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Light-swing CO_2 capture: photoirradiation-based chemical CO_2 release based on photoisomerization of azobenzene-amine/guanidine derivatives†

Ryo Murakami, * Keitaro Shiota,‡ Ayaka Uchida‡ and Fuyuhiko Inagaki *

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The world is committed to reducing CO_2 emissions, and research on CO_2 capture and effective utilization is being actively studied. Among the methods in development, direct air capture (DAC) is classified as a negative emission technology and has attracted significant study. The current problem with CO_2 capture technologies for decarbonization is their cost due to the high separation energy required to release CO_2. We have developed a new light-swing method that can potentially utilize a natural source of energy, *i.e.*, sunlight, as an alternative to temperature- and pressure-swing methods. Herein, we report photoirradiation-based CO_2 capture based on photoisomerization of azobenzene-amine and guanidine derivatives. The visible light-swing CO_2 absorption and release system using azobenzene-guanidine has shown potential in DAC systems owing to its reusability. A plausible mechanism for CO_2 release under light irradiation involves photoisomerization from *trans*- to *cis*-azobenzene in which steric repulsion with other molecules is the driving force, and CO_2 is released due to the functional disruption of intermolecular interactions. This concept demonstrates the potential of using various photokinetic molecules as a driving force for light-swing CO_2 capture.

1. Introduction

CO_2 capture,[1–6] a technology that captures CO_2 directly from the atmosphere or from exhaust gases is one of the most important methods for decarbonization. In the well-studied chemical absorption method using amines, CO_2 and an absorbent are combined through a chemical reaction. There are several types of CO_2 capture methods, including carbon capture and storage (CCS),[7,8] which captures CO_2 from the exhaust gases from thermal power plants, direct air capture (DAC),[9–22] which captures atmospheric CO_2, and bioenergy with carbon capture and storage (BECCS),[23,24] which captures CO_2 produced in biomass power generation. In all of these methods, low-concentration CO_2 [exhaust gas: *ca.* 1–15 vol%, air: *ca.* 400 ppm] is recovered with absorbent/adsorbent (amines, *etc.*), and then CO_2 is released and concentrated by heating or decompression.

In the chemical absorption method using amines,[25] the reaction proceeds exothermically through a neutralization reaction between the base, amine, and the acid (CO_2). On the other hand, when CO_2 is released, the reaction becomes endothermic, requiring energy from the outside to release/concentrate CO_2. This enormous separation energy is a major issue for general CO_2 capture technologies. One of the reasons for this large separation energy is the water content. For example, we found that monoethanolamine (MEA),[14] which is a benchmark for CO_2 absorbents, absorbed CO_2 and moisture in air to form $1(CO_2)\cdot 3(MEA)\cdot 3(H_2O)$. Theoretically, two molecules of amine should react with one molecule of CO_2, providing $1(CO_2)\cdot 2(\text{amine})$ [*e.g.*, $2 \times \text{R-NH}_2 + CO_2 \rightarrow \text{R-NH-COO}^-\cdot{}^+\text{H}_3\text{N-R}$]. Thus, the CO_2 absorption efficiency of the amine is reduced due to the water content, resulting in an increase in the separation energy. In addition, extra thermal energy for moisture content during CO_2 release/concentration is required. It was thought that the presence of water was unavoidable because amines are hydrophilic groups and CO_2 is soluble in water, as exemplified by carbonated water. However, we[26–28] recently found that aralkyl amines with hydrophobic phenyl groups near the amine can selectively absorb CO_2 in air without moisture. This technology eliminates the necessity for extra energy related to water content when releasing CO_2.

The ultimate challenge in CO_2 capture by chemical absorption is how to avoid wasting energy during the dissociation of amines and CO_2. As far as we know, there are currently three methods of dissociating CO_2: (a) a thermal-swing method by heating,[29] (b) a pressure-swing method[30,31] by depressurization

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Faculty of Pharmaceutical Sciences, Kobe Gakuin University, 1-1-3 Minatojima, Chuo-ku, Kobe, Hyogo 650-8586, Japan. E-mail: finagaki@pharm.kobegakuin.ac.jp, rmurakami@pharm.kobegakuin.ac.jp

