A New Naphthalimide Derivative as a Selective Fluorescent and Colorimetric Sensor for Fluoride, Cyanide and CO₂

Minji Lee, Sunjung Jo, Dayoung Lee, Zhaochao Xu, Juyoung Yoon

PII: S0143-7208(15)00159-X
DOI: 10.1016/j.dyepig.2015.04.029
Reference: DYPI 4751

To appear in: Dyes and Pigments

Received Date: 14 February 2015
Revised Date: 18 April 2015
Accepted Date: 18 April 2015


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Highlights

- A new naphthalimide derivative 1 showed selective UV/vis absorption and fluorescence changes with $F^-$ and $CN^-$.  

- Colorimetric and fluorescence changes of chemosensor 1 with $F^-$ or $CN^-$ were revived upon exposure to $CO_2$.  

- We demonstrated a novel anion-activated sensing strategy for $CO_2$.  

A New Naphthalimide Derivative as a Selective Fluorescent and Colorimetric Sensor for Fluoride, Cyanide and CO₂

Minji Lee,†a Sunjung Jo,†a Dayoung Lee,a Zhaochao Xu,a,b and Juyoung Yoon*a

aDepartment of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea.

bDalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

jyoon@ewha.ac.kr; zcxu@dicp.ac.cn

†contributed equally to this work

Abstract: A new naphthalimide derivative 1 is reported as an anion-activated CO₂ 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 CO₂ revived the original color and fluorescence, so that distinct “On-Off-On” fluorescence emission changes were observed, for this anion-activated CO₂ sensing mechanism.
Keywords: carbon dioxide sensor, fluoride ion sensor, cyanide ion sensor, fluorescent sensor, colorimetric sensor, anion recognition

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 greenhouse effect, CO₂ detection and fixation have been an important issue [8]. Besides the above environmental aspect, CO₂ plays a key role in human physiology, so CO₂ detection is also very important for medical diagnosis. Recently, a few attempts to sense CO₂ 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-induced deprotonation of the amine moiety, and subsequent reaction with CO₂ [9a]. Polydiacetylenes, composed of two monomers with amine and imidazolium groups, are also used as colorimetric and fluorescent chemosensors for CO₂ [9b]. Recently, our group also reported a novel
fluoride ion-activated strategy for the detection of CO$_2$, in which benzo[b]imidazole 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 CH$_3$CN, 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 on silica gel (230-400 mesh). $^1$H NMR and $^{13}$C 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

*N*-[(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-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 (SiO$_2$, CH$_2$Cl$_2$/MeOH, 99:1, v/v), to give 2 as a brown solid, in 55% yield (700 mg).

$^1$H-NMR (CDCl$_3$, 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).

$^{13}$C-NMR (CDCl$_3$, 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 C$_{16}$H$_{13}$BrN$_2$O$_6$ [M$^+$] 407.9957, found 407.9963.

*N*-[(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-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 (SiO$_2$, CH$_2$Cl$_2$/MeOH, 98:2, v/v), to give 1 as a yellow powder, in 80% yield (90 mg).
$^1$H-NMR (CDCl$_3$, 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), 6.69 (d, $J = 8.4$ Hz, 2H), 8.36 (d, $J = 8.4$ Hz, 2H). $^{13}$C-NMR (CDCl$_3$, 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 C$_{22}$H$_{30}$N$_3$O$_4$S$_2$ [MH$^+$] 464.1678, found 466.1676.

2.3 Preparation of solutions for fluorescent study

Stock solutions (10 mM) of CH$_3$CO$_2^-$, F$^-$, Cl$^-$, ClO$_4^-$, CN$^-$, NO$_3^-$, Br$^-$, I$^-$, H$_2$PO$_4^-$ and HSO$_4^-$ in CH$_3$CN were prepared. Stock solution of 1 (1 mM) was prepared in CH$_3$CN. Test solutions were prepared, by placing 15-30 µL of the probe stock solution into a test tube, adding an appropriate aliquot of each stock, and diluting the solution to 3 mL with CH$_3$CN. 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

As shown in Scheme 1, 2 was firstly synthesized from the treatment of 4-bromo-5-nitro-1,8-naphthalic anhydride and 2-(2-aminoethoxy)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.

