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Light-swing CO₂ capture: photoirradiation-based chemical CO₂ release based on photoisomerization of azobenzene-amine/guanidine derivatives†

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The world is committed to reducing CO₂ emissions, and research on CO₂ 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 CO₂ capture technologies for decarbonization is their cost due to the high separation energy required to release CO₂. 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 CO₂ capture based on photoisomerization of azobenzene-amine and guanidine derivatives. The visible light-swing CO₂ absorption and release system using azobenzene-guanidine has shown potential in DAC systems owing to its reusability. A plausible mechanism for CO₂ release under light irradiation involves photoisomerization from *trans*- to *cis*-azobenzene in which steric repulsion with other molecules is the driving force, and CO₂ 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 CO₂ capture.

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1. Introduction

CO₂ capture,^{1–6} a technology that captures CO₂ 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, CO₂ and an absorbent are combined through a chemical reaction. There are several types of CO₂ capture methods, including carbon capture and storage (CCS),^{7,8} which captures CO₂ from the exhaust gases from thermal power plants, direct air capture (DAC),^{9–22} which captures atmospheric CO₂, and bioenergy with carbon capture and storage (BECCS),^{23,24} which captures CO₂ produced in biomass power generation. In all of these methods, low-concentration CO₂ [exhaust gas: *ca.* 1–15 vol%, air: *ca.* 400 ppm] is recovered with absorbent/adsorbent (amines, *etc.*), and then CO₂ is released and concentrated by heating or decompression.

In the chemical absorption method using amines,²⁵ the reaction proceeds exothermally through a neutralization reac-

tion between the base, amine, and the acid (CO₂). On the other hand, when CO₂ is released, the reaction becomes endothermic, requiring energy from the outside to release/concentrate CO₂. This enormous separation energy is a major issue for general CO₂ 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 CO₂ absorbents, absorbed CO₂ and moisture in air to form 1(CO₂)-3(MEA)-3(H₂O). Theoretically, two molecules of amine should react with one molecule of CO₂, providing 1(CO₂)-2(amine) [*e.g.*, 2 × R-NH₂ + CO₂ → R-NH-COO⁻-H₃N-R]. Thus, the CO₂ 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 CO₂ release/concentration is required. It was thought that the presence of water was unavoidable because amines are hydrophilic groups and CO₂ 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 CO₂ in air without moisture. This technology eliminates the necessity for extra energy related to water content when releasing CO₂.

The ultimate challenge in CO₂ capture by chemical absorption is how to avoid wasting energy during the dissociation of amines and CO₂. As far as we know, there are currently three methods of dissociating CO₂: (a) a thermal-swing method by heating,²⁹ (b) a pressure-swing method^{30,31} by depressurization

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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 CO₂ dissociation. However, it is limited because CO₂ 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 CO₂ emission. The pressure-swing method requires CO₂ to be recovered under reduced pressure. However, in general, recovered CO₂ should be under pressurized conditions since it is expected to be stored and utilized. Therefore, re-pressurizing CO₂ 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 CO₂ release method using a light-induced pH swing approach³⁶ with spiropyran compounds. However, this method is limited to absorption of CO₂ with a concentration of 100%. From the perspective of green processes, it is neces-

ary to capture low-concentration CO₂ such as that contained in air or industrial exhaust gas.

Thus, we attempted to develop a new direct light-swing method that is applicable to low-concentration CO₂ capture. Herein, we report a photoirradiation-based CO₂ capture method involving photoisomerization of azobenzene-amine or guanidine derivatives (Scheme 1, bottom).

2. Results and discussion

2.1. Photoirradiation-based CO₂ release of azobenzene-amine

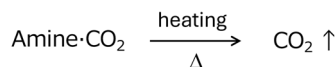
It is well known that photoirradiation of azobenzene^{37–41} causes geometric isomerization. Several conventional azobenzene-introduced CO₂ absorbers have been reported,^{42–44} but they are not adapted to visible light or CO₂ enrichment. Thus, we considered that the *trans* form of azobenzene bearing an aminomethyl group should selectively absorb CO₂, and the photoisomerized *cis*-form of aminomethyl-substituted azobenzene should release the absorbed CO₂ 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 Boc₂O 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 CO₂. 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 CO₂) 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 CO₂ 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 H₂O from aerial moisture, these amines absorbed aerial CO₂ only. Thus, the introduction of a hydrophobic azobenzene was effective for selective absorption of CO₂. As described in the Introduction, the ratio of amine to CO₂ should be 2 : 1. However, the relative amount of CO₂ was lower when using **o-3a** and **m-3b**. Because the concentration of CO₂ in the atmosphere is very low (ca. 0.03–0.06 vol%), the total amount of absorbed CO₂ may not reach the theoretical value.

