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# Light-swing CO<sub>2</sub> capture: photoirradiation-based chemical CO<sub>2</sub> release based on photoisomerization of azobenzene-amine/guanidine derivatives†

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The world is committed to reducing CO<sub>2</sub> emissions, and research on CO<sub>2</sub> 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<sub>2</sub> capture technologies for decarbonization is their cost due to the high separation energy required to release CO<sub>2</sub>. 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<sub>2</sub> capture based on photoisomerization of azobenzene-amine and guanidine derivatives. The visible light-swing CO<sub>2</sub> absorption and release system using azobenzene-guanidine has shown potential in DAC systems owing to its reusability. A plausible mechanism for CO<sub>2</sub> release under light irradiation involves photoisomerization from *trans*- to *cis*-azobenzene in which steric repulsion with other molecules is the driving force, and CO<sub>2</sub> 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<sub>2</sub> capture.

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## 1. Introduction

CO<sub>2</sub> capture,<sup>1–6</sup> a technology that captures CO<sub>2</sub> 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<sub>2</sub> and an absorbent are combined through a chemical reaction. There are several types of CO<sub>2</sub> capture methods, including carbon capture and storage (CCS),<sup>7,8</sup> which captures CO<sub>2</sub> from the exhaust gases from thermal power plants, direct air capture (DAC),<sup>9–22</sup> which captures atmospheric CO<sub>2</sub>, and bioenergy with carbon capture and storage (BECCS),<sup>23,24</sup> which captures CO<sub>2</sub> produced in biomass power generation. In all of these methods, low-concentration CO<sub>2</sub> [exhaust gas: *ca.* 1–15 vol%, air: *ca.* 400 ppm] is recovered with absorbent/adsorbent (amines, *etc.*), and then CO<sub>2</sub> is released and concentrated by heating or decompression.

In the chemical absorption method using amines,<sup>25</sup> the reaction proceeds exothermically through a neutralization reac-

tion between the base, amine, and the acid (CO<sub>2</sub>). On the other hand, when CO<sub>2</sub> is released, the reaction becomes endothermic, requiring energy from the outside to release/concentrate CO<sub>2</sub>. This enormous separation energy is a major issue for general CO<sub>2</sub> capture technologies. One of the reasons for this large separation energy is the water content. For example, we found that monoethanolamine (MEA),<sup>14</sup> which is a benchmark for CO<sub>2</sub> absorbents, absorbed CO<sub>2</sub> and moisture in air to form 1(CO<sub>2</sub>)-3(MEA)-3(H<sub>2</sub>O). Theoretically, two molecules of amine should react with one molecule of CO<sub>2</sub>, providing 1(CO<sub>2</sub>)-2(amine) [*e.g.*, 2 × R-NH<sub>2</sub> + CO<sub>2</sub> → R-NH-COO<sup>-</sup>-H<sub>3</sub>N-R]. Thus, the CO<sub>2</sub> 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<sub>2</sub> release/concentration is required. It was thought that the presence of water was unavoidable because amines are hydrophilic groups and CO<sub>2</sub> is soluble in water, as exemplified by carbonated water. However, we<sup>26–28</sup> recently found that aralkyl amines with hydrophobic phenyl groups near the amine can selectively absorb CO<sub>2</sub> in air without moisture. This technology eliminates the necessity for extra energy related to water content when releasing CO<sub>2</sub>.

The ultimate challenge in CO<sub>2</sub> capture by chemical absorption is how to avoid wasting energy during the dissociation of amines and CO<sub>2</sub>. As far as we know, there are currently three methods of dissociating CO<sub>2</sub>: (a) a thermal-swing method by heating,<sup>29</sup> (b) a pressure-swing method<sup>30,31</sup> by depressurization

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and (c) an electro-swing method<sup>32–35</sup> 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<sub>2</sub> dissociation. However, it is limited because CO<sub>2</sub> 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<sub>2</sub> emission. The pressure-swing method requires CO<sub>2</sub> to be recovered under reduced pressure. However, in general, recovered CO<sub>2</sub> should be under pressurized conditions since it is expected to be stored and utilized. Therefore, re-pressurizing CO<sub>2</sub> 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<sub>2</sub> release method using a light-induced pH swing approach<sup>36</sup> with spiropyran compounds. However, this method is limited to absorption of CO<sub>2</sub> with a concentration of 100%. From the perspective of green processes, it is necessary

to capture low-concentration CO<sub>2</sub> 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 CO<sub>2</sub> capture. Herein, we report a photoirradiation-based CO<sub>2</sub> capture method involving photoisomerization of azobenzene-amine or guanidine derivatives (Scheme 1, bottom).

