

Full Research Paper

Colorimetric and Fluorescent Sensing of SCN⁻ Based on *meso*-Tetraphenylporphyrin/*meso*-Tetraphenylporphyrin Cobalt(II) System

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Received: 27 February 2007 / Accepted: 22 March 2007 / Published: 30 March 2007

Abstract: An approach for colorimetric and fluorescent sensing of thiocyanate (SCN⁻) has been proposed based on the competitive-displacement strategy between *meso*-tetraphenylporphyrin (TPP) and *meso*-tetraphenylporphyrin cobalt(II) (CoTPP). In THF-water solution, TPP emits strong fluorescence at 651 nm; however, the fluorescence was quenched stepwise by CoTPP, and then restored by SCN⁻, the detection limit is 6.0×10^{-4} M. The recognition of SCN⁻ could also be easily achieved by visual way since the assembly system showed significant color change by the anion. Both the fluorescence and the color change of the system exhibits remarkably high selectivity to SCN⁻ over a large series of anions. The interaction mechanisms among TPP, CoTPP and SCN⁻ were primarily investigated by fluorescence lifetime. The quenching of TPP fluorescence is attributed to the formation of TPP/CoTPP aggregates, and the fluorescence restoration is due to the binding of CoTPP with SCN⁻, releasing the free TPP. This simple system has the potential to be used as a latent fluorescent sensing approach for SCN⁻ for environmental analysis.

Keywords: Porphyrin; Fluorescent; Colorimetric; Sensor; Thiocyanate.

1. Introduction

There has been growing interests in the design of synthetic receptors for anions because of the important role of the analytes in biological and environmental fields, as well as food science [1]. As one of the important inorganic anions, SCN^- has made a great influence on both environment and the human body. It has been widely used in fabric dyeing, photographing, electroplating baths and so on [2]. SCN^- is also known to block the iodine uptake by the thyroid gland [3,4]. Several methods, such as chromatography [4,5], amperometry [3] and ion-selective electrodes [6,7], etc. have been previously reported in the literature for the assay of SCN^- . However, most of them require either sophisticated operation or time-consuming synthetic efforts. Therefore, there is still need for the development of a simple method for multipurpose determination of SCN^- .

Fluorescent sensor has its own advantages such as high sensitivity and easy operation [8]. In general, a fluorescent sensory molecule would involve the covalent linking of a receptor domain to a fluorescent fragment (i.e. the signaling unit) [9-12]. However, this synthetic work required elaborate design of the synthetic routes and many heavy and complicated synthetic steps. In this respect, the development of straightforward, low-cost and simple system for particular analytes should be of general interests. One is the use of non-covalent assembly approaches based on the competition indicator displacement between a fluorophore bonded to a receptor and a certain analyte [13-15]. When the receptor and fluorophore are carefully chosen, selective sensing event can be achieved.

Metalloporphyrins are one of the attractive candidates for anions receptor due to the high binding affinity of the metal center with the analytes [16-19]. It was found that in organic medium, the TPP fluorescence could be quenched in the presence of some metalloporphyrins [20, 21]. However, it has been taken little attention to restore the quenched fluorescence by other substrates which may be a potential anions sensing approach. With this in mind, our goal is to investigate whether this quenched TPP fluorescence can be restored, and further be used as a fluorescence recognition approach for anions in a suitable way. In this contribution, we reported our study on the interaction of TPP and CoTPP to develop an efficient colorimetric and fluorescent enhancement sensor for SCN^- . In the present case, CoTPP was used as SCN^- receptor and TPP acted as a fluorescent reporting unit, which does not require establishing any covalent linking between the fluorophore and the receptor but utilizes the fluorophore and receptor as such.

