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pH-responsive switching of near-infrared absorption of a diradical complex of Pt^{II} and 3,4-diaminobenzoate formed in aqueous solutions

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ABSTRACT

In alkaline aqueous solutions, 3,4-diaminobenzoate ($H_2(^2L^{PDA})^-$) reacts with Pt^{II} to form a 1:2 (Pt:L) complex that intensely absorbs near-infrared (NIR) light at 713 nm ($\varepsilon = 8.0 \times 10^4\ M^{-1}\ cm^{-1}$). The absorption disappeared at pH < 3 (in DMSO), showing pH-responsive switching of the NIR absorption. By comparing the NIR-absorbing behavior of this complex to that of a complex, $[Pt^{II}(^1L^{ISQ})_2]^{2-}$, containing the analogous phenylenediamine ligand [$(^1L^{ISQ})^{2-}$ = *o*-diiminobenzosemiquinonate radical], the complex can be formulated as $[Pt^{II}(^2L^{ISQ})_2]^{2-}$. The assignment of the entity was consistent with the redox and spectroelectrochemical behaviors and electronic spin resonance (ESR) spectroscopy. First, one-electron oxidation of $[Pt^{II}(^2L^{ISQ})_2]^{2-}$ formed an ESR-silent complex assignable to the dimeric complex $[\{Pt^{II}(^2L^{ISQ})(^2L^{IBQ})\}_2]^{2-}$ [$(^2L^{IBQ})$ = *o*-iminobenzoquinone form] in which the two radical centers at $(^2L^{ISQ})_2^-$ were antiferromagnetically coupled. Second, the one-electron reduced complex of $[Pt^{II}(^2L^{ISQ})_2]^{2-}$ exhibited an ESR signal attributed to $[Pt^{II}(^2L^{ISQ})(^2L^{PDA})]^{3-\cdot}$; 34% of the electronic spin was located at the Pt^{II} center rather than on the $(^2L^{ISQ})_2^-$ moiety. The pH-responsive switching-off of the NIR absorption was thus rationally explained by oxidation of $[Pt^{II}(^2L^{ISQ})_2]^{2-}$ to $[\{Pt^{II}(^2L^{ISQ})(^2L^{IBQ})\}_2]^{2-}$ by the increase of the rest potential of the solution in the lower pH region.

1. Introduction

In the field of bio-molecular imaging, fluorescent probes have been widely utilized since they are able to bind to a target molecule or tissue and respond to the microenvironment [1]. Recently, to achieve a high signal-to-noise (S/N) ratio, emission in the near-infrared (NIR) region (700–1200 nm) has drawn much attention because biological tissue is essentially transparent in this wavelength region allowing imaging of deep tissue [2]. In contrast, less attention has been paid to the application of NIR absorption to bio-imaging. However, in the field of applied spectroscopy, novel techniques based on NIR absorption such as optical coherence tomography (OCT) [3] and photoacoustic tomography (PAT) [4,5] are emerging, and are able to provide images with greater resolution (10 μm for OCT and <100 μm for PAT) at a depth of 5–10 mm (for PAT) to complement existing imaging modalities. In such techniques, contrasting agents play a pivotal role in enhancing the S/N ratio of the acquired images. So far, NIR-absorbing organic dyes [6] and nano-materials [7,8] have been utilized as contrasting agents, but there are no examples of metal complexes. In general, metal complexes have many advantages over dyes and nano-materials including ease of preparation by simple reaction of the metal ion and ligand, resistance to photobleaching, and feasibility in bio-conjugation (as compared to the case of nano-materials); in some cases they also provide very large molar absorptivity (ε). These features prompted us to design a metal complex suitable for NIR-absorption contrasting agent applications, which require that the complex is bio-compatible, i.e., water-soluble and able to undergo bio-conjugation. Very recently, we clarified that Pt^{II} ion and 3,4-diaminobenzenesulfonate (DBS, Scheme 1) formed a water-soluble complex $[Pt^{II}(^1L^{ISQ})_2]^{2-}$ with a large ε value of $1.1 \times 10^5\ M^{-1}\ cm^{-1}$ at 705 nm, which is attributed to the ligand-to-ligand charge-transfer (LLCT) transition (Scheme 2) [9]. Moreover, the NIR absorption can be switched on and off depending upon the pH of the solution. In order to add conjugating ability to the biomolecule without sacrificing water-solubility, we herein study the ability of 3,4-diaminobenzoic acid (DBA), which has a carboxy group as an anchor to bind to the biomolecule, to form an NIR-absorbing complex with Pt^{II} in aqueous solutions and report the pH-responsive switching of the NIR absorption and the mechanism using (spectro)electrochemical and ESR measurements.