## 2. Results and discussion

### 2.1. Photoirradiation-based CO<sub>2</sub> release of azobenzene-amine

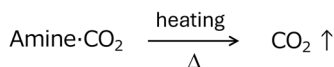
It is well known that photoirradiation of azobenzene<sup>37–41</sup> causes geometric isomerization. Several conventional azobenzene-introduced CO<sub>2</sub> absorbers have been reported,<sup>42–44</sup> but they are not adapted to visible light or CO<sub>2</sub> enrichment. Thus, we considered that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

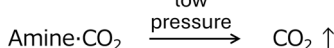
Therefore, the same experiments were conducted in a 1 vol% CO<sub>2</sub> atmosphere (99 vol% N<sub>2</sub>) with a higher CO<sub>2</sub> concentration (Fig. 1d). Under these conditions, the ratio of amine to CO<sub>2</sub> was 2 : 1, which matches the theoretical ratio.

#### General Chemical Desorption

##### 1. Thermal Swing



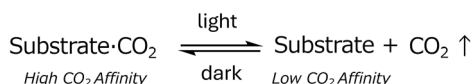
##### 2. Pressure Swing



##### 3. Electro Swing

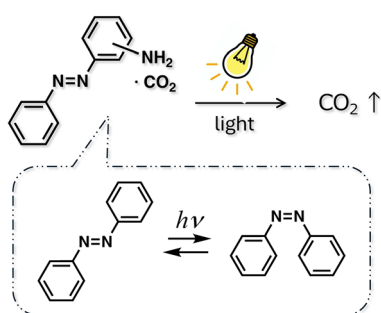


##### 4. Light-Driven pH Swing



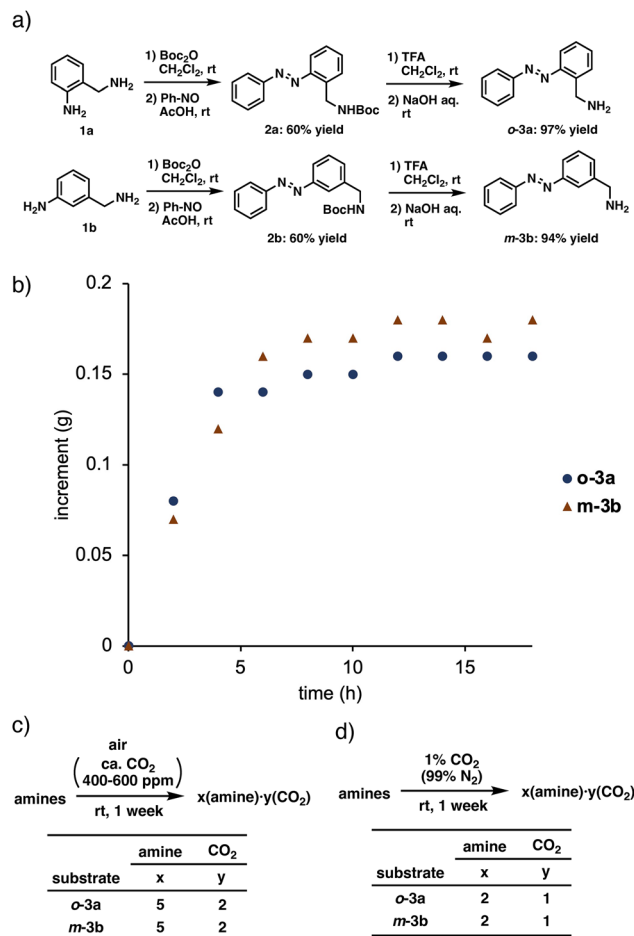
#### This work

##### Light Swing

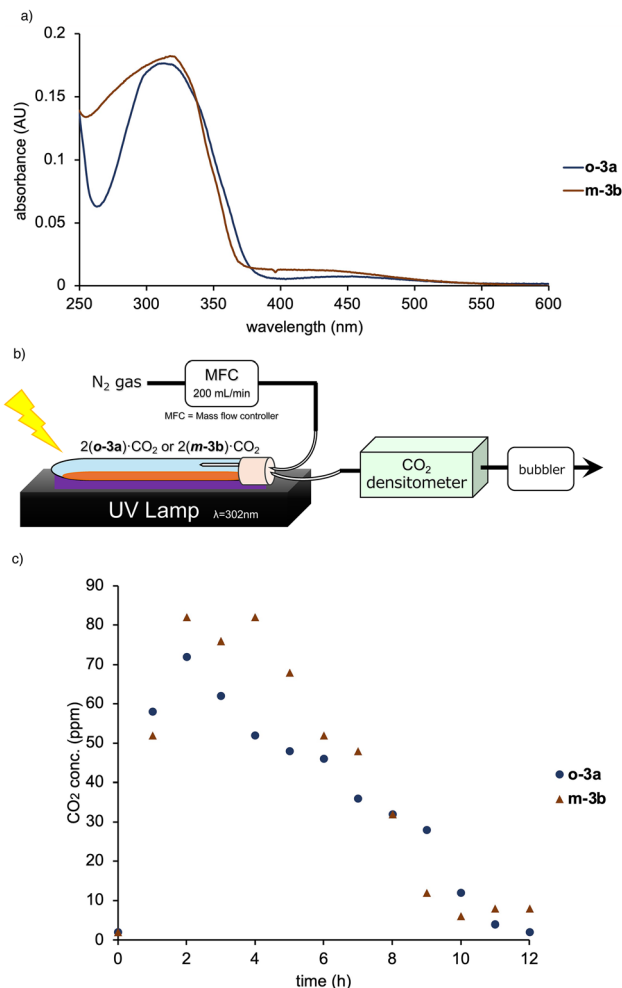