2. Results and Discussion

2.1. Fluorescence Quenching of TPP by Metalloporphyrins

Prior to application in fluorescence sensing of SCN^- anions, the effects of metalloporphyrins including *meso*-tetraphenylporphyrin zinc(II) (ZnTPP), *meso*-tetraphenylporphyrin manganese(II) (MnTPP) and CoTPP on the TPP fluorescence were first studied in the THF-water solution (Figure 1). In the absence of metalloporphyrin, TPP exhibited a strong emission peak at 651 nm. When CoTPP or MnTPP was added into the TPP solution, the TPP fluorescence significantly decreased. On the other hand, upon the addition of ZnTPP to the TPP solution, the fluorescence at 651 nm decreased concomitant with a new emission centered around 600 nm appearing, which might contribute to the emission of ZnTPP [22]. The quenching efficiencies, K_{sv} , of TPP by the three metalloporphyrins are

$4.01 \times 10^4 \text{ M}^{-1}$ (MnTPP), 1.54×10^5 (ZnTPP), and 3.14×10^5 (CoTPP). CoTPP display the strongest quenching.

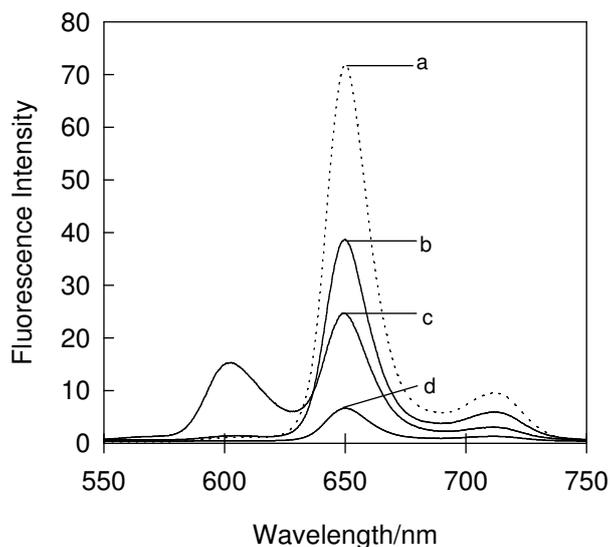


Figure 1. Effects of metalloporphyrins on the fluorescence emission spectrum of TPP in the THF-water solution. (a), without metalloporphyrin; (b), MnTPP; (c), ZnTPP and (d), CoTPP. $[\text{TPP}] = 2.5 \times 10^{-6} \text{ mol L}^{-1}$. $[\text{metalloporphyrin}] = 2.0 \times 10^{-5} \text{ mol L}^{-1}$. $\lambda_{\text{ex}} = 416 \text{ nm}$.

2.2. Restoration of TPP/CoTPP by Anions

To explore the utility of the TPP/CoTPP as anion-sensing approaches, the fluorescence responses of the system to anions were tested. It was found that the quenched fluorescence of TPP could be restored by anions.

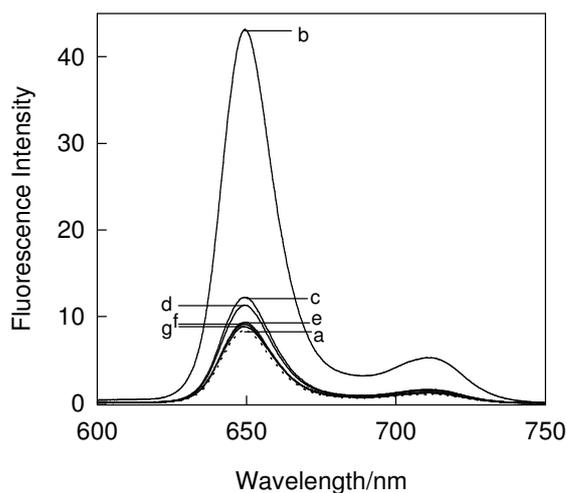


Figure 2. The fluorescence emission spectra of TPP/CoTPP system in the absence (a) and presence of selected anions (b, SCN^- ; c, NO_2^- ; d, Cl^- ; e, H_2PO_4^- ; f, F^- ; g, NO_3^-). $[\text{TPP}] = 2.5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{CoTPP}] = 2.0 \times 10^{-5} \text{ mol L}^{-1}$ and $[\text{anion}] = 2.8 \times 10^{-2} \text{ mol L}^{-1}$. $\lambda_{\text{ex}} = 416 \text{ nm}$.

