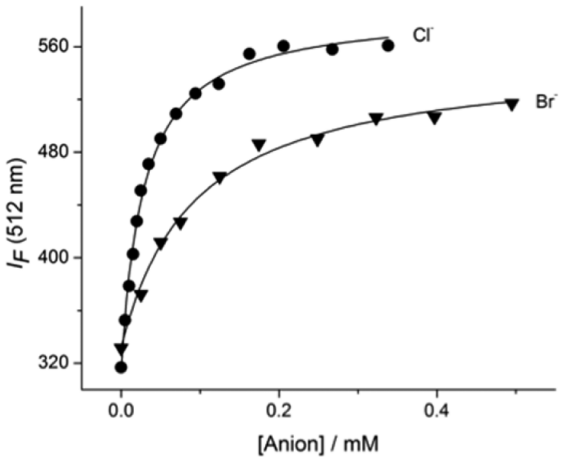

Figure 7. Profiles of emission titration experiments at 512 nm (λ_{ex} 360 nm) of buffered aqueous solutions (40 mM, MOPS at pH 7.0, 5 mM $CTA^+HSO_4^-$) of **4** (20 μM) by NaCl (0−0.3 mM) and NaBr (0−0.5 mM). The lines were obtained by fitting the data to the equilibrium model 1/1.

The chloride concentration was then calculated using the fitting equation derived from the emission titration experiment (Figure 5). A comparison between reported and determined chloride concentrations is given in Figure 8. The match

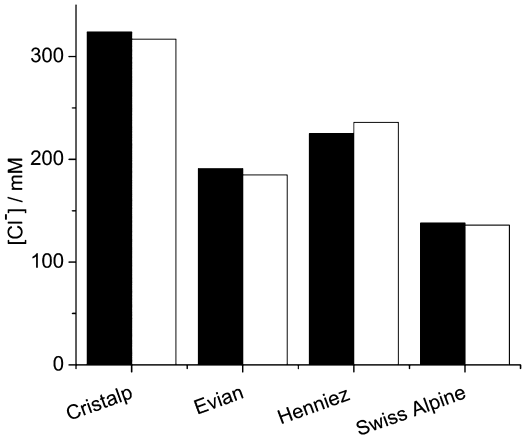

Figure 8. Reported (black bars) and determined (white bars) chloride concentrations of commercial mineral water samples. The measurements were carried out as described in the main text. The estimated error is ±10 μM.

between the two values is very good. It should be noted that the mineral waters contain several competing inorganic anions, some in the millimolar concentration range (e.g., bicarbonate and sulfate).

CONCLUSION

A cationic platinum pincer complex with the N,C,N-chelating ligand **4** can be used as an intrinsic luminescent chemosensor for the detection of chloride in aqueous solutions containing 50 vol % of an organic cosolvent (DMF or CH_3CN). Under these conditions, the addition of NaCl quenches the emission of **4**. On the other hand, a particularly high chloride affinity (K_a = (7.9 ± 0.8) × 10^4 M^{-1}) was found for buffered solutions containing the cationic surfactant $CTA^+HSO_4^-$. The green luminescence of neutral aqueous solutions of **4** containing $CTA^+HSO_4^-$ was turned on by addition of salts of inorganic

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anions, especially by NaCl. The optical change allows for detection of chloride in the micromolar concentration range with good selectivity over other common anions such as bromide, phosphate, and acetate. NMR experiments show that chloride anion is coordinated to platinum atom; additionally two short CH···Cl−Pt contacts are formed, which could result in the high affinity. This is supported by the crystal structure of chloro complex **2**. As a representative application, the chloride concentration in mineral water samples was determined. Overall, these results further highlight the utility of transition-metal-based receptors for anion recognition and sensing in water.

