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A new naphthalimide derivative as a selective fluorescent and colorimetric sensor for fluoride, cyanide and CO₂



PIĞMËNTS

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ABSTRACT

A new naphthalimide derivative 1 is reported as an anion-activated CO_2 chemosensor. Among the various anions, chemosensor 1 displayed selective colorimetric and fluorescence changes with F^- and CN^- . Hydrogen bonding interactions between amine groups and anions can be attributed to these changes. The exposure of CO_2 revived the original color and fluorescence, so that distinct "On-Off-On" fluorescence emission changes were observed, for this anion-activated CO_2 sensing mechanism. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Anion recognition has been of great interest, due to the key roles of anions in a wide range of chemical and biological processes [1]. Among them, the sensing of fluoride and/or cyanide is especially interesting, because of their biological and environmental importance. For example, fluoride ions are important in dental care, and the treatment of osteoporosis [2]. Cyanide is known as a toxic anion, due to its effects on numerous body functions, including the vascular, visual, and central nervous systems [3]. Accordingly, fluorescent and colorimetric methods for the detection of F^- [4,5], and CN^- [6,7] are popular research targets.

On the other hand, due to global warming and the green house effect, CO_2 detection and fixation have been an important issue [8]. Besides the above environmental aspect, CO_2 plays a key role in human physiology, so CO_2 detection is also very important for medical diagnosis. Recently, a few attempts to sense CO_2 via either colorimetric or fluorescence changes have been reported [9].

For example, Gunnlaugsson and coworkers reported that naphthalimide amine derivatives could fix CO₂, based on fluoride-

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induced deprotonation of the amine moiety, and subsequent reaction with CO_2 [9a]. Polydiacetylenes, composed of two monomers with amine and imidazolium groups, are also used as colorimetric and fluorescent chemosensors for CO_2 [9b]. Recently, our group also reported a novel fluoride ion-activated strategy for the detection of CO_2 , in which benzobisimidazolium derivatives show fluorescent and colorimetric changes during the above process [9c].

In this work, we synthesized a new naphthalimide derivative **1** as an anion-activated CO_2 sensor. First of all, chemosensor **1** showed selective colorimetric and fluorescence changes with F^- and CN^- in CH₃CN, which can be attributed to the strong hydrogen bonding interactions between amine groups and anions. Then, the exposure of CO_2 revived the original color, and in particular, fluorescence, resulting in distinct "On-Off-On" fluorescence emission changes. We believe this anion-activated CO_2 sensing strategy will be useful for obtaining selectivity for CO_2 detection.

2. Experimental

2.1. Materials and equipments

Unless otherwise noted, general methods were used, and materials were obtained from commercial suppliers, and were used without further purification. Flash chromatography was carried out



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Scheme 1. Synthesis of chemosensor 1.

on silica gel (230–400 mesh). ¹H NMR and ¹³C NMR spectra were recorded, using 300 MHz and 500 MHz. Chemical shifts were expressed in ppm, and coupling constants (*J*) in Hz.

UV absorption spectra were obtained by UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

2.2. Synthesis

2.2.1. N-[2-(2-hydroxyethoxy)ethyl]-4-bromo-5-nitro-1,8-naphthalimide 2

329 mg (3.1 mmol) of 2-(2-aminoethoxy)ethanol in 10 mL ethanol was added dropwise to a solution of 1 g (3.1 mmol) 4-



Fig. 1. UV/vis absorption changes of 1 (10 $\mu M)$ with various anions (10 equiv.) in CH_3CN.



