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Graphical Abstract



1	A Simple Turn-On Fluorescent Chemosensor for CO ₂ Based on Aggregation-Induced
2	Emission: Application as a CO ₂ Absorbent Screening Method
3	
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12	
13	Abstract
14	An α -cyanostilbene-based fluorescent chemosensor, which includes a primary amine, was developed
15	for the quantitative analysis of CO_2 in solution. (Z)-3-(4-(3-Aminopropoxy)phenyl)-2-(4-
16	nitrophenyl)acrylonitrile (1) reacts with CO_2 and enables a turn-on type CO_2 chemosensor with increased
17	fluorescence due to aggregation-induced emission. More importantly, 1 required no additives such as an amine
18	media for detecting CO_2 , and the limit of detection was estimated to be ~26 ppm. This system was successfully
19	applied to determine the relative efficiency of CO_2 absorbents dependent on the fluorescence change in 1. The
20	use of this chemosensor as a CO_2 absorbent screening method suggests that 1 may be used to develop a high-
21	throughput screening method for the evaluation of high-performance CO ₂ absorbents.
22	Key words: CO ₂ ; Fluorescent chemosensor; Aggregation-induced emission; CO ₂ absorbent screening; High
23	throughput screening

24 1. Introduction

25 CO_2 has been of international interest owing to environmental concerns with respect to CO_2 emissions, 26 because these have been reported to contribute to the greenhouse effect. This has made the detection of CO_2 an 27 important issue [1,2]. Moreover, the detection of CO_2 can provide useful applications for the development of 28 absorbents to reduce greenhouse gas emission, because CO₂ detection plays a key role in determining the 29 efficiency of CO_2 absorbents [3,4]. However, the development of CO_2 detection methods has been limited by the 30 inherent properties of CO₂, such as its inactiveness [5]. Electrochemical (EC), non-dispersive infrared (NDIR), 31 and gas chromatography-mass spectrometry (GC-MS) have been used as major protocols to detect CO₂, and are 32 being continuously improved. Unfortunately, these methods require time-consuming measurements and the use 33 of advanced and high-cost equipment [6-9].

34 As an alternative to these methods, fluorescent chemosensors have been attractive candidates due to 35 their simplicity, cost-effectiveness, and rapid detection capabilities [10-12]. In particular, several organic 36 molecule-based fluorescent chemosensors systems for CO₂ detection have been reported, due in part to their 37 ease of synthesis, high quantum yields, and biocompatibility [13]. For example, pH indicator-based fluorescent 38 chemosensors, such as 1-hydroxypyrene-3,6,8-trisulfonate (HPTS) and diketopyrrolopyrrole (DPP), have been 39 designed through a reversible equilibrium with carbonic acid [14,15]. Other examples are deprotonation-assisted 40 fluorescent chemosensors which are a combination of fluorescent dyes and a base, including triethylamine and 41 fluoride ions, respectively [16-18]. Furthermore, various aggregation-induced emission (AIE) fluorescent dyes 42 in amine media have been successfully applied to the detection of CO₂ through a mechanism where the amine 43 media reacts with CO_2 and results in the formation of a viscous carbamate ionic liquid (CIL) [19].

Chemosensor-based high-throughput screening (HTS) methods have several advantages over conventional screening methods because these methods are simple, fast, and cost effective. Therefore, these screening methods have been extensively used in the development of catalysts, drug candidates, and NO_x absorbents [20–23]. Although the aforementioned fluorescent chemosensors can be used as highly sensitive detectors of CO₂, they have a limitation when applied to screening the efficiency of CO₂ absorbents with the HTS method. Specifically, these chemosensors can require additives (i.e., amine media and bases) or are sensitive to pH changes. It is also important to reduce external interference, to develop an effective CO₂

absorbent screening method. Conventional CO_2 absorbents currently available in the industry tend to have unavoidable chemical influences, such as a change in pH or interference from amine derivatives present in the system. These influences can make it difficult to effectively evaluate the CO_2 absorbents. Therefore, it is highly desirable to develop a new chemosensor for CO_2 absorbent screening.