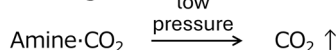
Therefore, the same experiments were conducted in a 1 vol% CO₂ atmosphere (99 vol% N₂) with a higher CO₂ concentration (Fig. 1d). Under these conditions, the ratio of amine to CO₂ was 2 : 1, which matches the theoretical ratio.

General Chemical Desorption

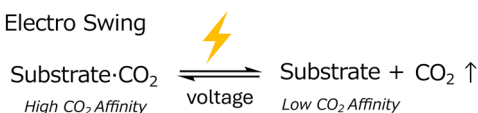
1. Thermal Swing



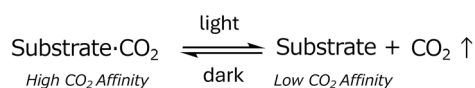
2. Pressure Swing



3. Electro Swing

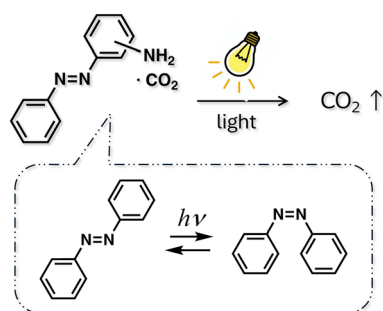


4. Light-Driven pH Swing



This work

Light Swing



Scheme 1 Types of CO₂ release in chemical absorption.



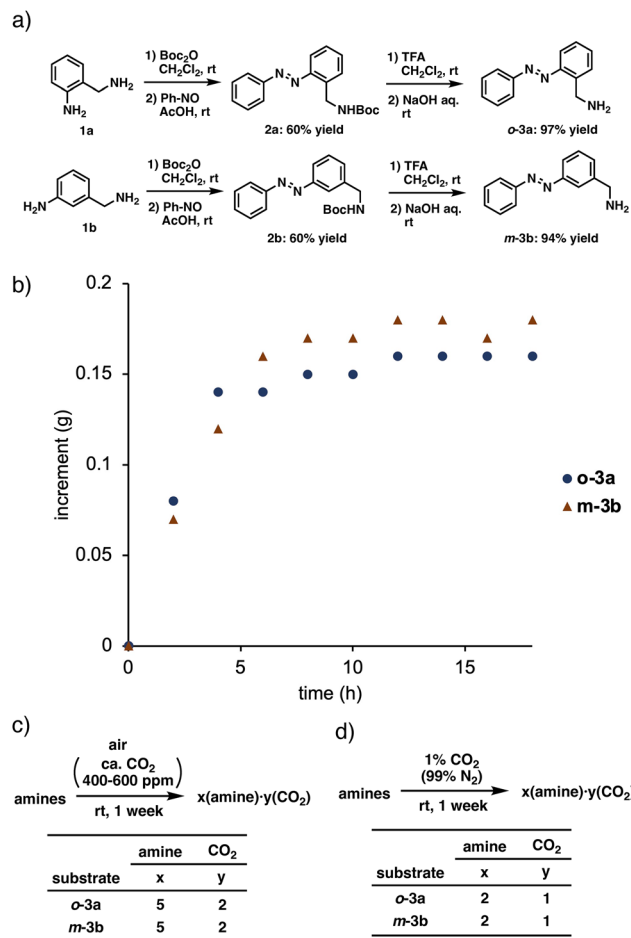


Fig. 1 Synthesis of and CO₂ absorption by azobenzene-amines. (a) Syntheses of azobenzene-amine derivatives. (b) Increase in mass of azobenzene-amines (10 mmol, 2.11 g) in air at room temperature upon absorbing aerial CO₂. (c) Composition ratio by elemental analysis of azobenzene-amines in air. (d) Composition ratio by elemental analysis of azobenzene-amines in 1% CO₂.

We next focused on CO₂ release upon photoirradiation. In order to select the appropriate wavelength for the irradiating light, UV-vis measurements of CO₂-absorbed aminomethylazobenzene (amine : CO₂ = 2 : 1) were performed (Fig. 2a). For both amines (*o*-3a and *m*-3b), the maximum absorption wavelength was around 300 nm (*o*-3a: $\lambda_{\text{max}} = 313$ nm, *m*-3b: $\lambda_{\text{max}} = 315$ nm).