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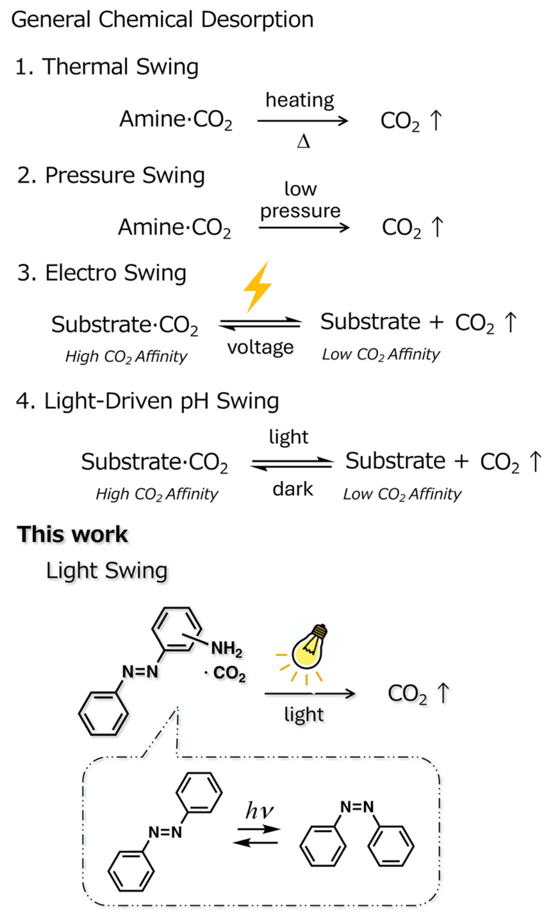
‡ These authors contributed equally to this work.

and (c) an electro-swing method[32–35] using an electrochemically activated redox compound (Scheme 1, top). In the thermal-swing method, the use of existing thermal energy sources such as industrial waste heat and geothermal heat has been actively studied. This is attractive in that it does not require generation of the energy necessary for CO_2 dissociation. However, it is limited because CO_2 must be recovered near the heat source. It also has the problem of sacrificing the efficiency of the absorption phase to improve the efficiency of CO_2 emission. The pressure-swing method requires CO_2 to be recovered under reduced pressure. However, in general, recovered CO_2 should be under pressurized conditions since it is expected to be stored and utilized. Therefore, re-pressurizing CO_2 after decompression recovery is necessary, resulting in energy consumption. The electro-swing method also requires that significant energy is supplied by renewable electricity. To satisfy these energy requirements, light is one of the most accessible energy sources in an energized environment, and sunlight is a natural source of energy. The Liu group recently reported a CO_2 release method using a light-induced pH swing approach[36] with spiropyran compounds. However, this method is limited to absorption of CO_2 with a concentration of 100%. From the perspective of green processes, it is necessary to capture low-concentration CO_2 such as that contained in air or industrial exhaust gas.



Scheme 1 Types of CO_2 release in chemical absorption.

Thus, we attempted to develop a new direct light-swing method that is applicable to low-concentration CO_2 capture. Herein, we report a photoirradiation-based CO_2 capture method involving photoisomerization of azobenzene-amine or guanidine derivatives (Scheme 1, bottom).

