



Photoacid for releasing carbon dioxide from sorbent

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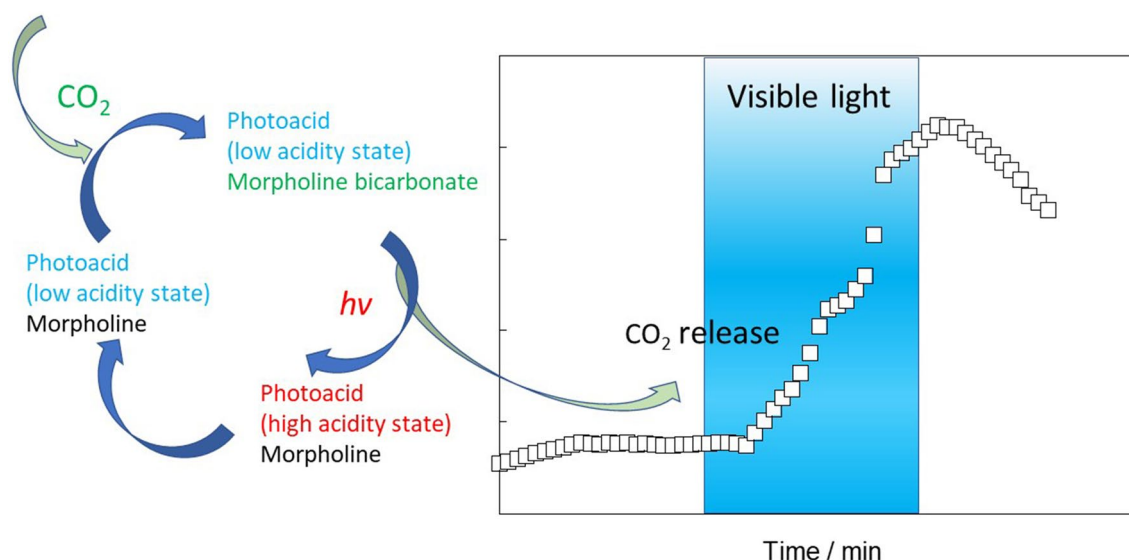
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Abstract

Carbon dioxide (CO₂) is the most important greenhouse gas that causes global warming. Different sorbents, e.g. amines have been applied to capture CO₂. Sorbent regeneration, which is currently conducted by thermal processes, is the most energy consuming step. In this work, we studied a photoacid, which can reversibly increase the acidity of a solution under light, and consequently lead to CO₂ release. The photoactivity, acidity and solubility of the photoacid was tuned for CO₂ release by structural design. The photoacid was mixed with morpholine, which is a well-studied amine for CO₂ capture. Results showed that an aqueous solution containing the mixture can repeatedly capture and release CO₂ under moderate irradiation of visible light. The CO₂ released was nearly the same to that was captured, which indicates the high efficiency of this method.

Graphical abstract



1 Introduction

Carbon dioxide (CO₂) is a major greenhouse gas, which leads to increased global temperature and catastrophic climate events. Different sorbents have been applied to capture

CO₂ [1–6]. In the process of CO₂ capture, sorbent regeneration is the most energy consuming step due to the high temperature required to overcome the thermodynamic stability of the CO₂-sorbent complexes, which is necessary for efficient CO₂ capture. Especially for the aqueous systems, the energy requirements are further increased by the high heat capacity of water. In addition, the high temperatures needed for sorbent regeneration can cause significant oxidation and thermal degradation of sorbents.

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Common sorbents are strong alkaline bases and amines. They react with CO_2 to form carbonates (bicarbonates) or carbamates. Both carbonates and carbamates are unstable under acidic (low pH) condition and release CO_2 . Therefore, changing pH is an effective method for releasing CO_2 at low temperature. However, it is not practical to repeatedly adding acids and bases for CO_2 release and capture. Using reversible photoacids, pH can be switched between basic and acidic condition with light. For example, our group have reported a series of metastable-state photoacids, which can reversibly change pH over 2 units under visible light. [7, 8] Using one of the photoacids, Bennett et al. demonstrated photo-release of CO_2 from a photoacid solution loaded with CO_2 [9]. Recently, Premadasa et al. reported that another metastable-state photoacid can be used for energy efficient direct air capture [10]. Photoenergy used for such process may be obtained from solar light or high-efficiency LED, which reduces the energy demand for sorbent regeneration.

