Inorganic Chemistry

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# Two Closely Related Iridium(III) Complexes as Colorimetric and Fluorometric Chemodosimeters for Nitrite in Aqueous Solution Operating along Different Modes of Action

Shu Qinghai,[†] Jan W. Bats,[‡] and Michael Schmittel*[,†]

[†]Center for Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein Strasse, D-57068 Siegen, Germany

[‡]Institut für Organische Chemie und Chemische Biologie, Johann Wolfgang Goethe-Universität, Max-von-Laue Strasse 7, D-60438 Frankfurt am Main, Germany

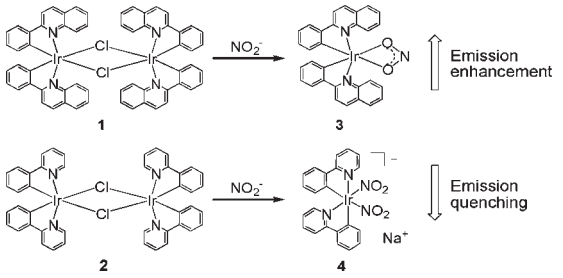
Supporting Information

**ABSTRACT:** Two closely related dual-channel chemodosimeters for nitrite in buffered aqueous acetonitrile were developed using $[(pq)_2IrCl]_2$ (**1**) and $[(ppy)_2IrCl]_2$ (**2**). In the UV−vis channel, the addition of nitrite caused visibly distinct color changes with both probes as a result of sizable absorption intensity enhancements. In the photoluminescence channel, the probes behaved oppositely upon the addition of nitrite. The emission was increased with **1**, while it was quenched with **2**. NMR and X-ray studies indicated that structurally very different $\eta^1$-nitrito-*N* and $\eta^2$-nitrito-*O*,*O*′ complexes were formed. Linear relationships for the quantification were obtained in both channels, allowing one to analyze for $NO_2^-$ in a range from $5 \times 10^{-5}$ to $2 \times 10^{-2}$ M.

Because nitrite is harmful to health because of possible carcinogenic effects,[1] its detection and quantification have become crucial in diverse fields,[2] including food, environmental, medicinal, and biological analytics. While colorimetric and fluorometric detection methods play a pivotal role in modern sensing[3] because they often allow for a rapid qualitative and quantitative assessment, few reports deal with nitrite sensing. The most common colorimetric method for nitrite detection still involves the reaction of nitrite with aromatic amines to yield an azo dye via the intermediate diazonium salt,[4] but the intricacy of the approach precludes a fast and easy quantification. Very recently, (2-arylethynyl)anilines were shown to react with nitrite in aqueous acidic media to produce yellow 4(1*H*)-cinnolones, thus setting up a rapid (5 min) chemodosimeter.[5] Other protocols use luminescence as its signal: e.g., nitrite was monitored by an $NO_x$ chemiluminescence analyzer that requires, however, prior reduction of nitrite to $NO_x$ by vanadium(III),[6a] iron(II), molybdenum(VI), and others.[6b] Clearly, many factors such as the reaction temperature, solution acidity, and intricate manipulation limit the sensitivity of such $NO_2^-$ detection. A photoluminescence (PL) sensing system was set up using membrane-bound rhodamine B,[6c] but the selectivity for nitrite versus chloride and sulfate was insufficient and the sensitivity was dependent on the pH. Finally, various polymer-based electrochemical sensors[7] and optodes[8] were used for quantification of $NO_2^-$.

Herein, we report on the two closely related iridium(III) complexes tetrakis(2-phenylquinoline-$C^2$,$N'$)($\mu$-dichloro)diiridium (**1**) and tetrakis(2-phenylpyridine-$C^2$,$N'$)($\mu$-dichloro)diiridium (**2**) as kinetic chemodosimeters for nitrite using either color or PL changes (see Scheme 1). Because disproportionation of $NO_2^-$ into NO and $NO_3^-$ is strongly favored in an acidic environment,[9] we performed all absorption and PL measurements in acetonitrile (ACN)/aqueous 0.1 M Tris-$ClO_4$ (50/50, v/v) at pH = 7.10. To the best of our knowledge, this is the first report of a one-step reaction PL probe for the sensitive and quantitative detection of nitrite.