Fig. 2. Fluorescence changes of 1 (10 μ M) upon the addition of various anions (10 eq.) in CH₃CN. ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm).

bromo-5-nitro-1,8-naphthalic anhydride [10] in 100 mL ethanol. The mixture was then heated at reflux for 4 h, and monitored by TLC. After the reaction was completed, the solvent was removed, under reduced pressure. The crude product was then purified by column chromatography (SiO₂, CH₂Cl₂/MeOH, 99:1, v/v), to give **2** as a brown solid, in 55% yield (700 mg). ¹H-NMR (CDCl₃, 250 MHz) δ 2.31 (s, 1H, O–H), 3.67 (s, 4H), 3.85 (t, J = 5.4 Hz, 2H), 4.44 (t, J = 5.4 Hz, 2H), 7.93 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.50 (d, J = 7.8 Hz, 1H), 8.72 (d, J = 7.8 Hz, 1H). ¹³C-NMR (CDCl₃, 62.5 MHz) δ 40.0, 61.78, 68.05, 72.23, 121.18, 122.22, 123.56, 124.38, 125.50, 130.55, 131.47, 132.53, 136.00, 151.33, 162.34, 163.10. HRMS (EI) calcd. for C₁₆H₁₃BrN₂O₆ [M⁺] 407.9957, found 407.9963.

2.2.2. N-[2-(2-hydroxyethoxy)ethyl]-4,5-di{[(2-methylthio)ethyl] amino}-1,8-naphthalimide

90 mg (1 mmol) of (methylthio)ethylamine was added to a solution of 100 mg (0.244 mmol) *N*-[2-(2-hydroxyethoxy)ethyl]-4-bromo-5-nitro-1,8-naphthalimide **2** in 5 mL 2-methoxyethanol, and then the mixture was heated to reflux for 5 h, and monitored by TLC. After the reaction was completed, the solvent was removed under reduced pressure. The product was then purified by column chromatography (SiO₂, CH₂Cl₂/MeOH, 98:2, v/v), to give **1** as a yellow powder, in 80% yield (90 mg). ¹H-NMR (CDCl₃, 250 MHz) δ 2.13 (s, 6H), 3.0 (t, *J* = 5.4 Hz, 4H), 3.45 (t, *J* = 5.4 Hz, 4H), 3.68 (s, 4H), 3.82 (t, *J* = 5.4 Hz, 2H), 4.38 (t, *J* = 5.4 Hz, 2H), 6.44 (s, 2H, N–H),



Fig. 3. Colorimetric (top) and fluorescence (bottom) changes of $1~(50~\mu M)$ with various anions (10 eq.) in CH_3CN.



Fig. 4. UV/vis absorption (a) and fluorescence titrations (b) of $1 (10 \ \mu\text{M})$ with various

6.69 (d, I = 8.4 Hz, 2H), 8.36 (d, I = 8.4 Hz, 2H). ¹³C-NMR (CDCl₃,

62.5 MHz) δ 14.46, 33.32, 39.05, 41.22, 61.88, 68.76, 72.22, 106.68,

111.33, 111.78, 132.24, 133.69, 152.14, 164.78. HRMS (FAB) calcd. for

amount of F⁻ in CH₃CN. ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm).

C₂₂H₃₀N₃O₄S₂ [MH⁺] 464.1678, found 466.1676.

2.3. Preparation of solutions for fluorescent study

Stock solutions (10 mM) of CH₃CO₂, F⁻, Cl⁻, ClO₄, CN⁻, NO₃, Br⁻, I^- , $H_2PO_4^-$ and HSO_4^- in CH₃CN were prepared. Stock solution of **1** (1 mM) was prepared in CH₃CN. Test solutions were prepared, by placing 15–30 uL of the probe stock solution into a test tube, adding an appropriate aliquot of each stock, and diluting the solution to 3 mL with CH₃CN. For all measurements, excitation was at 440 nm. Excitation and emission slit widths were 3 nm/1.5 nm, respectively.

3. Results and discussion

3.1. Synthesis

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As shown in Scheme 1, 2 was firstly synthesized from the treatment of 4-bromo-5-nitro-1,8-naphthalic anhydride and 2-(2aminoethoxy)ethanol [10] in ethanol, at reflux for 4 h in 55% yield, after column chromatography. 2 was then reacted with (methylthio)ethylamine, to give the desired product **1** in 80% yield, after column chromatography.

The compounds **1** and **2** were fully characterized by NMR, and high resolution FAB mass spectroscopy.