**Scheme 1** Types of CO<sub>2</sub> release in chemical absorption.





**Fig. 1** Synthesis of and CO<sub>2</sub> 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<sub>2</sub>. (c) Composition ratio by elemental analysis of azobenzene-amines in air. (d) Composition ratio by elemental analysis of azobenzene-amines in 1% CO<sub>2</sub>.



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

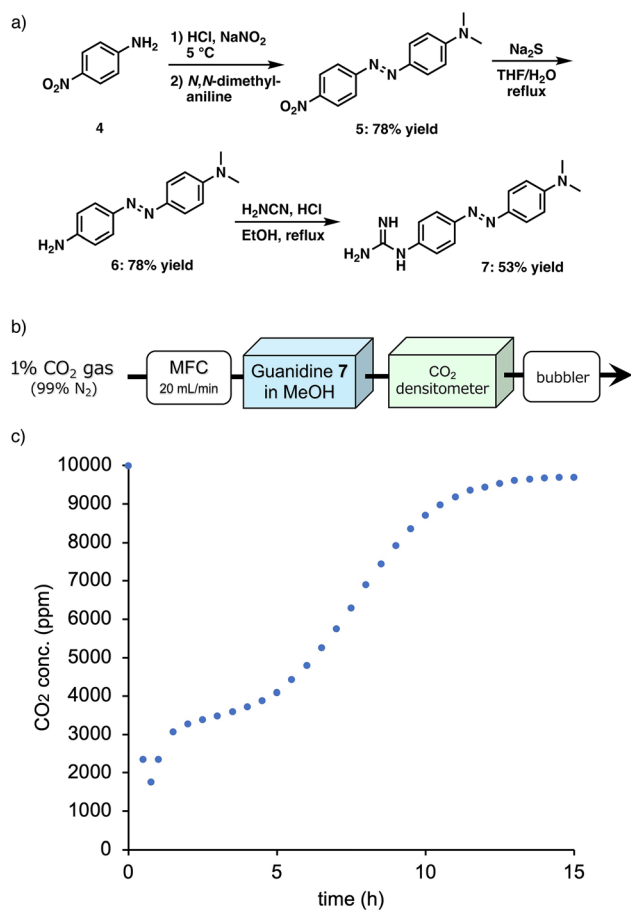
We next focused on CO<sub>2</sub> release upon photoirradiation. In order to select the appropriate wavelength for the irradiating light, UV-vis measurements of CO<sub>2</sub>-absorbed aminomethylazobenzene (amine:CO<sub>2</sub> = 2:1) were performed (Fig. 2a). For both amines (**o-3a** and **m-3b**),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

To confirm CO<sub>2</sub> release under light irradiation, the device in Fig. 2b was designed and used. A test tube containing CO<sub>2</sub>-absorbed aminomethylazobenzene (**o-3a** and **m-3b**; amine:CO<sub>2</sub> = 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<sup>-1</sup>) using a mass flow controller (MFC). The CO<sub>2</sub> concentration in the outlet gas was measured over time using a CO<sub>2</sub> densitometer (Fig. 2c). As expected, CO<sub>2</sub> release was observed for both compounds, and the maximum release concentrations were around 70–80 ppm.