To confirm CO₂ release under light irradiation, the device in Fig. 2b was designed and used. A test tube containing CO₂-absorbed aminomethylazobenzene (*o*-3a and *m*-3b; amine : CO₂ = 5 : 2; derived from 10 mmol of amine) was placed on a UV lamp ($\lambda = 302$ 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 CO₂ concentration in the outlet gas was measured over time using a CO₂ densitometer (Fig. 2c). As expected, CO₂ release was observed for both compounds, and the maximum release concentrations were around 70–80 ppm.

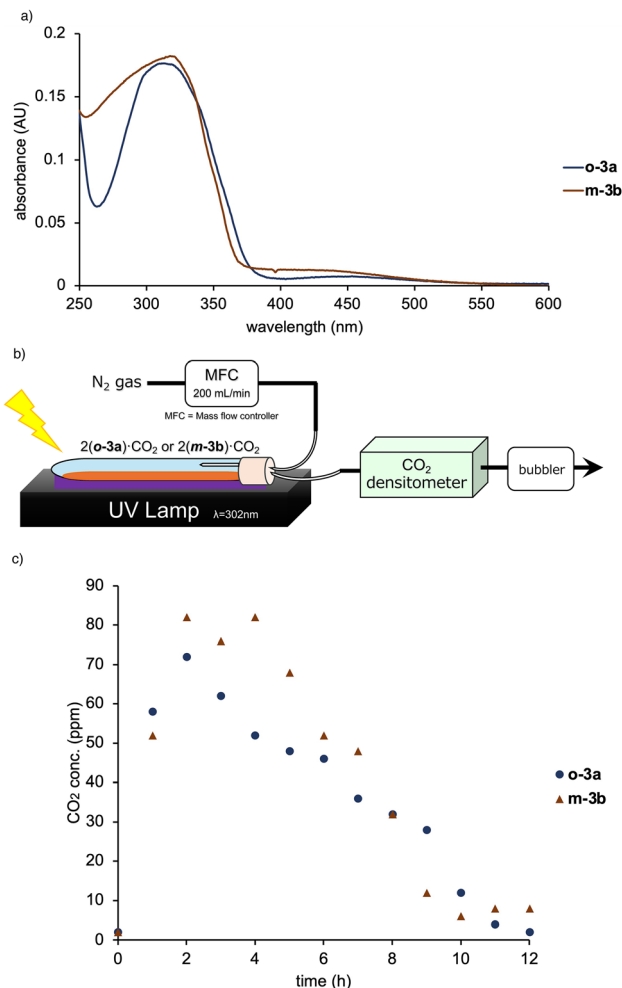


Fig. 2 CO₂ desorption from CO₂-absorbed azobenzene-amines under photoirradiation. (a) UV-vis measurements of CO₂-absorbed *o*-3a and *m*-3b (amine : CO₂ = 5 : 2). (b) Device for CO₂ release from CO₂-absorbed amines under UV irradiation ($\lambda = 302$ nm). (c) CO₂ concentration in outlet gas using device under UV irradiation.

2.2. Photoirradiation-based CO₂ 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 CO₂ absorption. To avoid the introduction of an amine at the benzylic position, a new structure was designed with a more basic guanidino group²¹ on the phenyl group of azobenzene. 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 CO₂. Although the reason is unclear, solid state guanidine 7 might not be able to absorb CO₂ due to the specific surface area. After several