**Scheme 1. Sensing Mechanism of 1 and 2 for Nitrite in Aqueous Solution**




**1** and **2** are usually used as starting materials for a variety of luminescent iridium compounds.[10] Because of the relatively weak Ir−Cl bond in the two dimers, we assumed that they may be well suited for the sensing of anions through substitution.

To test the aptness of **1** and **2** (10 $\mu$M) for anion sensing, UV−vis absorption measurements were carried out after the addition of 2000 equiv of various anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $NO_3^-$, $SO_4^{2-}$, $CO_3^{2-}$, and $NO_2^-$) in acetonitrile (ACN)/aqueous buffer (50/50, v/v). Notably, both **1** and **2** showed significant absorption intensity enhancements only for nitrite (see Figure 1). Immediately after the addition of nitrite (2000 equiv), the color changed from red to orange-yellow for **1** and from greenish to almost colorless for **2** because of small changes of the absorption wavelengths (Figure 1). Below, for quantification of both kinetic dosimeters (Figures S9 and S10 in the Supporting Information, SI), a reaction time (4 h) is chosen that fits both low and high $c_{analyte}$.

**Received:** August 12, 2011
**Published:** October 14, 2011

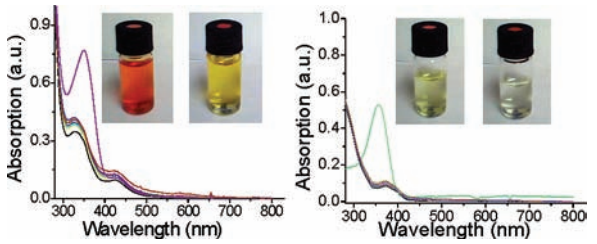



**Figure 1.** Absorption spectra of 10 $\mu$M solutions of **1** (left) and **2** (right) upon the addition of 2000 equiv of various anions [$F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $NO_3^-$, $SO_4^{2-}$, $CO_3^{2-}$, and $NO_2^-$ in 0.1 M Tris-$ClO_4$/ACN (50/50, v/v), pH = 7.10]. Insets: Visible color changes of **1** (left) and **2** (right) for the naked eye before and after the addition of nitrite.

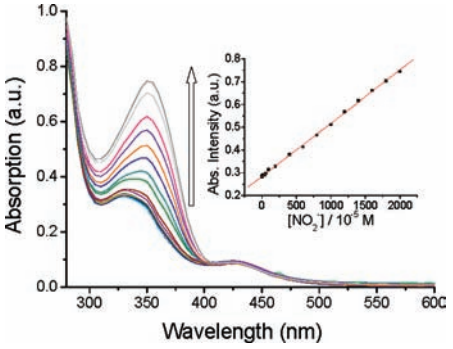



**Figure 2.** UV−vis absorption titration of **1** (10 $\mu$M) upon the addition of various equivalents of nitrite in 0.1 M Tris-$ClO_4$/ACN (50/50, v/v), pH = 7.10. Inset: Linear correlation of the absorption intensity at $\lambda$ = 353 nm versus concentration of nitrite.

Because no relevant UV−vis changes were seen after the addition of other anions, i.e., $F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $NO_3^-$, $SO_4^{2-}$, and $CO_3^{2-}$, some of which are important as constituents in food and drinking water,[6] all anions were evaluated in competition experiments (Figures S1 and S2 in the SI). No interference with the detection of nitrite was found. Linear relationships between the absorption intensity and amount of nitrite were established for both **1** and **2** (Figures 2 and S3 in the SI) that allow for quantification over a wide range of concentration with a detection limit of 50 $\mu$M (3.45 $\mu$g $mL^{-1}$).

In the PL channel, a valuable diagnostic enhancement by 350% was observed upon the addition of nitrite to a 10 $\mu$M solution of probe **1** (Figure 3). The titration provided a good linear relationship between the PL intensity and equivalents of nitrite (up to 2000 equiv). Thus, quantification of nitrite in aqueous solution was possible using **1** as a luminescent probe (see Figure 3, inset). As in the UV−vis channel, $F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $H_2PO_4^-$, $NO_3^-$, $BF_4^-$, $SO_4^{2-}$, and $CO_3^{2-}$ did not interfere with nitrite. As a rigorous test, the selective PL detection of nitrite using **1** was challenged in competition experiments (Figure 4). In none of the cases did the presence of other anions interfere substantially.