Figure 2 shows the effects of different anions on the fluorescence restoration of TPP/CoTPP. When SCN^- was added to the TPP/CoTPP solution, remarkable fluorescence enhancement was observed.

Although the fluorescence emission increases at 651 nm are also noted in the presence of NO_2^- , Cl^- and H_2PO_4^- , the restoration values were smaller than that observed by SCN^- . The restored fluorescence intensity was 5.2-fold that of the original quenched fluorescence value of TPP/CoTPP system by addition of SCN^- at $2.8 \times 10^{-2} \text{ mol L}^{-1}$, the values of NO_2^- , Cl^- and H_2PO_4^- are 1.5-fold, 1.4-fold and 1.1-fold that of the original quenched fluorescence values, respectively. Other investigated anions such as F^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and HCOO^- had low effects on the TPP/CoTPP fluorescence restoration under the same conditions, and temperature ranging from 10°C to 30°C made no significant influence on the experimental results.

2.3. Binding Interactions of CoTPP with Anions and SCN^- Selectivity

To further clear out the high selective fluorescence response of TPP/CoTPP to SCN^- , the binding interactions of CoTPP with anions were studied by UV-Vis spectroscopy. In the THF-water (8/2, v/v) solution, the potassium salts of Cl^- , CO_3^{2-} , F^- , HCOO^- , H_2PO_4^- , NO_2^- , NO_3^- , SCN^- and SO_4^{2-} were used to evaluate the anion binding ability of CoTPP.

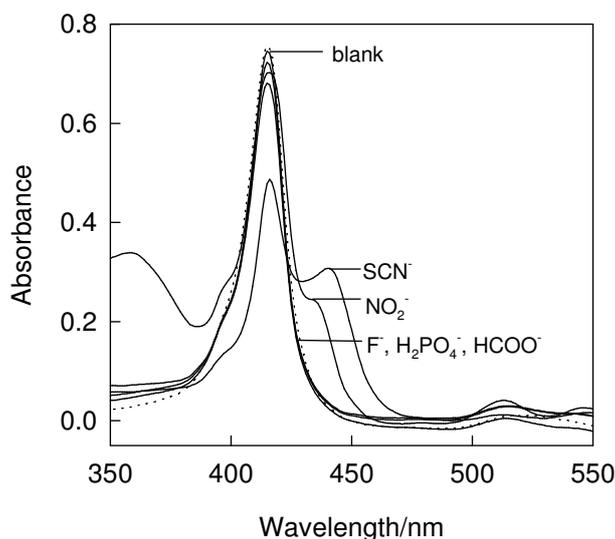


Figure 3. Effects of different anions on the UV-Vis spectra of CoTPP in THF aqueous solution.

[CoTPP] = $5.0 \times 10^{-6} \text{ mol L}^{-1}$. [anion] = $2.8 \times 10^{-2} \text{ mol L}^{-1}$.

Figure 3 shows the UV-Vis absorption spectra of CoTPP upon additions of $2.8 \times 10^{-2} \text{ mol L}^{-1}$ of the selected anions. In the THF aqueous solution, CoTPP displays a maximum absorption peak at 416 nm. When different anions were added into the solution, the porphyrin showed different response behaviors. In the presence of NO_2^- , a little change in the CoTPP absorption spectrum at 416 nm was observed, indicating the existence of weak interaction between NO_2^- and the CoTPP. By contrast, when SCN^- was added to the THF aqueous solution, significant decreases of absorbance around 416 nm accompanied with the intense bands centered at 442 nm appeared. No absorption spectral change was detected upon the additions of Cl^- , F^- , NO_3^- , H_2PO_4^- , SO_4^{2-} , CO_3^{2-} and HCOO^- to the THF aqueous solution of CoTPP. The results showed the high selective interaction of CoTPP with SCN^- compared with other investigated anions.