## 2.2. Photoirradiation-based CO<sub>2</sub> 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<sub>2</sub> absorption. To avoid the introduction of an amine at the benzylic position, a new structure was designed with a more basic guanidino group<sup>21</sup> on 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<sub>2</sub>. Although the reason is unclear, solid state guanidine **7** might not be able to absorb CO<sub>2</sub> due to the specific surface area. After several

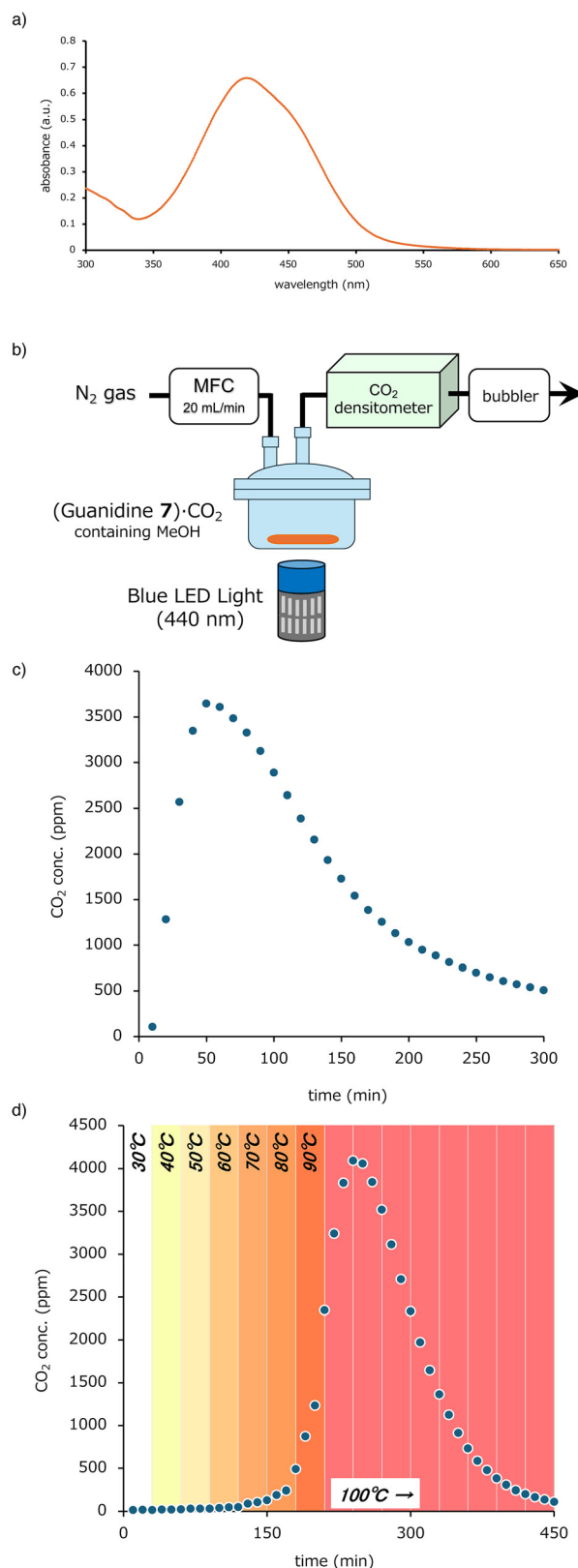




**Fig. 3** Synthesis of and  $\text{CO}_2$  absorption by azobenzene-guanidine **7**. (a) Synthesis of azobenzene-guanidine derivative **7**. (b) Device for measuring  $\text{CO}_2$  absorption of **7** under 1%  $\text{CO}_2$  flow. (c)  $\text{CO}_2$  concentration in outlet gas.