**Scheme 1.** Synthesis of chemosensor 1.

### 3.2 Results and Discussion

The selectivity of chemosensor 1 (10 μM) 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 to 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].

**Fig. 1** UV/vis absorption changes of 1 (10 μM) with various anions (10 equiv.) in CH₃CN.

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

**Fig. 2** Fluorescence changes of 1 (10 μM) upon the addition of various anions (10 eq.) in CH₃CN. (λ_ex = 440 nm, Slit width: 3 nm/1.5 nm)
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. 3** Colorimetric (top) and fluorescence (bottom) changes of 1 (50 µM) with various anions (10 eq.) in CH\(_3\)CN.

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 CH\(_3\)CN-H\(_2\)O (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 suppressed 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.

**Fig. 4** UV/vis absorption (a) and fluorescence titrations (b) of 1 (10 µM) with various amount of F\(^-\) in CH\(_3\)CN. (λ\(_{ex}\) = 440 nm, Slit width: 3 nm/1.5 nm)

The partial \(^1\)H 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\textsuperscript{−}, and then it showed significant downfield shift to 13.12 ppm, with $\Delta \delta$ of 5.82. On the other hand, H\textsubscript{b} at 6.86 ppm and H\textsubscript{c} at 8.21 ppm displayed significant upfield shifts, to 6.12 ppm and 7.67 ppm, respectively. These data support that strong hydrogen bonding interactions between amine protons and F\textsuperscript{−}, or even deprotonation of amine proton can occur, which can be attributed to the upfield shifts of H\textsubscript{b} and H\textsubscript{c}.

**Fig. 5** Partial $^1$H NMR spectra of 1 (2 mM) in DMSO-$d_6$ upon the addition of F\textsuperscript{−}.

Finally, these complexes were further exposed to CO\textsubscript{2} gas. As shown in Fig. 6, the addition of CO\textsubscript{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\textsubscript{2} (Fig. 7), from which the “On-Off-On” emission changes were obtained, during this F\textsuperscript{−} activated system. The detection limit of this system for CO\textsubscript{2} was calculated to be 2.04 $\times$ 10$^{-7}$ M (Fig. S9). We believe unstable N-CO\textsubscript{2} adduct is converted to HCO\textsubscript{3}\textsuperscript{−}, which can generate compound 1 resulting in fluorescence enhancement. Similar mechanism is proposed in previous reports [9a and 9g].

**Fig. 6** UV/Vis spectral changes of 1 (10 $\mu$M) upon bubbling with different volumes of CO\textsubscript{2} in the presence of 4 equiv. of F. Inset: Photograph showing the color changes corresponding to the UV spectral changes.

**Fig. 7** Fluorescence emission changes of 1 (10 $\mu$M) upon bubbling with different volumes of CO\textsubscript{2} in the presence of 4 equiv. of F. Inset: Photograph showing the color changes corresponding to the UV spectral changes.
4. Conclusion

In conclusion, a fluoride activated colorimetric and fluorescence sensing of CO\textsubscript{2} is reported in the current work. A new naphthalimide derivative 1 was synthesized from 4-bromo-5-nitro-1,8-naphthalic anhydride, in two steps. The title chemosensor showed selective UV/vis and fluorescence changes for F\textsuperscript{-} and CN\textsuperscript{-}. Upon exposure to CO\textsubscript{2}, 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 CO\textsubscript{2} sensing using naphthalimide will prove a useful strategy for CO\textsubscript{2} detection methods.

Acknowledgments

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (CRI No. 2012R1A3A2048814). Z.X. thanks financial supports from the National Natural Science Foundation of China (21276251, 21422606).

References


[10] (a) Xu Z, Baek K-H, Kim HN, Cui J, Qian X, Spring DR, Shin I, Yoon J. Zn$^{2+}$–Triggered Amide Tautomerization Produces a Highly Zn$^{2+}$–Selective,
Captions for Figures and Scheme


Fig. 1 UV/vis absorption changes of 1 (10 μM) with various anions (10 equiv.) in CH$_3$CN.

