Tetrahedron Letters 52 (2011) 2645-2648

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet



A fluorescent ammonia sensor based on a porphyrin cobalt(II)-dansyl complex

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ARTICLE INFO

Article history: Received 17 January 2011 Revised 7 March 2011 Accepted 10 March 2011 Available online 16 March 2011

Keywords: Cobalt(II)porphyrin Dansylpiperazine Axial ligand Ammonia Fluorescence enhancement

ABSTRACT

Detecting and measuring the concentration of ammonia is of interest in many scientific and technological areas. A porphyrin based cobalt(II) complex with a dansyl fluorophore has been synthesized and investigated as a 'turn-on' fluorescent ammonia sensor. Over sixfold increase in fluorescence emission occurs upon the treatment of NH_3 to [Co(TPP)(Ds-pip)] sensor solution, resulting from NH_3 -induced displacement of the axially coordinated fluorophore.

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1. Introduction

Ammonia has been widely used in the production of explosives, fertilizers, and as an industrial coolant,¹ the excess presence of ammonia in the atmosphere, however, creates potential hazards to human being and ecosystems. Ammonia is toxic to many aquatic organisms even in very low concentrations and inhalation of only a small dose of ammonia vapor causes acute poisoning to people. Detecting and measuring the concentration of ammonia is of interest in many scientific and technological areas. Although electrochemical ammonia sensors are widely used in environmental monitoring, automotive and chemical industry,² in recent years, several new approaches have been reported, including optical gaseous ammonia sensors.^{1,3–9} They utilize the reaction of ammonia vapor with either a pH-dependent dye material or a pH-sensitive film,^{7,10} which undergoes a suitable color change.

Our method in developing sensors that utilize the formation of transition-metal ammonia complexes to trigger a change in fluorescence is based on a strategy that takes advantage of the well-known fluorescence-quenching properties of transition metal complexes with partially filled d-shells. In particular, we have been exploring systems in which reaction of NH_3 with a transition-metal complex containing a coordinated fluorophore conjugate results in removal of the fluorophore from the coordination sphere with

concomitant fluorescence turn-on. Fluorescence enhancement is generally preferred over fluorescence quenching when monitoring an analyte. Herein, we report that NH₃ can displace a axial fluorophore ligand bound to cobalt(II) complex with concomitant fluorescence increase (Scheme 1). The observed fluorescence response of these cobalt–fluorophore conjugates may ultimately allow their use for measuring NH₃ vapor in atmosphere.

2. Results and discussion

Metalloporphyrins have been used as colorimetric gas sensors based on characteristic color changes, resulting from coordination of analytes at the metal center.^{11–14} The metal center of M(II)porphyrins and M(II)-phthalocyanines possesses coordinatively unsaturated axial sites, which are potentially used in catalysis or development of sensor. In the adsorbed state, the underlying metal surface can occupy one of the axial sites and, as an additional ligand, influence the electronic structure of the metal center. The nature of this interaction, which is the main focus of this paper, has been studied previously, in particular on the example of the coordinated cobalt ion.¹⁵ Moreover, the axial ligation properties of the metalloporphyrins can be utilized for the self-organization of the molecules.

Fluorescence quenching upon recognition of the analyte is not only disadvantageous for a high signal output but also hampers temporal separation of spectrally similar complexes with timeresolved fluorometry.¹⁶ Thus, it is of interest that the recognition of NH₃ by the sensor does increase the fluorescence. To enhance

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Scheme 1. Mechanism of fluorescence enhancement of [Co(TPP)(Ds-pip)] complex upon the addition of ammonia.

the fluorescence intensity of the sensor system upon treatment of NH₃, one needs to carefully design the sensor molecule containing a fluorophore so that the photoinduced intramolecular electron transfer (PET) responsible for fluorescence quenching is maximized in the sensor itself, whereas the PET is minimized in the NH₃bound state of the sensor. To find such molecule, we chose few metal complexes and tested with 10 µM concentration of fluorophore solution. In the absence of metal complex, the emission spectrum of the Ds-pip has one strong peak at 500 nm. When the fluorophore reacts to metal complex solutions, the emission peak decreases (Fig. 1). Among all the complexes tested, cobalt(II)tetraphenylporphyrin [Co(TPP)] complex showed a largest quenching effect than other metal complexes. Using this large quenching behavior of cobalt(II)porphyrin complex, we decided to prepare a fluorescence ensemble system based on a Ds-pip ligand, which can function as a new class of synthetic sensor for NH₃.