EXPERIMENTAL SECTION

General Considerations. All reagents for synthesis and analysis were of analytical grade and were used without further purification: *N*-Phenyl-*o*-phenylenediamine (Sigma-Aldrich), isophthaloyl dichloride (Sigma-Aldrich), K_2PtCl_4 (99%, Precious Metals Online), silver triflate (Sigma-Aldrich), 3-(*N*-morpholino)propanesulfonic acid (MOPS, Sigma-Aldrich), cetyltrimethylammonium hydrogensulfate ($CTA^+HSO_4^-$, Aldrich), sodium chloride extra pure (Acros Organics 99.99%), sodium bromide (Fluka 99.9%), sodium fluoride (Fluka, 99.9%), sodium acetate (Sigma-Aldrich, 99.5%), sodium nitrate (Aldrich, 99.9%), sodium nitrite (99.9% ACS reagent), sodium phosphate monobasic dihydrate (Aldrich 99.0%), sodium sulfate (Aldrich 99.9% ACS reagent), sodium bicarbonate (Sigma-Aldrich 99.5%), sodium pyrophosphate decahydrate (Sigma-Aldrich 99.0%). MOPS buffer solution (40 mM, pH 7.0) was prepared with double-distilled water. Stock solutions of anions were prepared in MOPS buffer (40 mM, pH 7.0). A stock solution of complex **4** (2.0 mM) containing CTA (5.0 mM) was made with double-distilled water. Luminescence spectra were recorded on a Varian Cary Eclipse spectrophotometer equipped with a thermostated cell holder. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer at 400 and 100 MHz, respectively. Electrospray ionization mass spectra were obtained with a Waters CapLC-coupled Micromass Q-ToF Ultima ESI instrument. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer.

1,3-Bis(2-*N*-phenylbenzimidazolyl)benzene (1). Ligand **1** was prepared by a reported procedure:[23] isophthaloyl dichloride (1.02 g, 5.0 mmol) was added to a solution of *N*-phenyl-*o*-phenylenediamine (1.85 g, 10 mmol) in *N*-methyl-2-pyrrolidinone (25 mL). The reaction mixture was stirred under an atmosphere of dinitrogen at room temperature for 2 h, and then the temperature was raised to 50 °C for another 2 h. After it was cooled, the mixture was poured into cool water (100 mL). The white precipitate was filtered off, washed with water, and dried under vacuum to give the diamide in 90% yield. Ligand **1** was obtained by cyclodehydration at 290 °C under an atmosphere of dinitrogen for 2 h, followed by sublimation at 300−310 °C at reduced pressure. Yield: 1.25 g, 60%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90 (s, 1H), 7.81 (d, J = 7.4 Hz, 2H), 7.55−7.44 (m, 8H), 7.36−7.20 (m, 11H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 152.1, 143.7, 137.9, 137.3, 131.1, 130.7, 130.4, 129.2, 128.6, 127.9, 123.9, 123.4, 120.4, 111.0 (one signal was not detected). ESI-MS: $[M + H]^+$ 463.18. Anal. Calcd for $C_{32}H_{22}N_4$ (462.18): C, 83.09; H, 4.79; N, 12.11. Found: C, 83.01 H, 4.83; N, 12.06.

Complex 2. A mixture of N,C,N-chelating ligand **1** (462 mg, 1.0 mmol) and K_2PtCl_4 (421 mg, 1.0 mmol) in acetic acid (40 mL) was heated under reflux for 24 h. After cooling and concentrating under vacuum, the residue was purified by column chromatography on silica gel with dichloromethane/chloroform (1/1 v/v) as eluent to give complex **2** as a red crystalline powder (590 mg) in 85% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.05 (d, J = 9.6 Hz, 2H), 7.72−7.68 (m, 6H), 7.61−7.57 (m, 4H), 7.47 (t, J = 7.7 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.0, 161.2, 141.2, 135.8, 134.0, 131.7, 130.5, 130.4, 127.8, 124.9, 124.4, 124.0, 122.1, 118.6, 110.6. ESI-MS: $[2]^+$ 656.42. Anal. Calcd for $C_{32}H_{21}ClN_4Pt$ (691.11): C, 55.53; H, 3.06; N, 8.10. Found: C, 55.51; H, 3.05; N, 8.04.

Complex 3. The iodo complex **3** was obtained by reaction of complex **2** (300 mg, 0.43 mmol) with 20 equiv of KI in DMF/CH_3OH (1/9 v/v, 30 mL) at 70 °C for 48 h. After the mixture was cooled, a yellow precipitate was isolated by filtration. Recrystallization from dichloromethane and diethyl ether gave the product in the form of yellow crystals suitable for X-ray diffraction (310 mg) in 92% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.58 (d, J = 8.6 Hz, 2H), 7.75−7.69 (m, 6H), 7.60−7.54 (m, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.71 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.8, 162.6, 142.2, 136.6, 134.5, 131.6, 131.2, 130.8, 128.3, 125.3, 124.8, 124.5, 122.9, 121.6, 111.0. ESI-MS: $[3]^+$ 656.42. Anal. Calcd for $C_{32}H_{21}IN_4Pt$ (783.05): C, 49.05; H, 2.70; N, 7.15. Found: C, 49.01; H, 2.79; N, 7.09.