Our group have been developing the photoacids suitable for regeneration of CO_2 sorbent. As described above, the photoacid must be reversible and capable of generating a large pH change. Given that the sorbent must have high basicity to capture CO_2 , the dark acidity of the photoacid, which is the acidity without irradiation, must be low. Otherwise, the photoacid releases proton to the sorbent without irradiation, and reduces its capability of CO_2 capture. Previous work of our group showed that indazole type of photoacids have low dark acidity comparing to the commonly used merocyanine photoacid [11, 12] (Fig. 1). For example, the merocyanine photoacid used by Bennett mentioned above, has a pK_a about 6 in the dark [13], which makes it difficult to pair with basic sorbents. For comparison, an indazole photoacid was reported to have a dark pK_a near 10. [12] However, there are two major drawbacks of indazole photoacid. Its photoreaction often generates significant portion of the *cis*-isomer instead of the spiro (SP) isomer [11]. Since the *cis* isomer is less acidic than SP, the effective photoacidity is reduced. In addition, the rigid conjugated structure leads to low solubility especially in water.

2 Results and discussion

Photoacid **1** (Fig. 1) was designed to solve these problems. It possesses a SO_3^- on the indazole moiety, which greatly enhanced its solubility in water. For comparison, the indazole photoacid without this SO_3^- substituent is essentially insoluble in water, while the solubility of **1** in water is about 30 mM. An ester group was added to the benzothiazolium side. This electron withdrawing group reduces the electron density on the reactive carbon, and thus encourage the nucleophilic cyclization reaction, which forms the high-acidity SP. Photoacid **1** was prepared from indazole-7-aldehyde and 2-methyl-benzothiazole-5-carboxylic acid. Indazole-7-aldehyde was sulfonated using a literature procedure [11]. The methyl ester of benzothiazolium sulfonate was synthesized from the benzothiazole carboxylic acid in two steps. The aldehyde was then coupled with the benzothiazolium by a Knoevenagel reaction. The orange precipitate was recrystallized in water/ethanol to yield the final product **1**. The detailed procedure is described in the Experimental Section.

The photoreaction of **1** in aqueous solution was studied by UV–Vis absorption spectroscopy. As shown in Fig. 2, **1** has an absorption band in visible range with a λ_{max} at 415 nm. Upon irradiation with a 470 nm LED, the band decreased close to baseline, and a band peaked at 332 nm raised. Previous study of an indazole photoacid without the ester group showed that the major photoproduct in aqueous solution without any base was the *cis* isomer [11]. The absorption band of the *cis* isomer has a shoulder in the visible range, while the SP does not absorb in the visible range. The fact that the photoproduct of **1** showed little absorption in the visible range indicates that the major product is SP. To confirm this, the SP was generated by adding a drop of concentrated Na_2CO_3 to a solution of **1**. Addition of a strong base is a routine method to generate the SP form of a metastable state photoacid. As shown in Fig. 2, the shape of SP absorption band is close to that of the photoproduct of **1**. We also compared the absorption spectrum of the photoproduct with