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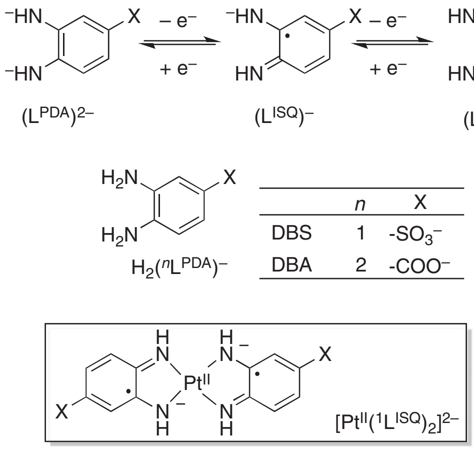
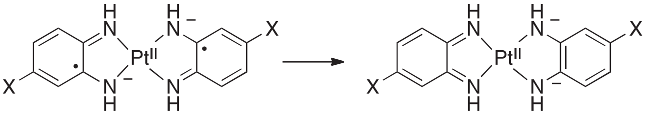


Scheme 1. Structures and redox states of the ligand and the diradical complex.



Scheme 2. Ligand-to-ligand charge transfer.

2. Experimental

2.1. Materials and methods

Potassium tetrachloroplatinate(II) was purchased from Nacalai Tesque (Kyoto). 3,4-Diaminobenzoic acid was purchased from Tokyo Chemical Industry Co. Ltd., (Tokyo). Tin(II) chloride dihydrate was purchased from Wako Pure Chemical Industries, Ltd. (Tokyo). All reagents were used without further purification. The electronic spectra were recorded with Shimadzu UV-3100PC and JASCO V-570 spectrometers. ^1H NMR spectra were obtained with a Bruker DPX-400 spectrometer using [D_6]-DMSO as the solvent and tetramethylsilane as an internal standard. The matrix-assisted laser desorption/ionization time-of-flight mass spectrum was measured with a Shimadzu AXIMA-CFR Plus spectrometer using 2,5-dihydroxybenzoic acid (DHBA) as the matrix. Cyclic voltammetric (CV) measurements were performed using a Hokuto Denko HAB-151 potentiostat with a glassy carbon working electrode (GCE), an $Ag/AgNO_3$ reference electrode (RE-7), and a Pt counter-electrode in a DMSO solution containing 2 mM NaOH to dissolve the complex and 0.1 M Bu_4NPF_6 as the supporting electrolyte under N_2. Spectroelectrochemistry was performed with Hokuto Denko HAB-151 and JASCO V-570 instruments using a spectroelectrochemical cell (SEC-C, 1 mm light path length) with a Pt mesh working electrode, a Pt counter-electrode, and an $Ag/AgNO_3$ reference electrode. The pH measurements were performed with a TOA HM-30 V pH meter with a G51–5421C combined electrode. The ESR spectra were recorded using a Bruker ESP-300 spectrometer and simulated using a program written in our laboratory.

2.2. $Na_2[Pt^{II}({}^2L^{ISQ})_2]$

The complex was prepared according to the method by Balch [10]. In brief, a solution of $K_2[Pt^{II}Cl_4]$ (0.051 g) in distilled water (*ca.* 1 mL) was added in small portions to an solution of DBA (0.038 g) in water (10 mL) and then aqueous NaOH was added to adjust the pH to 10.6. Stirring the mixture at room temperature for 24 h gave a dark-green precipitate, which was collected by filtration, washed with cold water, and dried *in vacuo* to afford $Na_2[Pt^{II}({}^2L^{ISQ})_2]$ as a powder [0.0512 g, 83% yield]. ^1H NMR (400 MHz, DMSO): $\delta = 7.11/7.12$ (d, $J = 8.72$ Hz, 1 H, ArH), 7.45 (dd, $J_1 = 8.59$, $J_2 = 1.40$ Hz, 1 H, ArH), 7.75 (d, $J = 1.40$ Hz, 1 H, ArH) ppm. MALDI-TOF MS (DHBA): *m/z* 562.53 $[M + Na]^+$.