55 α -Cyanostilbene, one of the AIE-based fluorogens, forms aggregates based on a stacking effect due to 56 π - π conjugation, resulting in the AIE phenomenon. Compared with that of traditional fluorogens, α -57 cyanostilbene has a more intense fluorescence emission which is paired with a good photostability in the 58 aggregated state, relative to a dilute solution [24]. Also, their photoluminescence property could be adjusted by 59 varying functional group of terminal aryl groups. Especially, the 4-nitro-4'methoxy- α -cyanostilbene showed a 60 remarkable difference of fluorescence intensity between solid and solution with a large Stokes shift [25]. 61 Furthermore, α -cyanostilbene can be easily designed as a turn-on type fluorescent chemosensor that can take 62 advantage of the AIE properties of this molecule, by introducing different functional groups to promote self-63 assembly [26]. Herein, the α -cyanostilbene derivative containing a primary amine group (1) is proposed as a 64 simple turn-on type AIE-based fluorescent chemosensor that does not require the use of additives for the 65 detection of CO₂ and for the design of a chemosensor-based HTS method for CO₂ absorbent screening. The 66 primary amine of 1 reacts with CO_2 to form carbamic acid [27,28], which interacts with other amine molecules 67 of 1 to form salt bridges [29]. This electrostatic interaction between the carbamate and ammonium salt induces 68 self-assembly and results in an enhancement in the fluorescence intensity due to the increase in size of the 69 aggregates of 1. Furthermore, bubbling N_2 into the solution induces the transformation of the carbamate salt to 70 the primary amine and CO₂ [30] which results in a decrease in the fluorescence, through the relaxation of the 71 aggregates. Therefore, this reversible turn-on type fluorescent chemosensor is reusable and allows for the 72 quantitative analysis of CO₂, measured by the increase in fluorescence emission, without the need for additives, 73 as shown in Scheme 1.



74

75

Scheme 1. Schematic illustration of compound 1-based CO₂ sensing

76 2. Experimental section

77 2.1. General

78 All the materials were purchased from commercial suppliers (Sigma-Aldrich, Tokyo Chemical 79 Industry, Alfa Aesar, and SHINYO) and were used without further purification. ¹H and ¹³C NMR spectra were 80 recorded on a Jeol 400 MHz NMR spectrometer. Mass spectra were obtained using an Agilent ESI-Q/TOF 81 (Quadrupole/Time-of-flight) mass spectrometer. Melting points were measured using a BUCHI Melting point 82 M-565 apparatus. Fluorescence spectra were recorded with a SCINCO FS-2 fluorescence spectrometer. 83 Absorption spectra were recorded with a JASCO V-630 UV-vis spectrometer. Fluorescence lifetime was 84 measured by an FLS-980 fluorometer (Edinburgh Instruments Ltd.) equipped with time-correlated single photon 85 counting (TCSPC) instruments (TCC2) and Red PMT (R928P-Hamamatsu Photonics K.K.). In gas experiments, 86 CO₂ gas flowed through an MKP TSC-200 mass flow controller (MFC), the size of aggregates was measured 87 using a Malvern Zetasizer Nano-ZS dynamic light scattering (DLS) instruments, and all the experiments were 88 performed in solution.

89 2.2. Synthesis of chemosensor



91

Scheme 2. Synthetic procedures for compound 1

92 2.2.1. Synthesis of **3**

93 **3** was synthesized according to previously reported procedures [31]. 3-bromopropylamine (2.07 g, 94 15.00 mmol) and triethylamine (8.36 mL, 60.00 mmol) were dissolved in dichloromethane (50 mL). After 95 stirring at room temperature for 30 min, di-tert-butyl dicarbonate (3.93 g, 18.00 mmol) was added, and stirred at 96 room temperature for 48 h. The solvent was removed under reduced pressure to give a white oily mixture. This 97 mixture was dissolved in ethyl acetate and washed with water and brine. Then, the organic layer was dried with 98 anhydrous sodium sulfate, and filtered. The organic layer was concentrated under reduced pressure to give a 99 white oil. The oil was purified by column chromatography (silica gel, hexane:ethyl acetate = 5:1 was used as the eluent) to yield **3** (1.22 g, 34%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 4.73 (s, 1H), 3.43–3.40 (t, J = 100 101 6.0 Hz, 2H), 3.27-3.22 (m, 2H), 2.06-1.99 (m, 2H), 1.42 (s, 9H).