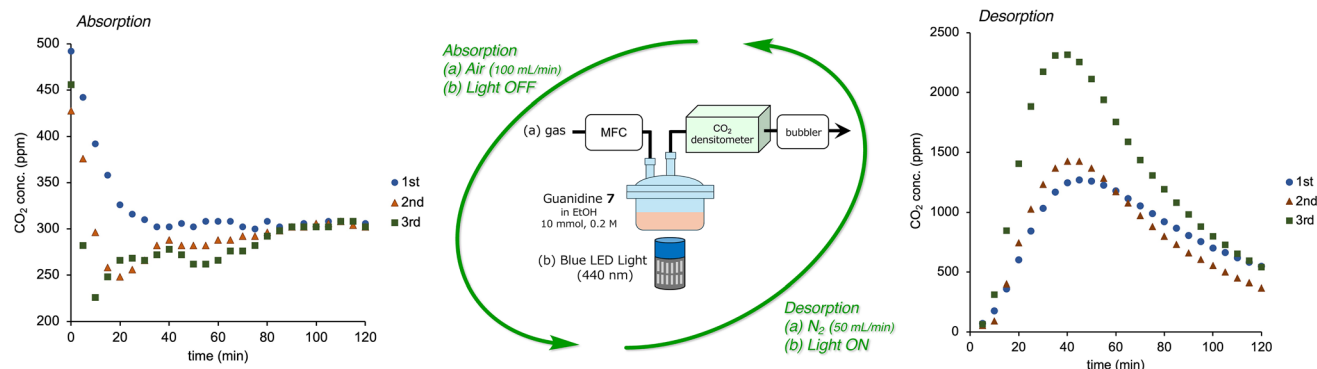
screenings, we found that guanidine **7** in MeOH absorbed 1%  $\text{CO}_2$ . Thereafter,  $\text{CO}_2$  absorption was conducted in MeOH solution. A mixed gas containing 1%  $\text{CO}_2$  and 99%  $\text{N}_2$  was flowed into guanidine **7** (3.0 mmol) in MeOH (100 mL) at a rate of  $20 \text{ mL min}^{-1}$  using an MFC, and the resulting  $\text{CO}_2$  concentration on the outlet side was measured over time (Fig. 3b). The flow rate was reduced from 200 to  $20 \text{ mL min}^{-1}$  due to concerns about solvent volatilization. After 45 min, the  $\text{CO}_2$  concentration decreased to a minimum of 1756 ppm, and then increased slowly (Fig. 3c). The amount of absorbed  $\text{CO}_2$  was calculated to be about 2.9 mmol, and the **7** :  $\text{CO}_2$  ratio was 1 : 1. After absorbing  $\text{CO}_2$ ,  $\text{CO}_2$ -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  $\text{CO}_2$  emission. The device is shown in Fig. 4b. The desiccator containing  $\text{CO}_2$ -absorbed guanidine **7** was irradiated with LED light under a  $\text{N}_2$  gas flow of  $20 \text{ mL min}^{-1}$  con-



**Fig. 4**  $\text{CO}_2$  desorption from  $\text{CO}_2$ -absorbed azobenzene-guanidine **7** under photoirradiation. (a) UV-vis measurements of  $\text{CO}_2$ -absorbed **7**. (b) Device for  $\text{CO}_2$  release from  $\text{CO}_2$ -absorbed **7** under photoirradiation (440 nm) (c)  $\text{CO}_2$  concentration in outlet gas using device under visible light irradiation. (d)  $\text{CO}_2$  desorption under thermal conditions without photoirradiation.