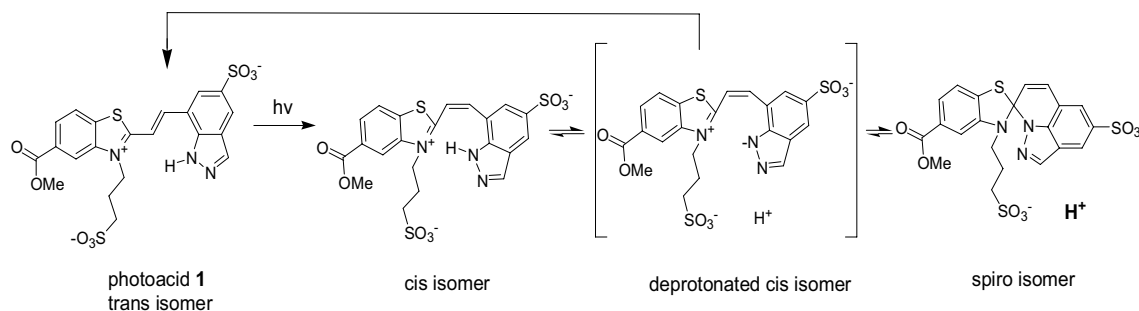


Fig. 1 Photoreaction of indazole photoacid **1**

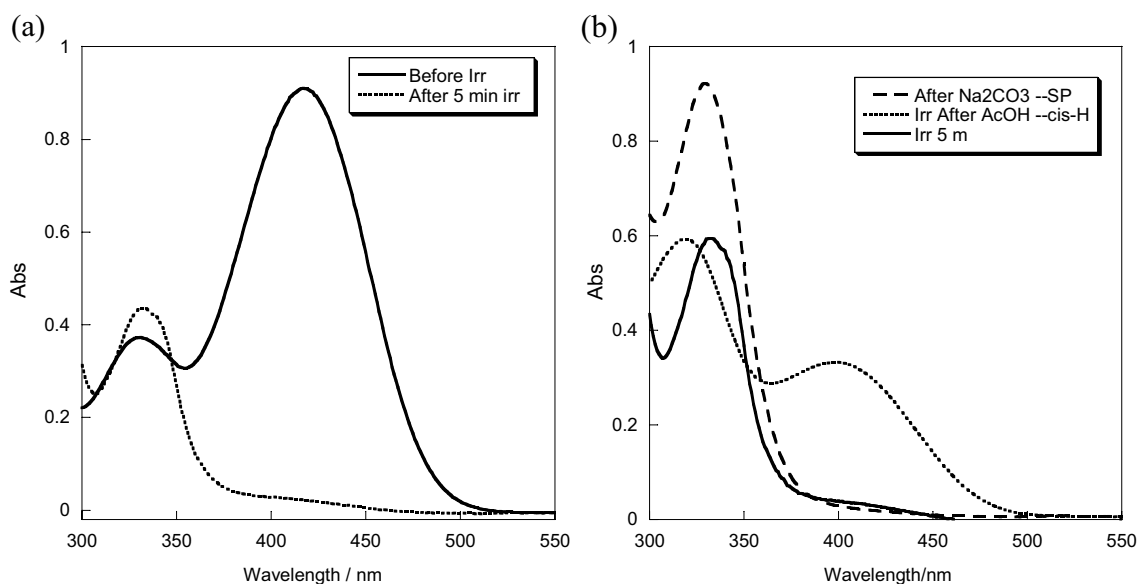


Fig. 2 **a** Absorption spectra of **1** in water before and after irradiation, **b** photoproduct of **1**, in acetic acidic solution (*cis-H*), and SP generated by addition of base

that of the *cis* isomer. Previous work showed that both *cis*-to-SP and *cis*-to-*trans* reactions have the deprotonated *cis* isomer as the major intermediate [11]. (Fig. 1) Under acidic condition, the *cis* isomer is stabilized due to protonation. Thus the *cis* isomer was generated by irradiating a solution of **1** mixed with acetic acid. Comparing the absorption spectra of *cis*, SP, and the photoproduct (Fig. 2) shows that the photoproduct was mostly SP, which was mixed with small portion of the *cis* isomer. This result shows that addition of an electron-withdrawing ester group on the benzothiazolium moiety indeed encourages the formation of SP.

The capability of changing pH with **1** was tested by measuring the pH of a 1 mM solution of **1** in distilled water. The initial pH was 6.55, which is in the common pH range of distilled water. Irradiating the sample with a 470 nm LED for 5 min reduced the pH to 3.88, which is 2.67 unit lower than the original pH. Keeping the sample in the dark after irradiation reversed the pH back to original level (6.47) in 45 min.

Given the promising properties of **1**, we studied its capability to induce CO₂ release from a sorbent. Amines are most commonly used sorbents for CO₂ capture. Morpholine is a secondary amine, which has been identified as a promising sorbent due to its high reactivity with CO₂ and relatively low stripper temperature [14–16]. In this study, we choose morpholine mostly because of relatively low pK_a (8.5) of its protonated form comparing to other commonly used amines, for example, ethanolamine (pK_a=9.5). The pK_a of the amine must be lower or close to that of the photoacid in the dark. If the pK_a of the amine is too high, the photoacid will transfer proton to the amine without irradiation, which results in

the formation of ammonium salt with less basicity than that of the amine and decreases the capability of CO₂ capture. To study the proton transfer between **1** and morpholine in the dark, a 1:1 morpholine/photoacid **1** solution was studied by NMR. The concentration of both was 10 mM. NMR analysis shows that 4/9 of **1** changed to the acidic SP due to proton transfer to morpholine. (Fig. 3) The other 5/9 kept the protonated *trans* conformation. The chemical shifts of the morpholine peaks are between that of morpholine and protonated morpholine, which confirms the partial protonation of morpholine. This result indicates that most of **1** can hold their protons in the presence of morpholine in the dark although a portion of **1** transferred protons to morpholine.

The mixture was loaded with CO₂ by gently bubbling CO₂ through a 3 mL solution of the mixture for two minutes. It was then left open in air for 1 h to achieve a pseudo equilibrium state with air. This step is important to reproducibly measure the CO₂ release as described below. The sample was then transferred to a glass chamber with an infrared sensor. (Fig. 4) After the reading of CO₂ was steady, irradiation was applied from outside of the glass chamber using a 470 nm LED with moderate power (~13 mW/cm²). The CO₂ released to the chamber was monitored using a head space method, which was also used in previous studies [9]. The concentration of CO₂ gas in the chamber was monitored by the sensor and compared to that of a standard. Not only this method directly measures the CO₂ gas released, but also it is suitable for studying relatively small samples with good sensitivity.

