

Probing Pb^{2+} cation via the iridium based phosphorescent dye

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Received 11 April 2007; accepted 21 June 2007
Available online 6 July 2007

Abstract

We demonstrate the concept of Pb^{2+} cation sensing using the emissive Ir(III) complex (**1**) based on the associated decrease of room-temperature phosphorescence upon forming the 1:1 adduct **1**- Pb^{2+} . Complex **1** bears two cyclometalated *N*-phenyl pyrazoles with pyrazoles residing at the mutual *trans* dispositions as well as one 3,5-di(pyridyl) pyrazolate chelate. X-ray structural analyses on the adduct **1**- Pb^{2+} confirm the key function of 3,5-di(pyridyl) pyrazolate as it forms chelate interaction with the metal analytes, while quenching of phosphorescent emission is probably due to the Pb^{2+} induced perturbation, which increases the intersystem crossing to another lower-lying triplet state for the host chromophore via an enhanced spin-orbit coupling.

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Keywords: Iridium; Phosphorescence; Pyridyl pyrazolate; Pb^{2+} ; Cation sensor

1. Introduction

Owing to their toxicity to human life, the identification of heavy metal ions in the environment remained to be an important issue. Among these, lead should be one of the most serious environmental concerns and health threats. It has been known that the toxicity of lead affects the kidneys, reproductive system, and nervous systems [1]. The FDA limit for lead in drinking water is 0.015 mg/L (7.2×10^{-8} M) [2]. Development of optical sensors for Pb^{2+} would thus help to clarify the Pb^{2+} ions in vivo as well as to monitor its concentration in the contaminated sources [3]. Recently, Chen et al. [1] used a coumarine derivative bearing an azacrown binding site as a new ratiometric fluorescent sensor for Pb^{2+} in acetonitrile, for which the specificity is attributed to the carbonyl lariat formation. Godwin et al. also reported a new ratiometric

fluorescent sensor for Pb^{2+} based on the dansyl-tetrapeptide framework [4]. In another approach, Czarnik et al. synthesized 9-anthracene derivatives bearing *N*-methylthiohydroxamate ligand, which is capable of quenching fluorescence in the uncomplexed form with certain selectivity [5]. Yoon et al. reported a new fluorescent sensor for Pb^{2+} based on rhodamine B, which displayed a good selectivity for Pb^{2+} in acetonitrile solution compared with other metal ions examined [6]. Although much work has been devoted in developing various fluorescent chemosensors for metal ions [4–6], there have been relatively few reports on the respective phosphorescence chemosensors [7,8]. Recently, extension was made to systems with third-row transition-metal complexes, among which the majority of these sensors comprised of a highly efficient phosphorescent entity, together with at least one crown ether substituent that allowed selective binding to the designated metal cations [9].

Typical signaling involves the switching of the non-emissive intra-ligand (³IL) $\pi\pi^*$ and metal-to-ligand charge transfer (³MLCT) states [8,10] such that positive luminescent response versus concentrations of metal cations, e.g.

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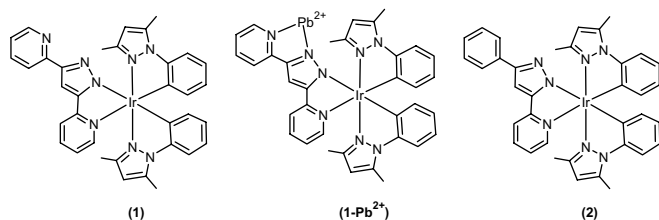
Ca^{2+} , Hg^{2+} or Pb^{2+} , can be obtained. Moreover, it may allow the design of “light-controlled ion switches”, for which the cation ejection from, e.g. the crown ether can be triggered by the effective reduction of electron donation at the receptor on excitation of the nearby chromophore [11]. As many of heavy metals are known as fluorescence quenchers via enhanced spin–orbit coupling [12], it is thus intriguing and of both fundamental and application importance to examine the interaction between environmental hazard metals such as Pb^{2+} (or Hg^{2+}) and heavy metal complexes that mainly exhibit room-temperature phosphorescence in solution due to the strong spin–orbit coupling effect.

Aiming at this goal, we present a novel phosphorescence sensor, in which an 3,5-di(pyridyl)pyrazole (py_2pz) moiety is attached to the heteroleptic Ir(III) complex (**1**). This design provides three inherent advantages [13]. First, the Ir(III) metal atom forms highly stable, octahedral coordinated structure and inherits strong phosphorescent emission due to the heavy atom effect induced by the Ir(III) metal center. Moreover, the ancillary cyclometalated *N*-phenyl pyrazole ligands, for which their $\pi\pi^*$ energy levels are far greater than those of the respective MLCT and other ligand-centered $\pi\pi^*$ excited states [14], enable both the HOMO and LUMO to reside predominantly on the ancillary py_2pz segment. Thirdly, the py_2pz fragment is attached to the Ir(III) metal center and then forming a neutral metal complex. Such a charge-neutral characteristic is similar to that of the Re(I) and Pt(II) based sensor complexes, but is in sharp contrast to most of the Ru(II) based polypyridyl sensors [15], for which the net cationic charge on the overall metal complex is expected to reside, in part, at the ligand site, giving a much reduced sensitivity in recognizing metal cations [16]. Finally, the nitrogen atoms of the py_2pz moiety would act as the effective donor site, allowing the direct recognition of the incoming cationic analytes. In other words, the py_2pz segment acts as crab chela and can potentially be used for distinguishing metal ions, simplifying the design strategy (see Scheme 1).