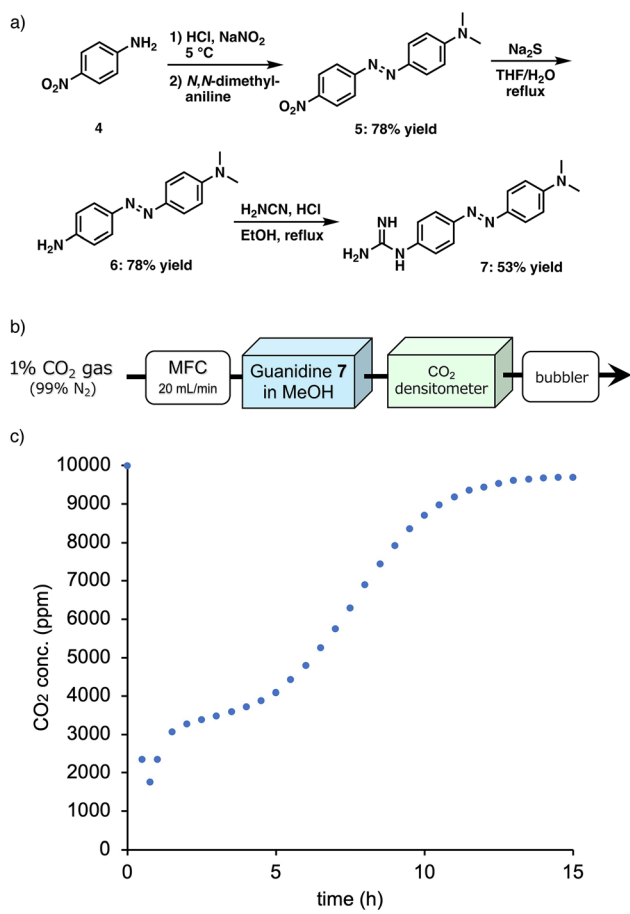


Fig. 3 Synthesis of and CO₂ absorption by azobenzene-guanidine 7. (a) Synthesis of azobenzene-guanidine derivative 7. (b) Device for measuring CO₂ absorption of 7 under 1% CO₂ flow. (c) CO₂ concentration in outlet gas.

screenings, we found that guanidine 7 in MeOH absorbed 1% CO₂. Thereafter, CO₂ absorption was conducted in MeOH solution. A mixed gas containing 1% CO₂ and 99% N₂ 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 CO₂ 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 CO₂ concentration decreased to a minimum of 1756 ppm, and then increased slowly (Fig. 3c). The amount of absorbed CO₂ was calculated to be about 2.9 mmol, and the 7 : CO₂ ratio was 1 : 1. After absorbing CO₂, CO₂-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 CO₂ emission. The device is shown in Fig. 4b. The desiccator containing CO₂-absorbed guanidine 7 was irradiated with LED light under a N₂ gas flow of 20 mL min⁻¹ con-

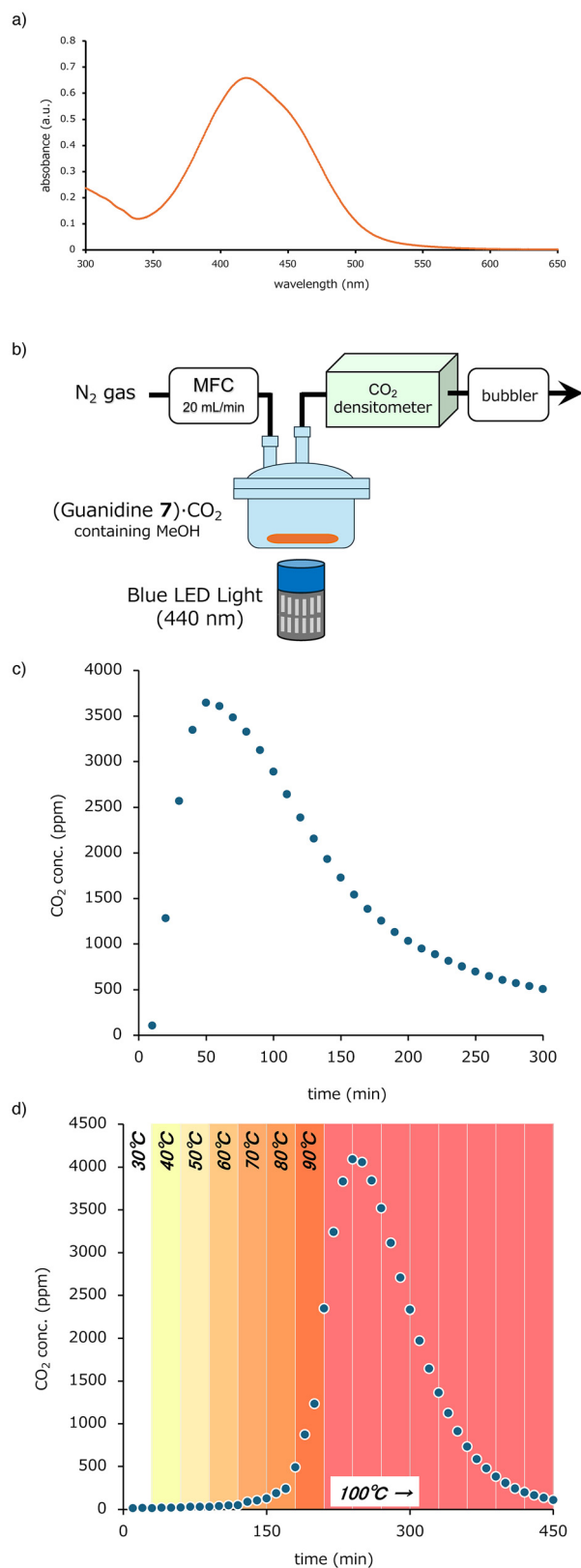
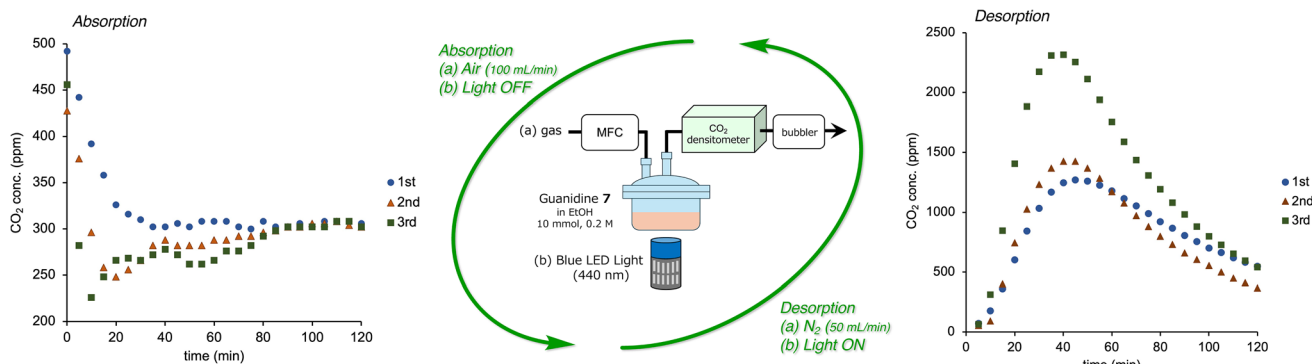