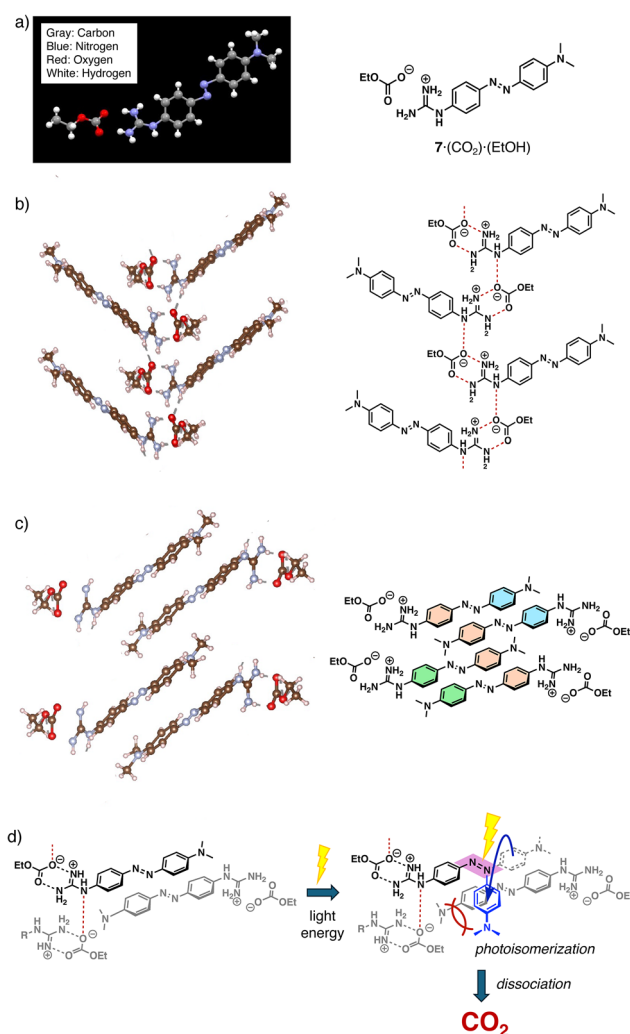


**Scheme 2** Recyclable visible light-swing CO<sub>2</sub> capture using azobenzene-guanidine **7** in air.

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

To elucidate the mechanism for CO<sub>2</sub> release under photoirradiation, a structural analysis of CO<sub>2</sub>-absorbed azobenzene-guanidine **7** in EtOH was performed. A single crystal



**Fig. 5** X-ray crystallographic analysis of **7**·(CO<sub>2</sub>)·(EtOH). (a) ORTEP drawing. (b) Intermolecular hydrogen bonding network. (c) Intermolecular  $\pi$ - $\pi$  stacking interaction. (d) Plausible mechanism for CO<sub>2</sub> 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**·(CO<sub>2</sub>)·(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 ( $\text{EtOC(=O)OH}$ ) derived from  $\text{CO}_2$  and EtOH formed ionic guanidine  $7 \cdot (\text{CO}_2) \cdot (\text{EtOH})$  composed of ethyl carbonate ( $\text{EtOC(=O)O}^-$ ) and guanidinium ( $\text{R-NHC(=NH}_2^+\text{)NH}_2$ ). Next, we focused on intermolecular interactions. As shown in Fig. 5b, a hydrogen bonding network involving  $\text{R-NHC(=NH}_2^+\text{)NH}_2$  and  $\text{EtOC(=O)O}^-$  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  $\text{CO}_2$  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,  $\text{CO}_2$  is released along with the production of EtOH.

### 3. Conclusion

In summary, a light-swing  $\text{CO}_2$  capture method based on photoisomerization reactions of azobenzene derivatives has been developed. In the case of azobenzene-amine **3**, it was possible to absorb  $\text{CO}_2$  not only at 1% concentration but also at atmospheric concentration (about 400 ppm). In addition,  $\text{CO}_2$  in air was selectively captured without moisture contamination.  $\text{CO}_2$ -absorbed **3** was found to release  $\text{CO}_2$  under UV irradiation. Although problems remain in terms of reusability, **3** showed that light energy has the potential to become a driving force for  $\text{CO}_2$  release. Based on these results, azobenzene-guanidine **7** was newly designed to overcome the issue of recyclability. In EtOH solution, **7** selectively absorbed  $\text{CO}_2$  in air to form  $7 \cdot (\text{CO}_2) \cdot (\text{EtOH})$  without moisture content. Desorption of  $\text{CO}_2$  from  $7 \cdot (\text{CO}_2) \cdot (\text{EtOH})$  occurred upon irradiation with visible light (440 nm). The results of  $\text{CO}_2$  release experiments under heating conditions indicated that light energy, and not thermal energy, caused the release of  $\text{CO}_2$ . A plausible mechanism for  $\text{CO}_2$  release under photoirradiation was proposed. From the results of an X-ray crystal structure analysis of  $7 \cdot (\text{CO}_2) \cdot (\text{EtOH})$ , it was considered that the key to  $\text{CO}_2$  release upon light irradiation was dissociation of aggregated  $7 \cdot (\text{CO}_2) \cdot (\text{EtOH})$  based on steric repulsion accompanying photoisomerization of the azobenzene moiety. Thus, we have developed a method for aerial  $\text{CO}_2$  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  $\text{CO}_2$  capture. In this study, light-swing  $\text{CO}_2$  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  $\text{CO}_2$  capture using other photoresponsive molecules

would be possible under various wavelength ranges. Further study on  $\text{CO}_2$  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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