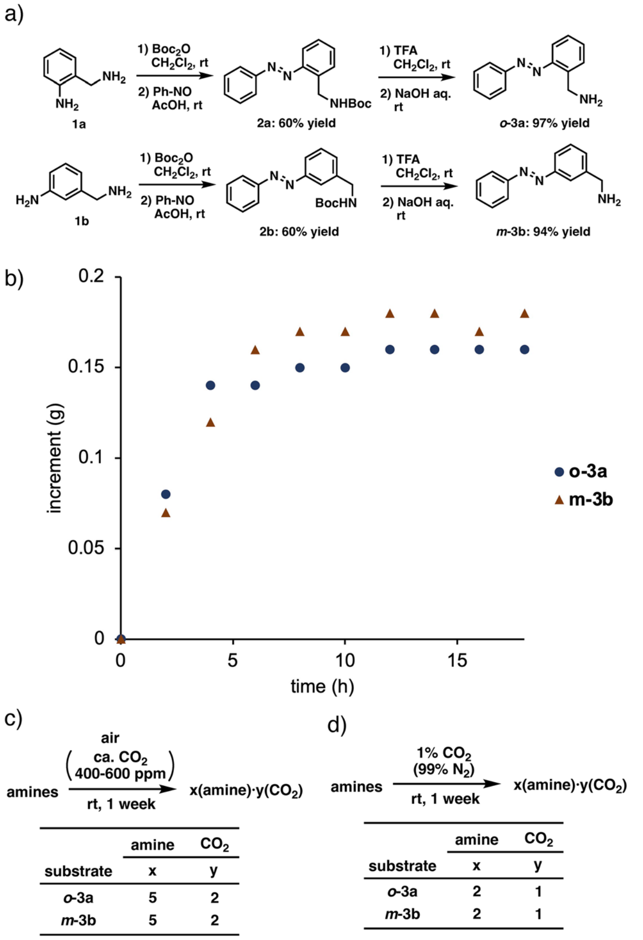
2. Results and discussion

2.1. Photoirradiation-based CO_2 release of azobenzene-amine

It is well known that photoirradiation of azobenzene[37–41] causes geometric isomerization. Several conventional azobenzene-introduced CO_2 absorbers have been reported,[42–44] but they are not adapted to visible light or CO_2 enrichment. Thus, we considered that the *trans* form of azobenzene bearing an aminomethyl group should selectively absorb CO_2, and the photoisomerized *cis*-form of aminomethyl-substituted azobenzene should release the absorbed CO_2 upon the structural change. Based on this hypothesis, azobenzene derivatives with an aminomethyl group were synthesized (Fig. 1a). Protection of the benzyl amino group in 2-aminomethylaniline with Boc_2O followed by dehydration condensation with nitrosoamine afforded *N*-protected 2-aminomethylazobenzene **2a** in 60% overall yield. Deprotection of the Boc group provided the desired 2-aminomethylazobenzene ***o*-3a** in 97% yield. 3-Aminomethylazobenzene ***m*-3b** was generated from 3-aminomethylaniline in similar yield using the same procedure.

With the required aminomethylated azobenzene derivatives in hand, we next examined their ability to absorb CO_2. For this experiment, 10 mmol of the aminomethylated azobenzene derivative (***o*-3a** or ***m*-3b**) was placed on a scale exposed to air (*ca.* 400–600 ppm CO_2) and weighed over time. The results are shown in Fig. 1b. In both cases, the mass gradually increased, reaching equilibrium after about 10 hours. To determine the composition of the mixture of substrate (***o*-3a** and ***m*-3b**) and air, elemental analyses were conducted (Fig. 1c). Samples collected after 1 week revealed that the mixture derived from ***o*-3a** contained CO_2 and ***o*-3a** at a ratio of 2 : 5. The composition ratio derived from ***m*-3b** was the same. Although general alkylamines absorbed a large amount of H_2O from aerial moisture, these amines absorbed aerial CO_2 only. Thus, the introduction of a hydrophobic azobenzene was effective for selective absorption of CO_2. As described in the Introduction, the ratio of amine to CO_2 should be 2 : 1. However, the relative amount of CO_2 was lower when using ***o*-3a** and ***m*-3b**. Because the concentration of CO_2 in the atmosphere is very low (*ca.* 0.03–0.06 vol%), the total amount of absorbed CO_2 may not reach the theoretical value.

Therefore, the same experiments were conducted in a 1 vol% CO_2 atmosphere (99 vol% N_2) with a higher CO_2 concentration (Fig. 1d). Under these conditions, the ratio of amine to CO_2 was 2 : 1, which matches the theoretical ratio.



c)

	amine	CO_2
substrate	x	y
o-3a	5	2
m-3b	5	2

d)

	amine	CO_2
substrate	x	y
o-3a	2	1
m-3b	2	1

Fig. 1 Synthesis of and CO_2 absorption by azobenzene-amines. (a) Syntheses of azobenzene-amine derivatives. (b) Increase in mass of azobenzene-amines (10 mmol, 2.11 g) in air at room temperature upon absorbing aerial CO_2. (c) Composition ratio by elemental analysis of azobenzene-amines in air. (d) Composition ratio by elemental analysis of azobenzene-amines in 1% CO_2.