Because of the comparable structures of **1** and **2** and their alike behavior in the absorption channel, we expected that **2** would show a similar performance in PL as **1**. Hence, it was quite astonishing to see that nitrite addition entailed an efficient quenching of the PL intensity of **2**, contrasting the significant emission increase found for **1** (see Figure S4 in the SI). To understand this difference, we reacted both complexes **1** and **2** in

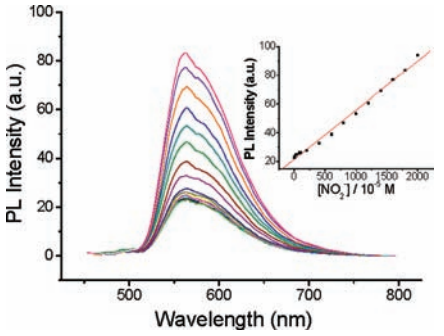



**Figure 3.** PL spectra of **1** (10 $\mu$M) upon the addition of various equivalents of nitrite in a Tris-$ClO_4$ buffer solution [ACN/buffer (50/50, v/v), pH = 7.10]; $\lambda_{exc}$ = 430 nm. Inset: Linear correlation of the emission intensity at $\lambda_{em}$ = 567 nm with the concentration of nitrite.

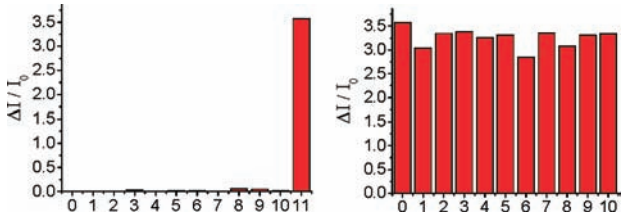



**Figure 4.** Left: PL ($\lambda_{em}$ = 567 nm) response of **1** (10 $\mu$M) with 2000 equiv of various anions. Right: PL spectra of **1** (10 $\mu$M) in the presence of nitrite (2000 equiv) and of other anions (2000 equiv). Conditions: 0.1 M Tris-$ClO_4$/ACN (50/50, v/v), pH = 7.10. Numbers: 0, none; 1, $F^-$; 2, $Cl^-$; 3, $Br^-$; 4, $I^-$; 5, $AcO^-$; 6, $H_2PO_4^-$; 7, $NO_3^-$; 8, $SO_4^{2-}$; 9, $CO_3^{2-}$; 10, $BF_4^-$; 11, $NO_2^-$.