Reaction of 1:1 molar ratio of [Co(TPP)] and Ds-pip in CH_2Cl_2 at room temperature afforded [Co(TPP)(Ds-pip)] (1) complex as dark purple color powder. Compound 1 was characterized by FT-IR, UVvisible and single crystal X-ray diffraction studies (Supplementary data). Especially, cubic shape single crystals of 1 were grown by vapor diffusion of CH_2Cl_2 solution of [Co(TPP)(Ds-pip)] into



Figure 1. Fluorescence response of $10\,\mu$ M solution of dansylpiperazine with different coordinated metal porphyrin complexes in CH₂Cl₂ (excitation: 340 nm; emission: 500 nm; slit width: 3 nm).

pentane over 3 days at room temperature. The structure of **1** is depicted in Figure 2 and interesting inter-atomic angles and distances of **1** are represented in Table S2 (Supplementary data). The cobalt atom has a distorted square pyramidal geometry. Co–N(1), Co–N(2), Co–N(3), and Co–N(4) distances are in the range of 1.981 and 1.992 Å, which are very common distances for the coordinate bond between Co(II) ion and the N donor ligands. Interestingly, Co–N(5) distances in **1**. The N(2)–Co–N(5) angle (87.41°) is smaller than those in other N–Co–N(5) angles (96.94°, 94.28°,



Figure 2. Thermal ellipsoid plot of [Co(TPP)(Ds-pip)] at 200 K in the *P*2(1)/*c* space group (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.



Figure 3. Fluorescence emission changes of **1** (single crystal) (10 μM) upon the addition of NH₃ (0–102 equiv) in CH₂Cl₂ (excitation: 340 nm; emission: 500 nm; slit width: 3 nm); (b) photograph under the irradiation at 365 nm, ((i) single crystal of **1**, (ii) single crystal of **1** + NH₃)); (c) fluorescence intensity changes upon addition of equivalents of ammonia in CH₂Cl₂.



Scheme 2. Proposed PET mechanism of fluorescence 'on-off-on' behavior of [Co(TPP)(Ds-pip)] complex upon the addition of NH₃.

and 95.08°), indicating that the cobalt atom locates above the porphyrin plane with N(1), N(2), N(3), and N(4) atoms.

The fluorescence emission changes of sensor **1** upon the addition of NH_3 are illustrated in Figure 3a. Addition of 0.2 equiv of NH_3 to **1** in CH_2Cl_2 induces an immediate strong fluorescent enhancement at ca. 500 nm. There is an increase of about 6-fold of emission intensity when 26 equiv of NH_3 was added to sensor **1** solution. Further addition causes no significant changes in the spectrum as a whole. The fluorescence emission intensity changes of **1** upon the addition of NH_3 can be viewable not only by instrument but also by naked eye (red \rightarrow green) (Fig. 3b). Based on our titration experimental result, the detection limit (LOD) of the sensor **1** is calculated to be ca. 40 nM (Fig. 3c).

Proposed photophysical mechanism to explain fluorescent 'onoff-on' switching of the sensor system has shown in Scheme 2. The demonstration of HOMO and LUMO levels clearly illustrate the direction of possible PET process in the compound **1**. The electron transfer from a metal complex (PET donor) to the excited fluorophore (PET acceptor) diminishes the fluorescence of original fluorophore resulting in '*switched off*. However, the PET fluorescence quenching process might be vanished upon formation of Cobalt(II)–porphyrin–NH₃ coordination complex due to the disassociation of axial fluorophore ligand, as a result, the fluorescence '*switched on*'. Hence, only the intensity of fluorescence is modulated upon NH₃ sensing, from these results it is clear that compound **1** is behaving like an ideal PET sensor.¹⁷

3. Conclusions

In conclusion, using quenching effect of a cobalt(II) ion, we developed simple fluorescence 'on-off-on' signal ensemble system for detection of NH₃, based on a dansylpiperazine(porphyrin–Co(II)) complex. The principle lying behind the so-called fluoro-ionophore work is based on an enhancement or decrease of fluorescence intensity of the system when the ionophore units bind guests. This has led to the design and synthesis of fluorescent reagents that are suitable for the detection of ions particularly important for environmental and biological applications. Among the known design principles for sensing, the displacement

(ensemble) approach is simple and convenient because a signaling unit (indicator) is bound to a binding site (receptor) by noncovalent interactions.¹⁸ There are several advantages of this approach because of the noncovalent binding between receptor and indicator: (1) No synthetic effort is required to chemically link an indicator and a receptor; (2) there is considerable freedom in the choice of an appropriate indicator; and (3) signal transduction is induced by the simple addition of an analyte to the receptor-indicator mixture.¹⁹ The fluorophore, dansylpiperazine, act as an axial ligand which coordinates with metal porphyrin complex through the piperazine nitrogen atom. The fluorescence emission intensity of compound 1 increases with gradual addition of NH₃ in dichloromethane in which NH₃ act as a nitrogen donor by replacing fluorophore. To the best of our knowledge, [Co(TPP)(Ds-pip)] is the first example of a metal complex capable of turn-on fluorescent detection of NH₃ under nonpolar conditions. From the results we concluded that compound **1** provides a very important contribution to the fast growing field of supramolecular gas sensing. Further applications of 1 and related derivatives for in vivo imaging/photophysical studies are currently in progress and will be reported in due course.

Acknowledgments

This work was supported by the Converging Research Center Program through the National Research of Korea (NRF) funded by the Ministry of Education, Science and Technology (Nos. 20090313 and 20090094261) and by a grant from the Fundamental R&D program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

Supplementary data

Supplementary data (experimental details for synthesis, fluorescence studies, X-ray studies and crystallographic data²⁰ of **1** (CIF) are provided) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.03.048.

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- 20. Cambridge Cystallographic Data Center deposition number: CCDC 798455. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 36033; e-mail: deposit@ccdc.cam.ac.uk).