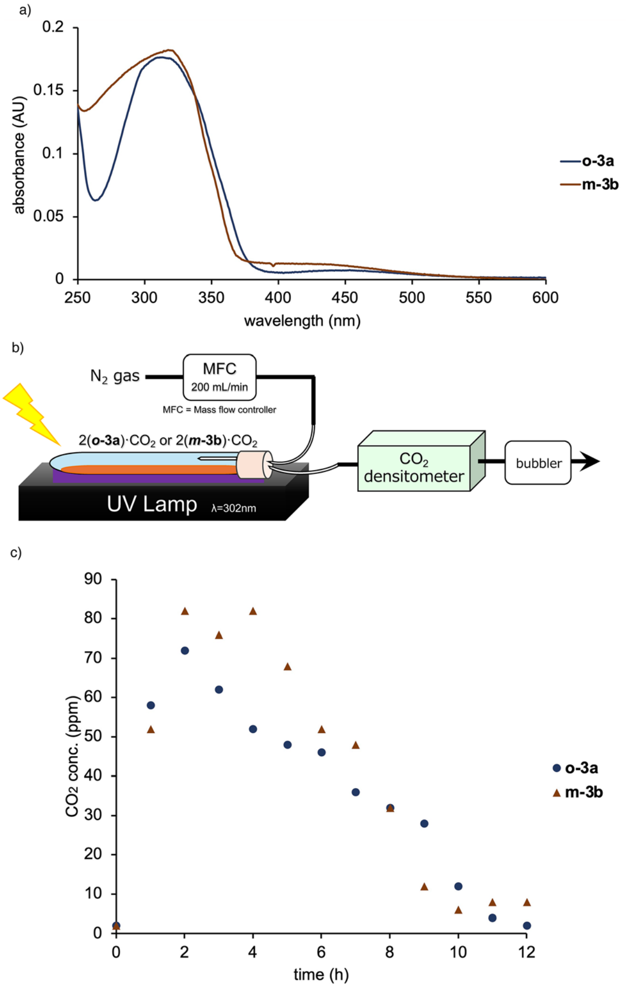


Fig. 2 CO_2 desorption from CO_2-absorbed azobenzene-amines under photoirradiation. (a) UV-vis measurements of CO_2-absorbed ***o*-3a** and ***m*-3b** (amine : CO_2 = 5 : 2). (b) Device for CO_2 release from CO_2-absorbed amines under UV irradiation (λ = 302 nm). (c) CO_2 concentration in outlet gas using device under UV irradiation.

We next focused on CO_2 release upon photoirradiation. In order to select the appropriate wavelength for the irradiating light, UV-vis measurements of CO_2-absorbed aminomethylazobenzene (amine : CO_2 = 2 : 1) were performed (Fig. 2a). For both amines (***o*-3a** and ***m*-3b**), the maximum absorption wavelength was around 300 nm (***o*-3a**: λ_{max} = 313 nm, ***m*-3b**: λ_{max} = 315 nm).

To confirm CO_2 release under light irradiation, the device in Fig. 2b was designed and used. A test tube containing CO_2-absorbed aminomethylazobenzene (***o*-3a** and ***m*-3b**; amine : CO_2 = 5 : 2; derived from 10 mmol of amine) was placed on a UV lamp (λ = 302 nm), and nitrogen gas was flowed into the UV-irradiated test tube at a constant flow rate (200 mL min^{-1}) using a mass flow controller (MFC). The CO_2 concentration in the outlet gas was measured over time using a CO_2 densitometer (Fig. 2c). As expected, CO_2 release was observed for both compounds, and the maximum release concentrations were around 70–80 ppm.

2.2. Photoirradiation-based CO_2 release from azobenzene-guanidine

While aniline, which has an amine directly bonded to the benzene ring, has lower basicity than normal alkyl amines, it has problems with CO_2 absorption. To avoid the introduction of an amine at the benzylic position, a new structure was designed with a more basic guanidino group[21] on the phenyl group. To increase the basicity of the guanidino group, guanidine **7** was selected as a candidate compound, in which a dimethylamino group was introduced opposite the phenyl group of azobenzene. Synthesis of guanidine **7** is shown in Fig. 3a. After reduction of the nitro group to an amino group to give **6** in 78% yield, the reaction of **6** with cyanamide gave the desired azobenzene-guanidine derivative **7** in 53% yield. In the initial trial, guanidine **7** did not absorb CO_2. Although the reason is unclear, solid state guanidine **7** might not be able to absorb CO_2 due to the specific surface area. After several