3.2. Results and discussion

The selectivity of chemosensor **1** (10 μ M) towards anions was first investigated upon addition of various anions (AcO⁻, F⁻, Cl⁻, ClO₄⁻, CN⁻, NO₃⁻, Br⁻, I⁻, H₂PO₄⁻ and HSO₄⁻, 10 equiv.) in CH₃CN (Fig. 1). The addition of F⁻ and CN⁻ induced red-shifts of their absorptions at 445 nm-450 nm, which can be attributed the increased internal charge transfer (ICT), due to the strong hydrogen bonding between amine groups and anions. Similar enhanced ICT effects were previously reported for naphthalimide derivatives [11].

When chemosensor 1 (10 μ M) was excited at 440 nm, selective fluorescence quenching effects were observed for F- and CN-(Fig. 2).

Naked eye colorimetric changes and pictures for fluorescence changes of chemosensor **1** with various anions are shown in Fig. 3. Pale yellow to dark yellow color changes were observed for F⁻, CN⁻ and AcO⁻. Similarly, there were clear fluorescence quenching effects for F⁻ and CN⁻.



Fig. 5. Partial ¹H NMR spectra of 1 (2 mM) in DMSO- d_6 upon the addition of F⁻.



Fig. 6. UV/Vis spectral changes of **1** (10 μ M) upon bubbling with different volumes of CO₂ in the presence of 4 equiv. of F⁻. Inset: Photograph showing the color changes corresponding to the UV spectral changes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 explains the UV/vis titrations and fluorescence titrations of chemosensor **1** with F⁻. The detection limits of chemosensor **1** for F⁻ and CN⁻ were calculated as 1.56×10^{-10} M and 2.47×10^{-5} M, respectively (Fig. S5 and S6).

We further checked the UV/vis absorption and fluorescence changes in CH₃CN–H₂O (99:1, v/v) (Fig. S7 and S8). Interestingly, only cyanide induced a new ICT peak in its UV/vis absorption spectrum and moderate fluorescence quenching effect. The UV/vis absorption and fluorescence changes for F- were supressed significantly probably due to the favourable solvation effect of F⁻ in the presence of water. However, when we increase the amount of H₂O, we could not observe any significant change with anions examined.

The partial ¹H spectra of **1** upon addition of F^- in DMSO- d_6 are shown in Fig. 5. Notably, the amine proton (H_a) at 7.30 ppm showed a severe broadness upon the addition of F^- , and then it showed significant downfield shift to 13.12 ppm, with $\Delta\delta$ of 5.82. On the other hand, H_b at 6.86 ppm and H_c at 8.21 ppm displayed significant



Fig. 7. Fluorescence emission changes of **1** (10 μ M) upon bubbling with different volumes of CO₂ in the presence of 4 equiv. of F⁻. Inset: Photograph showing the color changes corresponding to the UV spectral changes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

upfield shifts, to 6.12 ppm and 7.67 ppm, respectively. These data support that strong hydrogen bonding interactions between amine protons and F^- , or even deprotonation of amine proton can occur, which can be attributed to the upfield shifts of H_b and H_c .

Finally, these complexes were further exposed to CO_2 gas. As shown in Fig. 6, the addition of CO_2 moved the UV/vis absorption peak to 445 nm, resulting in colorimetric change to pale yellow. In addition, fluorescence enhancements were observed upon the addition of CO_2 (Fig. 7), from which the "On-Off-On" emission changes were obtained, during this F⁻ activated system. The detection limit of this system for CO_2 was calculated to be 2.04×10^{-7} M (Fig. S9). We believe unstable N–CO₂ adduct is converted to HCO₃, which can generate compound **1** resulting in fluorescence enhancement. Similar mechanism is proposed in previous reports [9a,9g].

4. Conclusion

In conclusion, a fluoride activated colorimetric and fluorescence sensing of CO_2 is reported in the current work. A new naphthalimide derivative **1** was synthesized from 4-bromo-5-nitro-1,8naphthalic anhydride, in two steps. The title chemosensor showed selective UV/vis and fluorescence changes for F⁻ and CN⁻. Upon exposure to CO₂, these changes could be removed. Colorimetric changes and clear "On-Off-On" fluorescence changes were observed during this process. We believe this unique anion activated CO₂ sensing using naphthalimide will prove a useful strategy for CO₂ detection methods.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.04.029.

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