3. Results and discussion

3.1. Complex formation and NIR absorption

The use of DBA as a spectrophotometric reagent for Pt^{II} in aqueous solutions was reported nearly half a century ago. However, the properties of the complex species as well as its electronic structure were not known except that it absorbed at 715 nm, had a 1:2 metal-to-ligand stoichiometry, and the electric charge was variable from negative to positive upon changing the pH [11]. In our study, the objective is to elucidate the NIR-absorption and the pH-dependent switching properties on the basis of the electronic structure of the complex. We first attempted to investigate the complexation behavior of DBA with Pt^{II} in aqueous solutions at pH 2–12. The complexation reaction, however, was too slow to be observed on a practical time scale suggesting that $[Pt^{II}Cl_4]^{2-}$ was very inert, which restricts the substitution of the Cl^- ligand with DBA. The pH of the aqueous solution was fixed at 6.5 to follow the time dependence of the absorption spectra (Fig. 1a). As can be seen, after 8 h of mixing, a small peak appeared at 713 nm, which was similar to the LLCT band of $[Pt^{II}({}^1L^{ISQ})_2]^{2-}$ at 705 nm characteristic of the diradical electronic structure [9]. This suggests that the diradical complex $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$ formed in the first step in the DBA–Pt^{II} system. Also, two other small peaks at 450 and 830 nm were evident and increased to reach a plateau at *ca.* 200 h (for 830 nm, see Fig. 1b). These absorption bands are akin to the ones at 420 and 822 nm, which correspond to the dimer of the mono-oxidized complex $[\{Pt^{II}({}^1L^{ISQ})({}^1L^{IBQ})\}_2]^{2-}$ [9]. This indicates that the once-formed $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$ was subsequently oxidized to the monoradical complex $[Pt^{II}({}^2L^{ISQ})({}^2L^{IBQ})]^{-\cdot}$ by air and then dimerized to $[\{Pt^{II}({}^2L^{ISQ})({}^2L^{IBQ})\}_2]^{2-}$ (Scheme 3). Since the peak at 713 nm assigned to the intermediary $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$ disappeared after 50 h (Fig. 1a and b), the first step of complexation appears to be much slower than the second step involving oxidation.

Since the DBS complex $[Pt^{II}({}^1L^{ISQ})_2]^{2-}$ showed pH-responsive switching of the NIR absorption via its oxidation and dimerization to $[\{Pt^{II}({}^1L^{ISQ})({}^1L^{IBQ})\}_2]^{2-}$ by the increased rest potential of the solution [9], we further attempted to switch on the NIR absorption of $[\{Pt^{II}({}^2L^{ISQ})({}^2L^{IBQ})\}_2]^{2-}$ obtained after 200 h of equilibration at pH 6.5. Surprisingly, when the pH of the solution was increased to 12.0 by the addition of NaOH, a large absorption band at 713 nm ($\varepsilon = 8.0 \times 10^4\ M^{-1}\ cm^{-1}$ as estimated from the inflection point of the molar ratio plot, Fig. 2) immediately appeared and the two bands at 450 and 830 nm disappeared (Fig. 2, inset). Seemingly, the dimeric complex $[\{Pt^{II}({}^2L^{ISQ})({}^2L^{IBQ})\}_2]^{2-}$ was reduced to give the original diradical complex $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$, which is attributable to the decrease in the rest potential of the solution upon the addition of NaOH [9]. Also, the composition of $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$ was unambiguously determined via the molar ratio method (Fig. 2): samples with varying [DBA]/[Pt^{II}] ratios were initially equilibrated for 200 h at pH 6.5 then NaOH was added to adjust the pH to 12.0, and the complex was additionally equilibrated for 1 day. The plot clearly shows that the metal-to-ligand ratio was 1:2 and confirms the composition of the diradical complex species as $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$.

In an attempt to further characterize the complex, the sodium salt of $[Pt^{II}({}^2L^{ISQ})_2]^{2-}$ was isolated from an aqueous solution of the reaction mixture of $[Pt^{II}Cl_4]^{2-}$ and PDA at pH 10.6, which was adjusted using NaOH. However, a single crystal of the complex with adequate quality for X-ray analysis was not obtained, which made us to pursue the solution-state study. Since the ^1H NMR spectrum of the complex in DMSO gave aromatic signals at