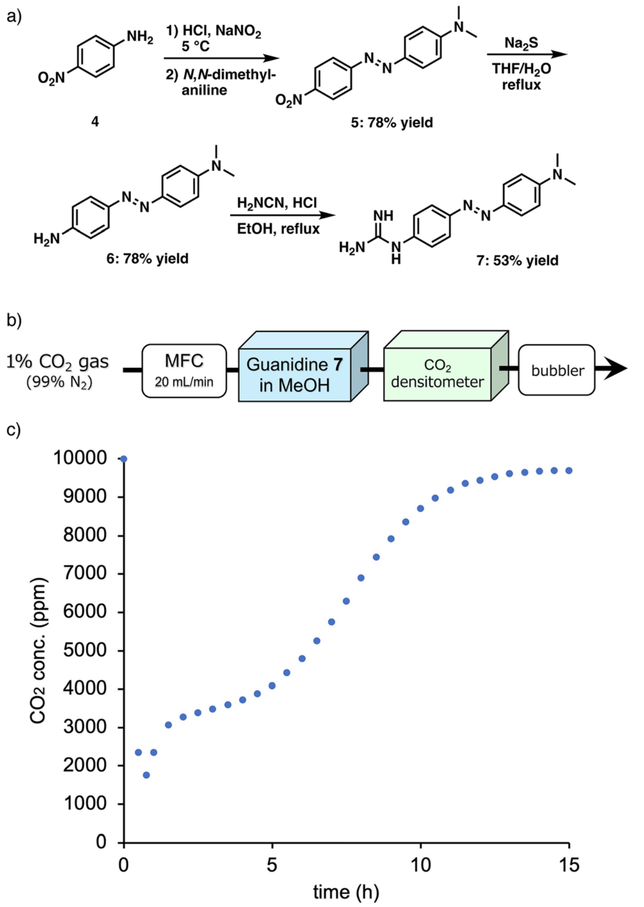


Fig. 3 Synthesis of and CO_2 absorption by azobenzene-guanidine **7**. (a) Synthesis of azobenzene-guanidine derivative **7**. (b) Device for measuring CO_2 absorption of **7** under 1% CO_2 flow. (c) CO_2 concentration in outlet gas.

screenings, we found that guanidine 7 in MeOH absorbed 1% CO_2. Thereafter, CO_2 absorption was conducted in MeOH solution. A mixed gas containing 1% CO_2 and 99% N_2 was flowed into guanidine 7 (3.0 mmol) in MeOH (100 mL) at a rate of 20 mL min^{-1} using an MFC, and the resulting CO_2 concentration on the outlet side was measured over time (Fig. 3b). The flow rate was reduced from 200 to 20 mL min^{-1} due to concerns about solvent volatilization. After 45 min, the CO_2 concentration decreased to a minimum of 1756 ppm, and then increased slowly (Fig. 3c). The amount of absorbed CO_2 was calculated to be about 2.9 mmol, and the 7 : CO_2 ratio was 1 : 1. After absorbing CO_2, CO_2-absorbed 7 was precipitated as a solid and could be filtered out from the mixture.

Next, UV measurements were performed in a EtOH solution using the filtered solid (Fig. 4a). The maximum absorption was found at a wavelength of 419 nm, which is in the visible region and is longer than that for azobenzene-amine **3**. Based on this result, a 440 nm blue LED light source was selected to investigate CO_2 emission. The device is shown in Fig. 4b. The desiccator containing CO_2-absorbed guanidine 7 was irradiated with LED light under a N_2 gas flow of 20 mL min^{-1} con-