The UV-Vis spectroscopy of CoTPP was followed as aliquots of SCN^- were added to the THF aqueous solutions of CoTPP (Figure 4). Stepwise addition of SCN^- led to significant decrease in the CoTPP absorption band at 416 nm with the concomitant formation of a new red-shifted absorption band at 442 nm through a clear isosbestic point at 426 nm. The well-defined isosbestic point indicates that a neat interconversion between the uncomplexed and complexed species occurs. By following the absorption change at 442 nm and a curve fitting analysis [23-24], the stoichiometry of CoTPP with SCN^- was estimated to be 1: 2 ($n = 2$, which denotes the association ratio of SCN^- to CoTPP), the corresponding association constant K , is $9.85 \times 10^3 \text{ mol}^{-2} \text{ L}^2$ (Figure 4, inset). The association constants of CoTPP with other anions are summarized in Table 1, CoTPP shows strongest affinity with SCN^- over other anions, which is the result of highly selective fluorescence response of TPP/CoTPP to SCN^- .

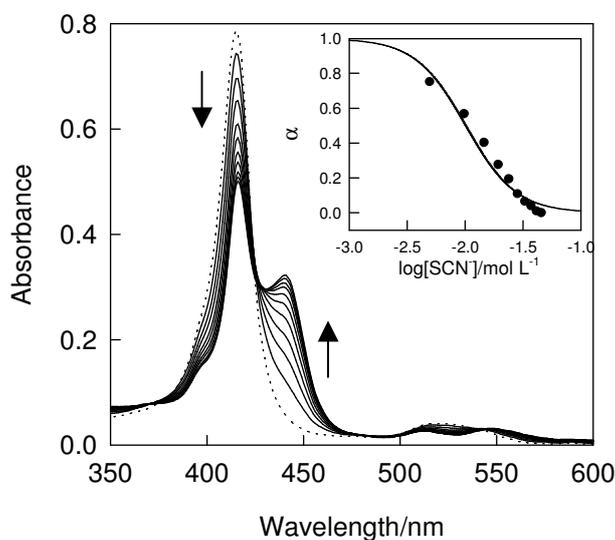


Figure 4. Absorption spectra of CoTPP in the presence of increasing amounts of SCN^- . The dashed line corresponds to CoTPP without anion. The concentration of SCN^- is 0, 5.0×10^{-3} , 9.0×10^{-3} , 1.3×10^{-2} , 1.75×10^{-2} , 2.2×10^{-2} , 2.6×10^{-2} , 3.0×10^{-2} , 3.4×10^{-2} , 3.7×10^{-2} and $4.2 \times 10^{-2} \text{ mol L}^{-1}$. $[\text{CoTPP}] = 5.0 \times 10^{-6} \text{ mol L}^{-1}$. Inset: Response parameter values (α) as a function of the logarithm of SCN^- concentrations. The association ratio of SCN^- to CoTPP, $n = 2$, and the association constant, $K = 9850 \text{ mol}^{-2} \text{ L}^2$ (• experimentally observed data points).

Table 1. Absorption Properties of CoTPP and Its Anion Complexes in the Visible Region, Association Constants K , and Response Selectivity of CoTPP to Anions.

Anions	λ_{\max} (nm)	ϵ^a , 10^4 ($\text{cm}^{-1} \text{mol}^{-1} \text{L}$)	K ($\text{mol}^{-2} \text{L}^2$)	Response selectivity ^b
SCN^-	442	6.30	9850	1
NO_2^-	436	4.88	1387	1.8×10^{-2}
CO_3^{2-}	442	0.64	763	7.4×10^{-4}
HCOO^-	442	0.28	154	1.3×10^{-4}
H_2PO_4^-	442	0.22	538	1.5×10^{-3}
F^-	442	1.31	287	2.7×10^{-4}
Cl^-	442	4.16	774	2.6×10^{-3}
SO_4^{2-}	442	0.41	-- ^c	-- ^c
NO_3^-	442	2.33	--	--
H_2PO_4^-	442	0.14	--	--
$\text{P}_2\text{O}_7^{2-}$	442	0.28	--	--
$\text{C}_2\text{O}_4^{2-}$	442	1.22	--	--

^a ϵ is the extinction coefficient of CoTPP-anion complex in the presence of $2.8 \times 10^{-2} \text{ mol L}^{-1}$ correspondent anions.