Fig. 4 CO₂ desorption from CO₂-absorbed azobenzene-guanidine 7 under photoirradiation. (a) UV-vis measurements of CO₂-absorbed 7. (b) Device for CO₂ release from CO₂-absorbed 7 under photoirradiation (440 nm) (c) CO₂ concentration in outlet gas using device under visible light irradiation. (d) CO₂ desorption under thermal conditions without photoirradiation.





Scheme 2 Recyclable visible light-swing CO₂ capture using azobenzene-guanidine 7 in air.

trolled by an MFC, and the CO₂ concentration on the outlet side was measured over time. As shown in Fig. 4c, CO₂ release occurred immediately after irradiation, and up to 3644 ppm of CO₂ 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 CO₂ was not simply due to the heat from the light source, CO₂ 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 CO₂ concentration in the outlet gas was measured (Fig. 4d). CO₂ was gradually released at 70 °C, and high levels of CO₂ emission were found at temperatures above 90 °C. However, no CO₂ release was observed when heating at around 40 °C. Therefore, it is clear that CO₂ 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 CO₂ capture, DAC (lower CO₂ concentration) and recyclability were examined (Scheme 2). For the first CO₂ absorption, air was flowed (100 mL min⁻¹) into guanidine 7 (10 mmol) in EtOH (50 mL) using an MFC, and the resulting CO₂ 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 CO₂ desorption cycle, CO₂-absorbed guanidine 7 in EtOH was irradiated with LED light (440 nm) under flowing N₂ gas (50 mL min⁻¹) using an MFC, and the CO₂ concentration on the outlet side was measured over time. Subsequently, CO₂ absorption/release operations were performed in the same manner, and each CO₂ concentration was measured three times in total. No significant change in atmospheric CO₂ absorption performance was found for the recycled (2nd and 3rd cycle) guanidine 7. In addition, under irradiation by visible light, CO₂ was released during all three cycles, with the highest release concentration recorded in the 3rd cycle. Although the reason is unclear, some EtOH volatilization may have increased the efficiency of CO₂ release.