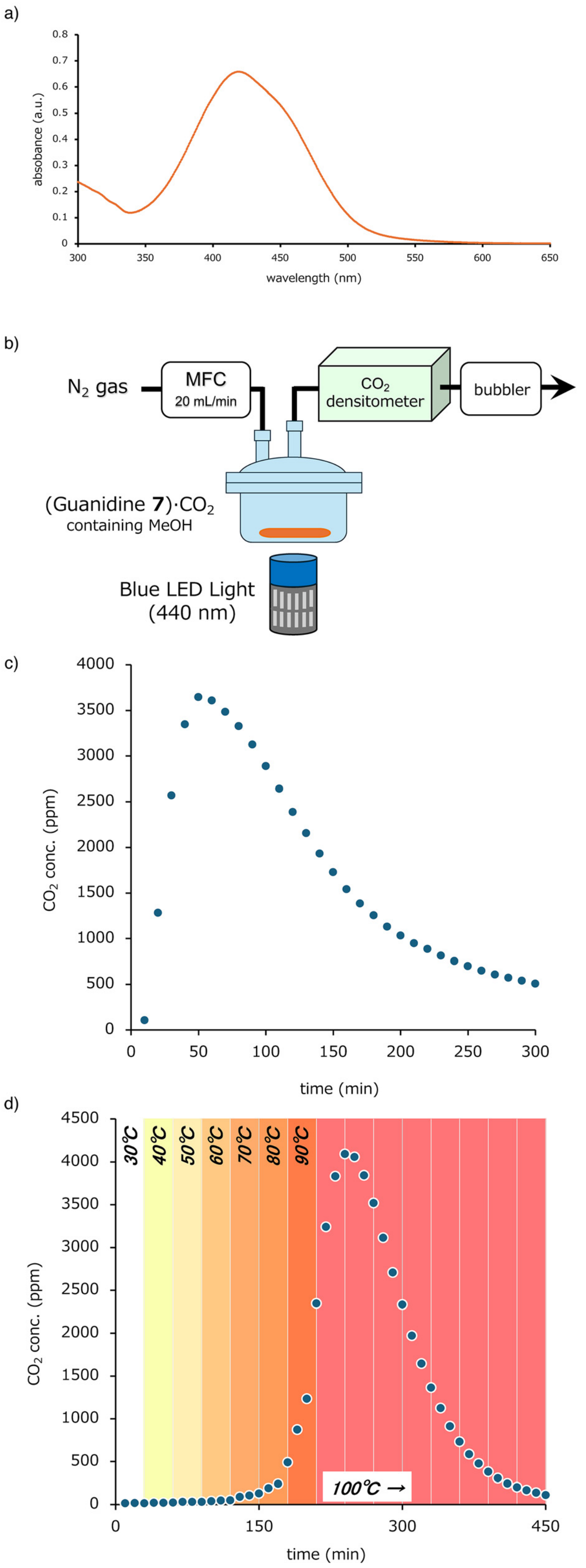
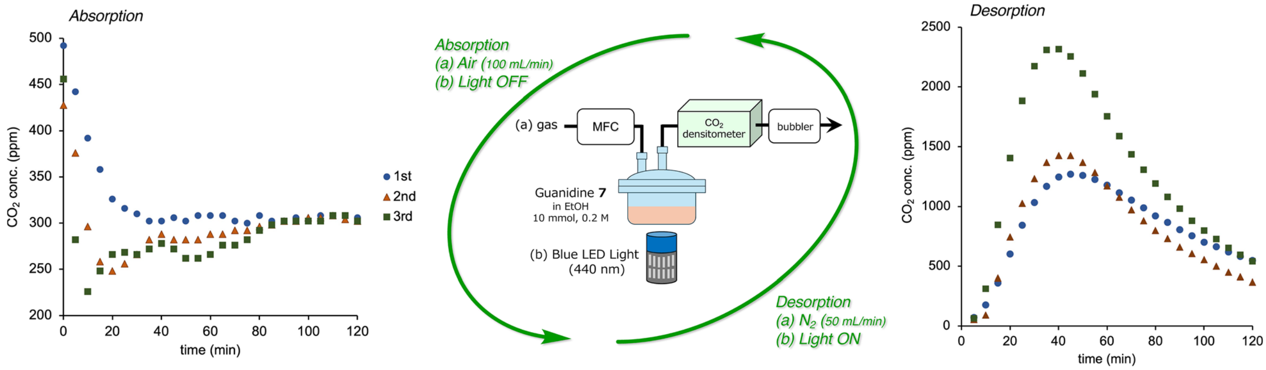


Fig. 4 CO_2 desorption from CO_2-absorbed azobenzene-guanidine **7** under photoirradiation. (a) UV-vis measurements of CO_2-absorbed **7**. (b) Device for CO_2 release from CO_2-absorbed **7** under photoirradiation (440 nm) (c) CO_2 concentration in outlet gas using device under visible light irradiation. (d) CO_2 desorption under thermal conditions without photoirradiation.