102 2.2.2. Synthesis of **2**

103 2 was synthesized according to previously reported procedures [32]. To a mixture of 4-104 hydroxybenzaldehyde (2.00 g, 16.40 mmol) and 4-nitrobenzyl cyanide (2.66 g, 16.40 mmol) in absolute ethanol 105 (40 mL), was added piperidine (2.43 mL, 24.60 mmol) in portions over 30 min. The reaction mixture was stirred 106 at room temperature for 6 h, cooled to 0 °C, and filtered. The precipitate was washed with ethanol. The brown colored solid was dissolved in ethyl acetate and washed with water and brine. The organic layer was dried with 107 108 anhydrous sodium sulfate, and filtered. Then, the organic layer was concentrated under reduced pressure to give 109 a yellow solid. The solid was recrystallized from ethanol to afford 2 (3.98 g, 91%) as a yellow solid. ¹H-NMR 110 (400 MHz, DMSO-*d*₆) δ 10.48 (s, 1H), 8.34–8.32 (m, 2H), 8.17 (s, 1H), 8.00–7.93 (m, 4H), 6.97–6.93 (m, 2H); 111 mp 202-204 °C.

112 2.2.3. Synthesis of **1**

113 A mixture of (Z)-3-(4-hydroxyphenyl)-2-(4-nitrophenyl)acrylonitrile (0.27 g, 1.00 mmol) and anhydrous 114 potassium carbonate (0.15 g, 1.10 mmol) in dimethylformamide (5 mL) was stirred at room temperature for 10 115 min, followed by the addition of 3 (1.19 g, 5.00 mmol). The reaction mixture was then stirred at 70 $^{\circ}$ C for 20 h, 116 and cooled to room temperature slowly. The reaction mixture was poured into water and allowed to stand for 6 h. 117 The precipitate was filtered and dried to give an orange-colored solid. The solid was dissolved in chloroform 118 and washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, filtered, and 119 concentrated under reduced pressure to give an orange solid. The solid was purified by column chromatography 120 (silica gel, chloroform:methanol = 100:1 was used as the eluent) to yield a yellow solid. The material was used for the next reaction without any further purification. To the material (0.70 g, 1.65 mmol) in ethyl acetate (60 121 122 mL) was added hydrogen chloride gas until no further precipitation occurred; then, the reaction mixture was 123 slowly cooled to 0 °C. The precipitate was filtered and dried to give a yellowish solid. The solid was dissolved 124 in water (300 mL) and stirred at room temperature for 30 min. Then, a 1 M aqueous solution of sodium hydroxide was added until the pH reached approximately 8. The yellow precipitate was extracted with 125 126 chloroform and washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, and 127 filtered. Then, the organic layer was concentrated under reduced pressure to give 1 (0.36 g, 68%) as a greenish 128 brown solids. ¹H-NMR (400 MHz, CDCl₃) δ 8.31–8.28 (m, 2H), 7.95–7.93 (m, 2H), 7.83–7.80 (m, 2H), 7.60 (s, 1H), 7.03–6.99 (m, 2H), 4.16–4.14 (t, J = 6.0 Hz, 2H), 2.96–2.92 (t, J = 6.6 Hz, 2H), 2.00–1.94 (m, 2H); ¹³C-129 NMR (100 MHz, CDCl₃) δ 161.94, 147.56, 145.15, 141.20, 132.05 (2C), 126.41 (2C), 125.70, 124.41 (2C), 130 131 117.85, 115.19 (2C), 106.12, 66.28, 39.07, 32.82; ¹H-NMR (400 MHz, THF-*d*₈) δ 8.31–8.28 (m, 2H), 8.03–7.99 (m, 2H), 7.96–7.93 (m, 3H), 7.08–7.04 (m, 2H), 4.18–4.15 (t, J = 6.4 Hz, 2H), 2.84–2.80 (t, J = 6.6 Hz, 2H), 132 1.90–1.83 (m, 2H); ¹³C-NMR (100 MHz, THF-*d*₈) δ 162.93, 148.35, 145.64, 142.05, 132.55 (2C), 127.02 (2C), 133 126.73, 124.72 (2C), 118.14, 115.59 (2C), 106.49, 39.44, 33.85; mp 87-90 °C; ESI-MS m/z calculated for 134 135 $C_{38}H_{34}N_4O_6 [M+H]^+$ 324.1343, found 324.1337.