To elucidate the mechanism for CO₂ release under photoirradiation, a structural analysis of CO₂-absorbed azobenzene-guanidine 7 in EtOH was performed. A single crystal

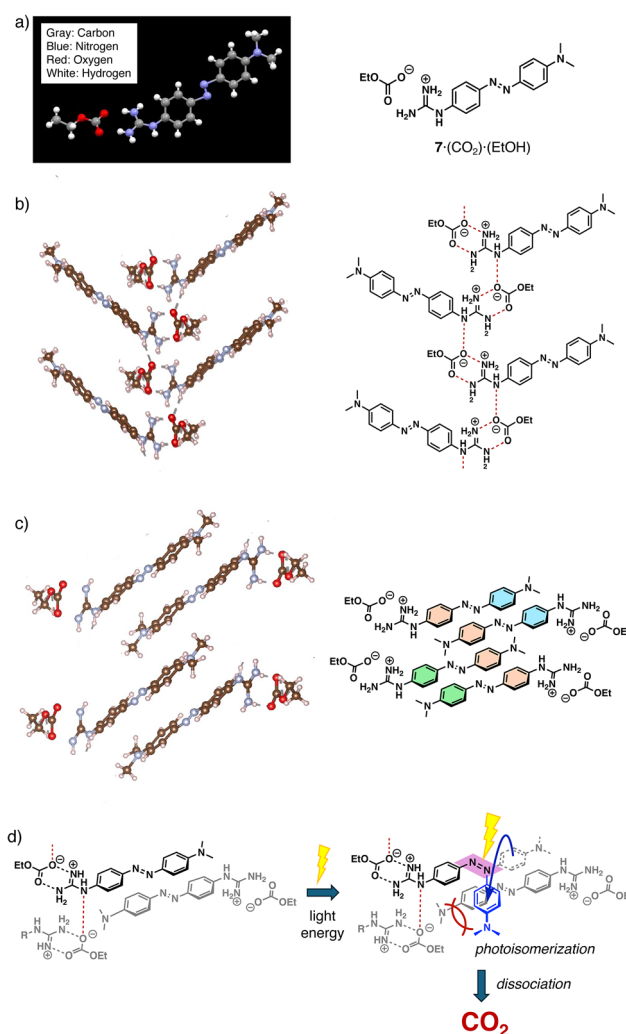


Fig. 5 X-ray crystallographic analysis of 7·(CO₂)·(EtOH). (a) ORTEP drawing. (b) Intermolecular hydrogen bonding network. (c) Intermolecular π - π stacking interaction. (d) Plausible mechanism for CO₂ release under photoirradiation.

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·(CO₂)·(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 CO₂ and EtOH formed ionic guanidine 7·(CO₂)·(EtOH) composed of ethyl carbonate (EtOC(=O)O⁻) and guanidinium (R-NHC(=NH₂⁺)NH₂). Next, we focused on intermolecular interactions. As shown in Fig. 5b, a hydrogen bonding network involving R-NHC(=NH₂⁺)NH₂ and EtOC(=O)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 CO₂ 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, CO₂ is released along with the production of EtOH.

3. Conclusion

In summary, a light-swing CO₂ capture method based on photoisomerization reactions of azobenzene derivatives has been developed. In the case of azobenzene-amine **3**, it was possible to absorb CO₂ not only at 1% concentration but also at atmospheric concentration (about 400 ppm). In addition, CO₂ in air was selectively captured without moisture contamination. CO₂-absorbed **3** was found to release CO₂ under UV irradiation. Although problems remain in terms of reusability, **3** showed that light energy has the potential to become a driving force for CO₂ release. Based on these results, azobenzene-guanidine **7** was newly designed to overcome the issue of recyclability. In EtOH solution, **7** selectively absorbed CO₂ in air to form 7·(CO₂)·(EtOH) without moisture content. Desorption of CO₂ from 7·(CO₂)·(EtOH) occurred upon irradiation with visible light (440 nm). The results of CO₂ release experiments under heating conditions indicated that light energy, and not thermal energy, caused the release of CO₂. A plausible mechanism for CO₂ release under photoirradiation was proposed. From the results of an X-ray crystal structure analysis of 7·(CO₂)·(EtOH), it was considered that the key to CO₂ release upon light irradiation was dissociation of aggregated 7·(CO₂)·(EtOH) based on steric repulsion accompanying photoisomerization of the azobenzene moiety. Thus, we have developed a method for aerial CO₂ 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 CO₂ capture. In this study, light-swing CO₂ 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 CO₂ capture using other photoresponsive molecules

would be possible under various wavelength ranges. Further study on CO₂ 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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