Scheme 2 Recyclable visible light-swing CO_2 capture using azobenzene-guanidine **7** in air.

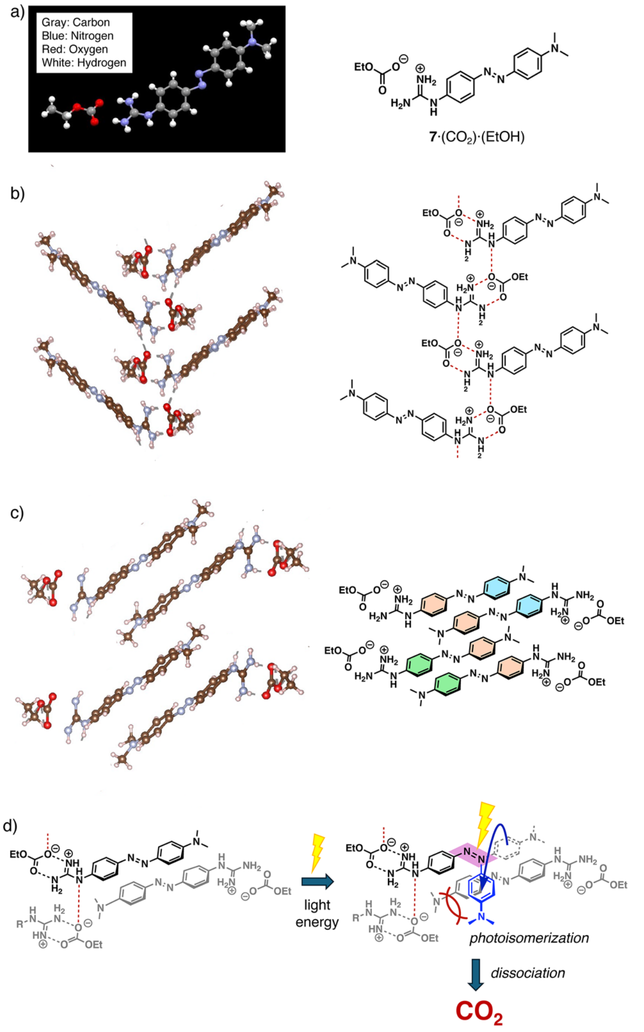


Fig. 5 X-ray crystallographic analysis of **7**·(CO_2)·(EtOH). (a) ORTEP drawing. (b) Intermolecular hydrogen bonding network. (c) Intermolecular π–π stacking interaction. (d) Plausible mechanism for CO_2 release under photoirradiation.

trolled by an MFC, and the CO_2 concentration on the outlet side was measured over time. As shown in Fig. 4c, CO_2 release occurred immediately after irradiation, and up to 3644 ppm of CO_2 was released at 50 min. In this system, heat was generated by the light source, and the temperature in the desiccator was about 40 °C. To confirm that the release of CO_2 was not simply due to the heat from the light source, CO_2 release under heating conditions using the same solid was investigated. Using the same equipment as in Fig. 4b, the desiccator was gradually heated (10 °C per 30 min) with an oil bath instead of being irradiated by light, and the CO_2 concentration in the outlet gas was measured (Fig. 4d). CO_2 was gradually released at 70 °C, and high levels of CO_2 emission were found at temperatures above 90 °C. However, no CO_2 release was observed when heating at around 40 °C. Therefore, it is clear that CO_2 release under light irradiation is caused by light energy rather than by thermal energy from the light source.

As a final challenge for light-swing CO_2 capture, DAC (lower CO_2 concentration) and recyclability were examined (Scheme 2). For the first CO_2 absorption, air was flowed (100 mL min^{-1}) into guanidine 7 (10 mmol) in EtOH (50 mL) using an MFC, and the resulting CO_2 concentration on the outlet side was measured over time. In this examination, EtOH instead of MeOH was chosen for practical recycling studies due to its lower volatility and toxicity. After 40 h, the air flow was stopped. For the first CO_2 desorption cycle, CO_2-absorbed guanidine 7 in EtOH was irradiated with LED light (440 nm) under flowing N_2 gas (50 mL min^{-1}) using an MFC, and the CO_2 concentration on the outlet side was measured over time. Subsequently, CO_2 absorption/release operations were performed in the same manner, and each CO_2 concentration was measured three times in total. No significant change in atmospheric CO_2 absorption performance was found for the recycled (2^{nd} and 3^{rd} cycle) guanidine 7. In addition, under irradiation by visible light, CO_2 was released during all three cycles, with the highest release concentration recorded in the 3^{rd} cycle. Although the reason is unclear, some EtOH volatilization may have increased the efficiency of CO_2 release.