Complex 4. A mixture of complex **3** (200 mg, 0.25 mmol) and silver triflate (70 mg, 0.27 mmol) in DMF/CH_3OH (1/9 v/v, 20 mL) was stirred at room temperature overnight. Subsequently, the reaction mixture was filtered through Celite 540 and the solvent was removed under reduced pressure to give a brown powder. Complex **4** was obtained by recrystallization from CH_3OH in 81% yield (169 mg). ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3OD, 1/1 v/v): δ 7.94 (m, 3H), 7.82−7.72 (m, 6H), 7.64−7.54 (m, 7H), 7.46 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 6.76 (t, J = 8.4 Hz, 1H), 6.42 (d, J = 7.7 Hz, 2H). ^{19}F NMR: −80.0 ppm. ^{13}C NMR (100 MHz, CD_2Cl/CD_3OD, 1/1 v/v): δ 161.4, 140.2, 136.5, 134.5, 133.1, 132.1, 131.6, 128.5, 126.7, 125.8, 125.7, 125.1, 121.4 (q, J_{CF} = 310 Hz; only the two major signals of the quartet were observed), 116.3, 112.7 (one signal was not detected). ESI-MS: $[4]^+$ 656.42; $[4(CH_3OH)]^+$ 697.17. Anal. Calcd. for $C_{34}H_{25}F_3N_4O_4PtS$ (837.12): Cal. C, 48.75; H, 3.01; N, 6.69. Found: C, 48.73; H, 3.05, N, 6.61.

Luminescence Emission Measurements. Titration experiments were performed by adding aliquots of stock solutions of anions as sodium salts to buffered aqueous solutions (40 mM, MOPS at pH 7.0) of complex **4** (20 mM) containing $CTA^+HSO_4^-$ (5.0 mM). After addition of anions, the solution was equilibrated for 5 min at room temperature before recording the emission spectrum (excited at 360 nm) using a quartz cuvette. Experiments in DMF/H_2O or CH_3CN/H_2O were carried out accordingly, but without $CTA^+HSO_4^-$. The resulting data were fitted to an equation describing a 1/1 complexation[24] using the nonlinear least-squares treatment with Microcal Origin version 8.0 program. The UV−visible spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer at room temperature. Luminescence quantum yields were determined using an aqueous solution of quinine sulfate containing H_2SO_4 (0.5 M) as standard (Φ = 0.546; excited at 360 nm).[25] The refractive indexes used for the mixtures CH_3CN/H_2O (1/1 v/v, x_{MeCN} = 0.345) and DMF/H_2O (1/1 v/v, x_{DMF} = 0.180) were taken from the literature.[26] Phosphorescence lifetime measurements were performed on the same Cary Eclipse fluorescence spectrophotometer and off-gate detection. The selectivity experiments were performed with stock solutions of the respective NaX and Na_2X salts (100 mM) in MOPS buffer (40 mM, pH 7.0). The analyses of commercial mineral water samples were performed as follows: an aliquot (700 μL) of the degassed water sample was added to a buffered aqueous solution containing complex **4** and CTA (final concentrations: [**4**], 20 μM; [XCTA], 5.0 mM; [MOPS], 20 mM; pH 7.0). The emission intensities at 512 nm (excited at 360 nm) were recorded, and the chloride concentration was calculated using the fitting equation derived from the emission titration experiment (Figure 5).

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in Table S1 (Supporting Information). Data collections for complex **2** and **3** were performed at low temperature using Mo Kα radiation on a Bruker APEX II CCD instrument. Semiempirical[27] absorption correction was applied to all data sets. Structure solutions, refinements, and geometrical calculations have been carried out by SHELXTL.[28] All structures were refined using full-matrix least-squares methods on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with U_{iso}

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= aU_{eq} (where a is 1.5 for $-CH_3$ and $-OH$ moieties and 1.2 for others). Crystallographic data for the two crystal structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 969988−969989. X-ray crystallographic data in CIF format are available in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files givingcrystallographic data for **2** and **3**, ^{1}H and ^{13}C NMR spectra of **1**−**4**, ^{19}F NMR spectrum of **4**, UV−vis absorption spectra of complex **4** in aqueous media, emission spectra of **4** in the presence of inorganic anions in neutral micellar aqueous system, time-dependent ^{1}H NMR spectra of **4** in CD_2Cl_2, spectrophotometric titration of **4** by NaCl in DMF/water, and UV−vis absorption spectra of aqueous solutions of **4** in the presence and absence of chloride containing the surfactant $CTA^+HSO_4^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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