136 2.3. Optimization of solvent polarity

137 To obtain the optimized system for AIE phenomenon, the change in solvent polarity was taken with 138 THF and hexane. All sample solutions (1 mL) were prepared by increasing the hexane to THF volume ratio with

- 10% units. The final concentration of 1 in each sample solution was maintained at 1 mM. All the fluorescence
 spectra were obtained by a SCINCO FS-2 fluorescence spectrometer after bubbling each sample with CO₂ (80 mL) and without CO₂. Excitation wavelength, 365 nm; slit widths, 10/10 nm; emission wavelength, 565 nm.
- 142 *2.4. General sampling method*
- 143 THF and hexane were degassed by bubbling them with N_2 for 30 min before use. The final 144 concentration of the sample solution was 1 mM of **1** in the THF:hexane (1:9, v/v) system (900 µL hexane + 100 145 µL of 10 mM **1** stock). All the sample solutions were degassed before measurements were taken.
- 146 2.5. Measurement of the size change of the aggregates

147 The size change of the aggregates was measured by DLS, following the above general sampling 148 method. Based on the CO_2 and N_2 titration, the control solution was bubbled with N_2 (10 mL) and the sample 149 solution was bubbled with CO_2 (0.09 mL).

150 *2.6. CO*² *titration*

All the fluorescence spectra for the CO_2 titration of **1** were obtained by a SCINCO FS-2 fluorescence spectrometer following the above general sampling method: excitation wavelength, 365 nm; slit widths, 10/10 nm; and emission wavelength, 565 nm. The injected volume of CO_2 gas was changed using an MFC with 0.01 mL units.

155 2.7. Test of reversibility of 1

The fluorescence spectra of **1** (1 mM, 1 mL) with an amount of CO_2 associated with AIE behavior were observed in the THF:hexane (1:9, v/v) system: excitation wavelength, 365 nm; slit widths, 10/10 nm; and emission wavelength, 565 nm. Based on the CO_2 and N_2 titration, the same sample solution was bubbled with CO_2 (0.09 mL) and N_2 (10 mL). The change in the fluorescence spectra upon bubbling each gas another time was subsequently measured.

161 2.8. CO₂ absorbents screening method based on 1

162 The stock solutions were prepared in THF. The final sample solutions (1 mL) were composed of 1 (1 163 mM) and a CO₂ absorbent (1 mM), and were prepared using stock solutions of 1 (20 mM) and the CO₂

absorbent (20 mM). The control sample was composed of degassed hexane (900 μ L) + stock solution of **1** (20 mM, 50 μ L) + degassed THF (50 μ L), and the other samples were composed of degassed hexane (900 μ L) + stock solution of **1** (20 mM, 50 μ L) + stock solution of the CO₂ absorbent (20 mM, 50 μ L). After bubbling CO₂ (0.09 mL) through each sample, all the fluorescence spectra of the samples containing CO₂ absorbents were normalized relative to the control sample: excitation wavelength, 365 nm; slit widths, 10/10 nm; and emission wavelength, 565 nm.

170

171 **3. Results and discussion**

172 The change in solvent polarity was first conducted to utilize the designed molecule (1) as a fluorescent 173 chemosensor for CO_2 . The excellent solubility of 1 in pure THF led to no fluorescence detection, whereas the 174 solution of only hexane resulted in poor solubility and excessive aggregates, leading to uneven fluorescence 175 emission. Therefore, a combination of THF and hexane was required to optimize the solvent polarity for the 176 introduction of the AIE phenomenon. According to the absorption spectrum in THF (Fig. S1), the excitation 177 wavelength obtained at 365 nm demonstrated optimal fluorescence intensities. As the hexane to THF ratio 178 gradually increased, with the concentration of 1 maintained at 1 mM, the normalized fluorescence intensity was 179 plotted at 565 nm (Fig. 1b). As a result, the optimized THF:hexane (1:9, v/v) system was chosen, as it produced 180 the maximum emission for CO_2 detection.