To elucidate the mechanism for CO_2 release under photoirradiation, a structural analysis of CO_2-absorbed azobenzene-guanidine 7 in EtOH was performed. A single crystal was obtained from an EtOH solution of 7 at room temperature in air. An X-ray crystal structure analysis of this crystal revealed that the product was 7·(CO_2)·(EtOH) (Fig. 5a), which is consistent with the elemental analysis results for the solids observed in Fig. 3. Neutralization between guanidine **7** and ethyl hydrogen carbonate (EtOC(=O)OH) derived from CO_2 and EtOH formed ionic guanidine **7**·(CO_2)·(EtOH) composed of ethyl carbonate (EtOC(=O)O^-) and guanidinium (R-NHC(=NH_2^+)NH_2). Next, we focused on intermolecular interactions. As shown in Fig. 5b, a hydrogen bonding network involving R-$\underline{\mathrm{N}}\underline{\mathrm{H}}$C(=$NH_2^+$)$NH_2$ and EtOC(=O)$\underline{\mathrm{O}}^-$ in adjacent molecules was identified. Also, p–p interactions between benzene moieties in the overlapped azobenzenes were observed (Fig. 5c). Based on these results, a plausible mechanism for CO_2 release under photoirradiation is proposed as shown in Fig. 5d. Under photoirradiation, *trans*-azobenzene is converted to *cis*-azobenzene. The formation of *cis*-azobenzene causes steric repulsion with other molecules, disrupting the intermolecular interactions. As a result of the dissociation of *cis*-azobenzene from the aggregated molecules, CO_2 is released along with the production of EtOH.

3. Conclusion

In summary, a light-swing CO_2 capture method based on photoisomerization reactions of azobenzene derivatives has been developed. In the case of azobenzene-amine **3**, it was possible to absorb CO_2 not only at 1% concentration but also at atmospheric concentration (about 400 ppm). In addition, CO_2 in air was selectively captured without moisture contamination. CO_2-absorbed **3** was found to release CO_2 under UV irradiation. Although problems remain in terms of reusability, **3** showed that light energy has the potential to become a driving force for CO_2 release. Based on these results, azobenzene-guanidine **7** was newly designed to overcome the issue of recyclability. In EtOH solution, **7** selectively absorbed CO_2 in air to form **7**·(CO_2)·(EtOH) without moisture content. Desorption of CO_2 from **7**·(CO_2)·(EtOH) occurred upon irradiation with visible light (440 nm). The results of CO_2 release experiments under heating conditions indicated that light energy, and not thermal energy, caused the release of CO_2. A plausible mechanism for CO_2 release under photoirradiation was proposed. From the results of an X-ray crystal structure analysis of **7**·(CO_2)·(EtOH), it was considered that the key to CO_2 release upon light irradiation was dissociation of aggregated **7**·(CO_2)·(EtOH) based on steric repulsion accompanying photoisomerization of the azobenzene moiety. Thus, we have developed a method for aerial CO_2 capture using light energy. It is expected that by combining light at different wavelengths, various photokinetic molecules can be used to produce the driving force for light-swing CO_2 capture. In this study, light-swing CO_2 capture with the guanidine derivative required a large amount of solvent due to the solubility, and further improvement is necessary from a practical standpoint. However, we believe that the issue would be improved by introducing a functional group, which increases the solubility, into the substrate. In addition, this research suggests that the light-swing CO_2 capture using other photoresponsive molecules would be possible under various wavelength ranges. Further study on CO_2 capture based on longer wavelengths light is ongoing.

Author contributions

R. M. and F. I. designed the study, the main concept ideas, and the proof outline. K. S. and A. U. performed the experiments and analysed the data. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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