2. Experimental

2.1. General information and materials

Elemental analyses and Mass spectra (operating in FAB mode) were carried out at the NSC Regional Instrument Centre at National Chiao Tung University, Taiwan. ^1H



Scheme 1.

and ^{13}C NMR spectra were recorded on a Varian Mercury 400 instrument; chemical shifts are quoted with respect to internal standard Me_4Si . All synthetic manipulations were performed under N_2 atmosphere, while solvents were used as received. Synthesis of 3,5-di(2-pyridyl) pyrazole (py_2pz)H, 3-phenyl-5-(2-pyridyl) pyrazole (ppypz)H and 1-phenyl-3,5-dimethyl pyrazole (pdpz)H follows the procedures documented in the literature [17]. Treatment of (pdpz)H with $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ in refluxing methoxyethanol afforded the chloride bridged dimer $[(\text{pdpz})_2\text{IrCl}]_2$ in 75% yield [14]; it was then used for subsequent reactions without further purification.

2.2. Preparation of $[(\text{pdpz})_2\text{Ir}(\text{py}_2\text{pz})]$ (**1**)

A mixture of $[(\text{pdpz})_2\text{IrCl}]_2$ (150 mg, 0.13 mmol), 3, 5-di(2-pyridyl) pyrazole (py_2pz)H, 64 mg, 0.29 mmol) and Na_2CO_3 (93 mg, 0.88 mmol) in 2-methoxyethanol (25 mL) was heated to reflux for 6 hours. Excess of water was added after cooling the solution to room temperature. The precipitate was collected by filtration and subjected to silica gel column chromatography, eluting with a mixture of ethyl acetate and methanol (9:1). Pale yellow crystals of $[(\text{pdpz})_2\text{Ir}(\text{py}_2\text{pz})]$ (**1**) were obtained from repeated recrystallization using a mixture of THF and pentane at room temperature (49 mg, 0.065 mmol, 50%).

Spectral data of **1**: MS (FAB, ^{193}Ir): m/z 756 (M^+). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K): δ 8.43 (d, 1H, $J_{\text{HH}} = 4.8$ Hz), 7.99 (d, 1H, $J_{\text{HH}} = 7.6$ Hz), 7.84 (t, 1H, $J_{\text{HH}} = 7.8$ Hz), 7.63 (t, 1H, $J_{\text{HH}} = 7.6$ Hz), 7.60 (t, 1H, $J_{\text{HH}} = 8.0$ Hz) 7.53 (d, 1H, $J_{\text{HH}} = 5.6$ Hz), 7.47 (d, 1H, $J_{\text{HH}} = 8.0$ Hz), 7.42 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.39 (s, 1H), 7.07 (t, 2H, $J_{\text{HH}} = 6.4$ Hz), 6.95 (t, 1H, $J_{\text{HH}} = 8.0$ Hz), 6.86 (t, 1H, $J_{\text{HH}} = 8.0$ Hz), 6.75 (t, 1H, $J_{\text{HH}} = 7.6$ Hz), 6.65 (t, 1H, $J_{\text{HH}} = 7.6$ Hz), 6.28 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 6.23 (d, 1H, $J_{\text{HH}} = 8.0$ Hz), 6.20 (s, 1H), 6.16 (s, 1H), 2.75 (s, 3H, Me), 2.72 (s, 3H, Me), 1.50 (s, 3H, Me), 1.47 (s, 3H, Me). Anal. Calc. for $\text{C}_{35}\text{H}_{31}\text{IrN}_8$: C, 55.61; N, 14.82; H, 4.13. Found: C, 55.37; N, 14.46; H, 4.20%.

2.3. Preparation of $[(\text{pdpz})_2\text{Ir}(\text{ppypz})]$ (**2**)

A mixture of $[(\text{pdpz})_2\text{IrCl}]_2$ (200 mg, 0.17 mmol), 3-phenyl-5-(2-pyridyl) pyrazole (ppypz)H, 85 mg, 0.38 mmol) and Na_2CO_3 (214 mg, 0.21 mmol) in 2-methoxyethanol (25 mL) was heated to reflux for 6 h. Excess of water was added after cooling the solution to room temperature. The precipitate was collected by filtration and subjected to silica gel column chromatography, eluting with a mixture of ethyl acetate and methanol (9:1). Pale yellow crystals of $[(\text{pdpz})_2\text{Ir}(\text{ppypz})]$ (**2**) were obtained from repeated recrystallization using a mixture of THF and pentane at room temperature (68 mg, 0.009 mmol, 53%).

Spectral data of **2**: MS (FAB, ^{193}Ir): m/z 755 (M^+). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K): δ 7.91 (d, 1H, $J_{\text{HH}} = 7.6$ Hz), 7.82 (t, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.59 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.52 (d, 1H, $J_{\text{HH}} = 6.2$ Hz), 7.46 (d, 1H,

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