182 Fig. 1. (a) Normalized fluorescence spectra of 1 (1 mL, 1 mM) versus fraction of hexane in THF after bubbling with CO₂ (80

183 mL) and (b) plot of normalized fluorescence intensity of **1** (1 mL, 1 mM) at 565 nm, *versus* fraction of hexane in THF, 184 including hexane mixtures bubbled with CO_2 (80 mL, red) and without CO_2 (blue). Excitation wavelength, 365 nm; slit 185 widths, 10/10 nm.

186 To demonstrate the aggregation of 1, the size of the aggregates in the THF: hexane (1:9, v/v) solution 187 before and after bubbling with CO₂ were measured by DLS. The average particle diameter of the aggregates before bubbling with CO₂ was 86.99 nm (Fig. 2a), and that after bubbling with CO₂ was 774.1 nm (Fig. 2b), a 188 189 9-fold increase in size. These DLS data and other observed spectral changes show an increase in aggregation 190 when the solution was bubbled with CO₂, resulting in an increase in the fluorescence intensity of 1. Furthermore, the NMR study was conducted to elucidate the formation of carbamic acid by bubbled with CO₂. Each NMR 191 192 spectra of a solution of 1 were measured in THF- d_8 before and after bubbling with an excess CO₂. The ¹H-NMR 193 signal of α -proton of amine of 1 was shifted to downfield including a change of the splitting pattern from a triplet to a quartet after CO₂ bubbling (Fig. S5). Also the new peak at δ 158.60 was appeared after CO₂ bubbling 194 in ¹³C-NMR spectrum (Fig. S6). These results are in good agreement with previously reported NMR studies of 195 196 amine-based CO₂ absorption [33,34].





198 Fig. 2. Size analysis of aggregates in THF:hexane (1:9, v/v) (a) after bubbling with N₂ (10 mL) and (b) after bubbling with

199 CO₂ (0.09 mL).

207

The changes in the fluorescence spectra were measured as the volume of CO_2 introduced into the system was increased (as controlled using an MFC) in a solution of **1**. As the amount of CO_2 increased, the fluorescence of **1** gradually increased, as shown in **Fig. 3a**. The obtained fluorescence spectral changes for **1** tended to be proportional to the increase in CO_2 , which reached saturation when about 0.09 mL of CO_2 was added to a solution of **1** (**Fig. 3b**). Based on these results, the limit of detection of **1** was estimated to be ca. 26 ppm, as shown in **Fig. S2**. These results indicate that the quantitative measurement of CO_2 can be conducted through changes in the fluorescence intensity of **1**.





210 Since reversible chemosensors for CO₂ are likely to be used in environmental monitoring and irregular 211 and dynamic changes of CO_2 , it was very important to demonstrate the reversible behavior of 1. To obtain 212 reversible fluorescence spectral changes, an N₂ titration test was preferentially performed at the point where the 213 fluorescence intensities reached a maximum, as shown in Fig. S3. The reversible fluorescence changes were 214 measured when the solution was alternately bubbled with a certain volume of the two gases (CO2 and N2) that 215 saturated the fluorescence intensity of 1. As the volume of bubbled N2 increased after bubbling CO2, the 216 fluorescence of 1 decreased due to the release of the aggregates through the transformation of the carbamate salt 217 to the primary amine and CO_2 , by N_2 . Compared with the original fluorescence intensity, a similar fluorescence 218 intensity was observed upon bubbling CO_2 after bubbling N_2 in the second cycle. Therefore, CO_2 induced an

- increase in the fluorescence of $\mathbf{1}$, whereas N_2 reverted the fluorescence of $\mathbf{1}$ to its initial state. In multiple cycles,
- the fluorescence changes in 1 showed good reproducibility (Fig. 4).





Fig. 4. Normalized fluorescence intensity of 1 (1 mL, 1 mM) at 565 nm, in THF:hexane (1:9, v/v) with repeated bubbling of CO_2 (0.09 mL) and N_2 (10 mL). Excitation wavelength, 365 nm; slit widths, 10/10 nm.