^b The response selectivity = $K_{\text{anion}} (F_{\text{anion}} - F_0) / K_{\text{SCN}^-} (F_{\text{SCN}^-} - F_0)$, where K is the association constant of CoTPP with anions, F_0 denotes the fluorescence intensity at 651 nm of TPP/CoTPP system without anions and F_{anion} is the fluorescence intensity in the presence of $2.8 \times 10^{-2} \text{ mol L}^{-1}$ correspondent anions.

^c The association constant and the response selectivity can not be acquired at this condition.

Interestingly, the solution was initially pale red in color and changed to deep yellow when exposed to SCN^- (Figure 5). The color would go deeply as time passed. NO_2^- showed very pale green color which is consistent with the very slim change on UV-Vis spectrum. The results indicate that color changes can be used for a “naked-eye” detection of SCN^- .

**Figure 5.** Partial color changes of TPP/CoTPP solution upon addition of different anions, separately.

From the left to the right are in turn no anion, Cl^- , SCN^- , F^- , NO_3^- , H_2PO_4^- , SO_4^{2-} , CO_3^{2-} , NO_2^- and HCOO^- in double distilled water. $[\text{TPP}] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{CoTPP}] = 5.0 \times 10^{-6} \text{ mol L}^{-1}$ and $[\text{anion}] = 2.8 \times 10^{-2} \text{ mol L}^{-1}$.

2.4. Mechanism Studies for the Fluorescence Quenching and Restoration of TPP

In our experiment, it was not found that Zn^{2+} , Co^{2+} or Mn^{2+} significantly quenched the TPP fluorescence, which demonstrated that the fluorescence quenching of TPP by the metalloporphyrins was related to the interactions of the two porphyrins rather than the heavy atom effects. Fluorescence lifetime measurements were carried out to understand the mechanism of TPP fluorescence quenching and restoration. From Table 2 it can be seen that in the presence of CoTPP, the fluorescence lifetime of TPP

is almost unaffected, which suggests that the quenching between TPP and CoTPP contributes to the formation of TPP/CoTPP ground state aggregation instead of electron transfer (PET) or excited energy transfer. Because if it is PET process, electrons of the free-base porphyrin in singlet excited state will transfer to a low-spin empty orbit of cobalt(II) [25], which means the presence of CoTPP will undoubtedly decrease the fluorescence lifetime of TPP. In contrast, upon addition of SCN^- , it shows a slim lifetime enhancement. This result may due to the stabilization of the TPP excited state caused by SCN^- . In all the measurements the best fits were obtained by monoexponential decay functions, which indicated the homogeneity of the chromophore in the excited state [26].

Table 2. Time-Dependent Fluorescence Decay Data of TPP, TPP/CoTPP System Affected by SCN^- in THF Solution.

Compound ^a	τ (ns) ^b	χ^2
TPP	9.81 ± 0.06	1.102 ± 0.009
TPP/CoTPP	9.81 ± 0.02	1.128 ± 0.003
TPP/CoTPP + SCN^-	10.73 ± 0.20	1.177 ± 0.063

^a $[\text{TPP}] = 2.5 \times 10^{-6} \text{ mol L}^{-1}$ and $[\text{CoTPP}] = 5.0 \times 10^{-6} \text{ mol L}^{-1}$. $\lambda_{\text{ex}}/\lambda_{\text{em}} = 416 \text{ nm}/651 \text{ nm}$.