Fig. 2 Fluorescence changes of 1 (10 μM) upon the addition of various anions (10 eq.) in CH$_3$CN. ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm)

Fig. 3 Colorimetric (top) and fluorescence (bottom) changes of 1 (50 μM) with various anions (10 eq.) in CH$_3$CN.

Fig. 4 UV/vis absorption (a) and fluorescence titrations (b) of 1 (10 μM) with various amount of F$^-$ in CH$_3$CN. ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm)

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

Fig. 6 UV/Vis spectral changes of 1 (10 μM) upon bubbling with different volumes of CO$_2$ in the presence of 4 equiv. of F$^-$. Inset: Photograph showing the color changes corresponding to the UV spectral changes.

Fig. 7 Fluorescence emission changes of 1 (10 μM) upon bubbling with different volumes of CO$_2$ in the presence of 4 equiv. of F$^-$. Inset: Photograph showing the color changes corresponding to the UV spectral changes.

Fig. 1 UV/vis absorption changes of 1 (10 μM) with various anions (10 equiv.) in CH₃CN.
**Fig. 2** Fluorescence changes of 1 (10 μM) upon the addition of various anions (10 eq.) in CH$_3$CN. ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm)

**Fig. 3** Colorimetric (top) and fluorescence (bottom) changes of 1 (50 μM) with various anions (10 eq.) in CH$_3$CN.
Fig. 4 UV/vis absorption (a) and fluorescence titrations (b) of 1 (10 μM) with various amount of F<sup>-</sup> in CH<sub>3</sub>CN. (λ<sub>ex</sub> = 440 nm, Slit width: 3 nm/1.5 nm)

Fig. 5 Partial <sup>1</sup>H NMR spectra of 1 (2 mM) in DMSO-<i>d<sub>6</sub></i> upon the addition of F<sup>-</sup>. 
**Fig. 6** UV/Vis spectral changes of 1 (10 μM) 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.

**Fig. 7** Fluorescence emission changes of 1 (10 μM) 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.
Graphical Abstract

A New Naphthalimide Derivative as a Selective Fluorescent and Colorimetric Sensor for Fluoride, Cyanide and CO₂

Minji Lee, Sun-Jung Cho, Zhaochao Xu* and Juyoung Yoon*

Highlights

- A new naphthalimide derivative 1 showed selective UV/vis absorption and fluorescence changes with F⁻ and CN⁻.
- Colorimetric and fluorescence changes of chemosensor 1 with F⁻ or CN⁻ were revived upon exposure to CO₂.
- We demonstrated a novel anion-activated sensing strategy for CO₂.
Supporting Informations for “A New Naphthalimide Derivative as a Selective Fluorescent and Colorimetric Sensor for Fluoride, Cyanide and CO₂”

Minji Lee,†a Sun-Jung Cho,†a Dayoung Lee,a Zhaochao Xu*,ab and Juyoung Yoon*a

aDepartment of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea.

bDalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

jyoon@ewha.ac.kr; zcxu@dicp.ac.cn

† contributed equally to this work
Figure S1. $^1$H NMR (300 MHz) of compound 1 in CDCl$_3$.

Figure S2. $^{13}$C NMR (75 MHz) of compound 1 in CDCl$_3$. 
Figure S3. $^1$H NMR (300 MHz) of compound 2 in CDCl$_3$.

Figure S4. $^{13}$C NMR (75 MHz) of compound 2 in CDCl$_3$. 
Figure S5. Fluorescence intensity changes of 1 (10 μM) with F⁻ (as the tetrabutylammonium salt).

Figure S6. Fluorescence intensity change of 1 (10 μM) with CN⁻ (as the tetrabutylammonium salt).
**Fig S7.** UV/vis absorption changes of 1 (10 μM) with various anions (10 equiv.) in a mixed solution of CH$_3$CN and water (99:1, v/v).

**Fig S8.** Fluorescence change of 1 (10 μM) upon the addition of various anions (10 eq.) in a mixed solution of CH$_3$CN and water (99:1, v/v). ($\lambda_{ex} = 440$ nm, Slit width: 3 nm/1.5 nm)
Figure S9. Fluorescence intensity changes of 1 (10 μM) with firstly the addition of 4 equiv F⁻ (as the tetrabutylammonium salt) and then bubbling with various quantities of CO₂. (R=0.9965)