224 In terms of contributing to the efforts of reducing the impacts of global warming, the importance of 225 industrial application for capturing and fixing CO₂ has been emphasized. According to previous research, 226 various kinds of CO_2 absorbents have been studied to address these problems [35]. The evaluation of CO_2 227 absorbent efficiency is a key step in the development of CO_2 absorbents. The conventional screening methods 228 for absorbents require multistep processes, such as a screening test through a specific apparatus, a vapor-liquid 229 equilibrium test, and heat of reaction measurements [36]. Thus, it is highly meaningful to develop a selection 230 method with less limitations than the current methods, in the aspect of screening a large number of absorbent 231 candidates. When compared with conventional technologies, fluorescent chemosensors-based screening 232 methods have the advantages of a more economical method and a more rapid analysis. From this perspective, 233 the CO_2 chemosensor 1 was used to evaluate the efficiency of CO_2 absorbents. The efficiency of the CO_2 234 absorbents was expected to be indirectly measured through the change in fluorescence, based on the relative 235 CO_2 reactivity between the absorbent and 1. A strong CO_2 absorbent in the sample solution results in a weak 236 fluorescence of 1 because most of the CO_2 is captured by the absorbent rather than 1. In the opposite case,

- strong fluorescence emission of 1 suggests that 1 is preferentially capturing most of the CO₂ and exhibiting AIE
- behavior, as shown in **Scheme 3**.



239



Scheme 3. Schematic illustration of CO₂ absorbent screening

241 When comparing various CO₂ absorbents, alkanolamine derivatives were chosen to demonstrate the 242 proposed screening method, as they are widely used in current industrial technologies for the removal of CO₂, 243 due to their high affinity for CO_2 [4]. Each relative change in fluorescence indicates the ability of the CO_2 244 absorbent to capture CO_2 relative to 1, as shown in Fig. 5. Strong CO_2 absorbents, such as 2-piperidinemethanol 245 (PM) and monoethanolamine (MEA), showed little fluorescence change in solution, whereas a relatively weak CO₂ absorbent induced a strong fluorescence change. According to previous studies, the relative CO₂ absorbing 246 247 capacity of the CO_2 absorbents used in this experiment were as follows: 2-piperidinemethanol (PM) > 248 monoethanolamine (MEA) and N-methylethanolamine (MMEA) > diethanolamine (DEA) and 249 dimethylethanolamine (DMEA) > N-methyldiethanolamine (MDEA) > triethanolamine (TEA) [37-40]. The 250 findings of this study have a good correlation with these previously reported results. Therefore, this screening 251 method has the potential to be used for a variety of applications to distinguish CO₂ absorbents through relative 252 fluorescence changes.



253

Fig. 5. Normalized fluorescence intensity of 1 (1 mL, 1 mM) at 565 nm, after bubbling with CO₂ (0.09 mL) in THF:hexane
(1:9, v/v) using various CO₂ absorbents (1 mM). Excitation wavelength, 365 nm; slit widths, 10/10 nm.

256

257 4. Conclusion

258 α -Cyanostilbene with a primary amine as the reactive functional group was developed as an AIE-259 based fluorescent chemosensor (1) for CO₂ without the need of additives such as amine media and anions. This 260 CO₂-sensitive turn-on type signaling is based on the AIE phenomenon caused by the increase in size of the 261 aggregates after bubbling the solution with CO_2 . In addition, 1 showed excellent reversibility when alternately 262 bubbling CO2 and N2. Furthermore, 1 can also be utilized as a method for screening the relative efficiency of 263 CO_2 absorbents by comparing the changes in the fluorescence intensities. Thus, this method has the potential to 264 be used in a high-throughput screening (HTS) method to effectively select high-performance CO₂ absorbents 265 from a large number of candidates.

266

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271

- 272 Appendix A. Supplementary data
- 273 Supplementary data related to this article can be found at doi ****

274

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Highlights

- α-Cyanostilbene-based fluorescent chemosensor for CO₂ was developed by using AIE
- Chemosensor enables the detection of CO₂ with no additives, such as amine and anion
- This chemosensor was applied to determine the relative efficiency of CO₂ absorbents

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