^b Mean value \pm standard deviation (three determinations)

2.5. Preliminary Application

At the optimum experimental condition, the preliminary application of the present approach was tested by applying it in the determination of SCN^- concentration in three synthetic samples in the presence of other interferents. The synthetic samples were prepared on the basis of possible existing anions in physiological environment. The fluorescence titrations were carried out by adding a few microliters of the synthetic samples to TPP/CoTPP system, and the results were compared with those of SCN^- solutions without the interferents. The results are given in Table 3, and the recoveries of the three samples are 98.8~107.4 %.

Table 3. Recovery Studies of SCN^- from Synthetic Samples

Sample Composition (mM)	Determination (mM)	Recovery (%)
1 SCN^- , 14.1; F^- , 7.04; CO_3^{2-} , 7.04; HCOO^- , 7.04; Cl^- , 7.04, NO_3^- , 3.52.	14.8	105.0
2 SCN^- , 54.1; F^- , 27.0; CO_3^{2-} , 27.0; HCOO^- , 27.0; Cl^- , 27.0, NO_3^- , 13.5.	58.1	107.4
3 SCN^- , 96.8; F^- , 48.4; CO_3^{2-} , 48.4; HCOO^- , 48.4; Cl^- , 48.4, NO_3^- , 24.2.	95.6	98.8

3. Conclusion

In conclusion, a simple and efficient sensing approach capable of high selective colorimetric and fluorescent sensing of SCN^- has been proposed. In contrast to the traditional design of molecular receptors as chemical sensors based on geometric and electronic complementarity of the fluorophore-appended receptor to match that of the analyte, this simple approach needs no tedious synthetic efforts and obtains high selectivity. It has the potential to be explored as a SCN^- colorimetric and fluorescent sensing system. Furthermore, from a mechanism perspective, it will be helpful for providing more information to better understanding of porphyrin-based chemistry as well as, or at least the interactions between porphyrin units and anions.

4. Experimental Section

4.1. Materials

TPP and all kinds of metalloporphyrins were synthesized and purified in our laboratory according to the literatures [27-29]. The $1.0 \times 10^{-4} \text{ mol L}^{-1}$ stock solutions of porphyrins were prepared in THF. The concentrations of the porphyrins were determined by spectrophotometrically by using Beer's law and the corresponding absorptivity values. Below $4.0 \times 10^{-6} \text{ mol L}^{-1}$, the TPP absorption values in the THF-water (8/2, v/v) solution was increased with increasing in the TPP concentration, indicating there were no aggregations of TPP [30]. All organic solvents and the potassium salts of all kinds of anions were of analytical-grade. All salt solutions were prepared by doubly distilled water. The working solutions of the porphyrins were obtained by diluting the stock solution with THF and doubly distilled water. The substances described above were used as available without further purification.

4.2. Methods

Fluorescence emission spectra were acquired on a Hitachi F-4500 fluorescence spectrofluorometer (Kyoto, Japan) with the excitation and emission slits of 10.0 nm. Fluorescence lifetime measurements were carried out on Edinburgh Instruments FLS 920 (UK). The concentrations of TPP and CoTPP were $2.5 \times 10^{-6} \text{ mol L}^{-1}$ and $5.0 \times 10^{-6} \text{ mol L}^{-1}$, respectively. The excitation and emission wavelength was 416 and 651 nm, respectively. UV-Vis spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer (Kyoto, Japan). The fluorescence and absorption titrations of TPP/CoTPP system with the analytes were carried out by adding a few microliters of a stock solution of the materials to 1.0 mL of TPP/CoTPP solution with a quartz cell ($1.0 \times 1.0 \text{ cm}^2$ cross section). ^1H NMR spectra were recorded on an Invoa-400 spectrometer at 298 K. Samples for ^1H NMR analysis were prepared in 5 mm NMR tubes using CDCl_3 and $\text{CDCl}_3/\text{CD}_3\text{COCD}_3$ as solvent in the absence and presence of KSCN with tetramethylsilane (TMS) as internal standard.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (Grant No. 20475005) and the National Outstanding Youth Foundation of China (Grant No. 20525518) are gratefully acknowledged.

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