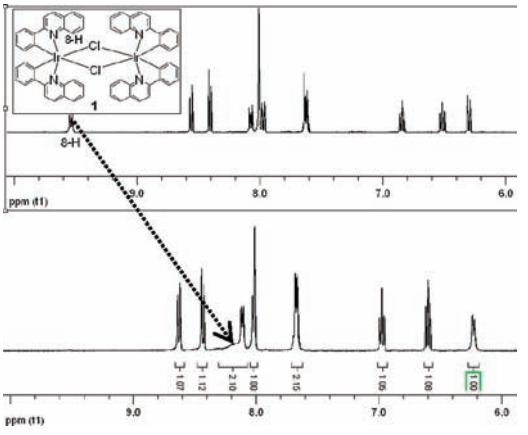



**Figure 5.** $^1$H NMR spectra of **1** (top) and **3** (bottom) in DMF-$d_7$.

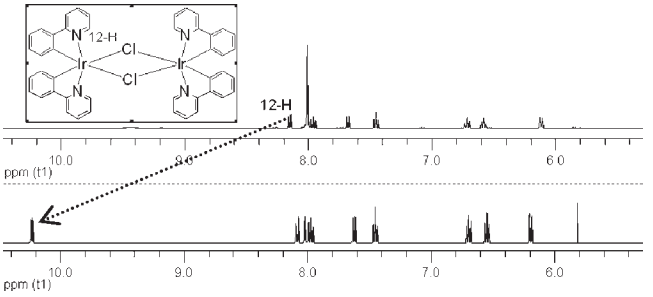



**Figure 6.** $^1$H NMR spectra of **2** (top) and **4** (bottom) in DMF-$d_7$.


dx.doi.org/10.1021/ic201753v |*Inorg. Chem.* 2011, 50, 10531–10533

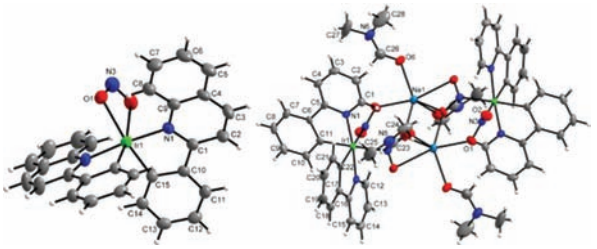


**Figure 7.** View of the molecular structure of **3** (left) and **4** (right) with the atomic numbering in the crystal. Color code: C, gray; H, white.

an ACN/water mixture with an excess of $NaNO_2$ at room temperature and isolated the products **3** and **4**, respectively. Both products show the same emission properties as those observed in the chemodosimeter reaction of **1** and **2** with nitrite; i.e., **3** is strongly luminescent, and **4** is almost dark.

From a comparison of the $^1$H NMR spectra of **3** and **4** with those of the starting materials, significant differential chemical shifts are obvious. For example, for **1** → **3**, proton 8-H is shifted by 1.4 ppm upfield along with broadening, while for **2** → **4**, proton 12-H is shifted downfield by 2.0 ppm (Figures 5 and 6). The vastly different behavior of **3** and **4** was readily understood after solving the X-ray structures of both products (Figure 7).

Single-crystal X-ray analysis indicated that nitrite addition led in both cases to Ir−Cl bond breakage. While in **3** a single nitrite ion is $\eta^2$-coordinated to the iridium(III) center in an isobidentate fashion via the two oxygen atoms ($d_{Ir-O}$ = 2.235 Å; see Figures 7 and S5 in the SI), the iridium center in **4** is linked to two nonequivalent nitrite ions via nitrogen coordination ($\eta^1$; $d_{Ir-N}$ = 2.134 and 2.148 Å; see Figures 8 and S7 in the SI). It is worth mentioning that $\eta^2$ coordination to iridium as in **3** has precedence with nitrate and carboxylic acids.[11] In **4**, the iridium is octahedrally coordinated, while the sodium countercation is coordinating to six oxygen atoms stemming from two *N*,*N*-dimethylformamide (DMF) molecules and three nitrite anions (two in an $\eta^1$ fashion and one in a bidentate manner). With this insight, the different $^1$H NMR shifts of the selected protons in Figures 5 and 6 may be attributed to a breakdown of the dimer structure in the process **1** → **3**, while a dimeric structure was maintained in **2** → **4**. The broadening of the $^1$H NMR signal of 8-H in **3** may originate from hydrogen bonding between 8-H and one oxygen atom of the nitrite ($d_{H\cdots O}$ = 2.259 Å).

Solvolysis studies on **1** and **2** (Figures S7 and S8 in the SI) suggest the following scenarios: (i) for **1**, hydrolysis is much slower than the reaction with nitrite. (ii) for **2**, hydrolysis precedes the slow reaction with nitrite. Thus, the different steric bulk of **1** and **2** might be a reason for the different products.

In summary, both iridium complexes **1** and **2** performed well as colorimetric chemodosimeters for nitrite in buffered aqueous solution. With **1**, excellent selectivity without interference and good quantification for nitrite was demonstrated in both the UV−vis (naked eye detection[12]) and PL channels. Both channels were operated on intensity enhancements and allowed one to establish a detection window from 50 $\mu$M to 20 mM. Intriguingly, for **2**, a different response was obtained in the PL channel, while its behavior in the UV−vis channel was comparable to that of **1**. With **2**, quenching of the emission was triggered upon the addition of nitrite. The difference was explained by two different coordination motifs for **1** and **2** with nitrite and distinct stoichiometries.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Synthesis, $^1$H and $^{13}$C NMR spectra, crystallographic details in CIF format, and additional spectroscopic material. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: schmittel@chemie.uni-siegen.de.

## ■ ACKNOWLEDGMENT

We are indebted to the DFG for continued financial support (Schm 647/17-1) and to the Universität Siegen for a stipend to S.Q.

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