As shown in Fig. 4, the reading of [CO₂] in the head space raised up ~5 min after the irradiation started. The delay is

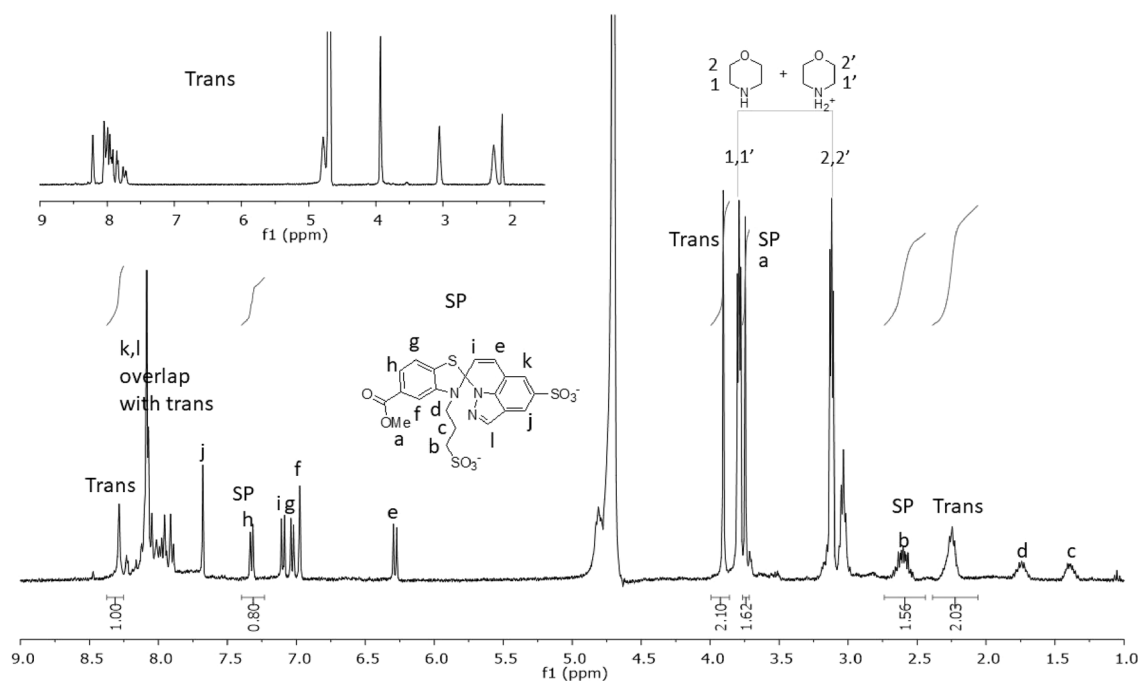


Fig. 3 ^1H NMR of photoacid **1**, which is a mixture of *trans* and SP, and morpholine in water. (NMR of **1** itself in water (*trans*) is shown as the inset for comparison. For the sake of clarity, only the integrations of three pairs of peaks are listed to show the ratio of *trans* and SP is about 5:4.)

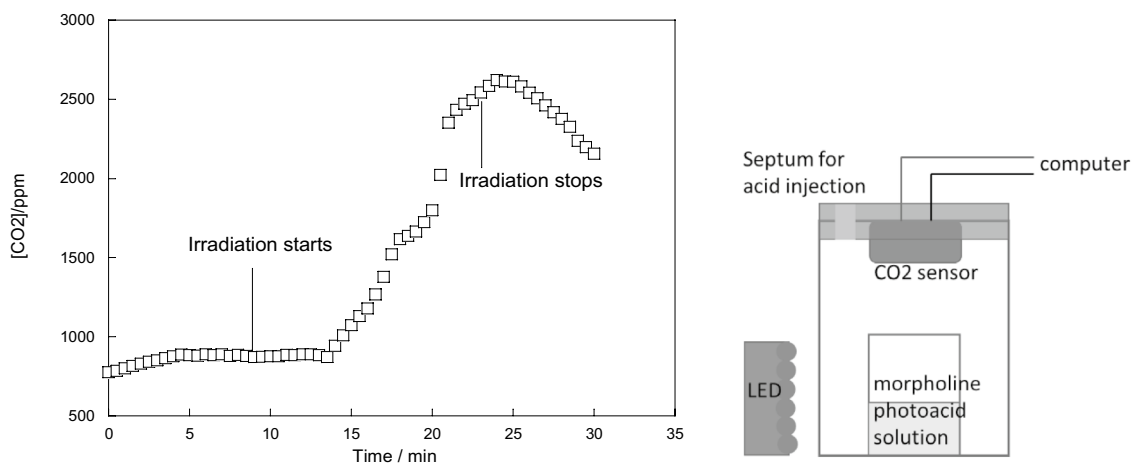


Fig. 4 Head space CO_2 concentration change upon irradiation to the photoacid morpholine solution (left) and setup of CO_2 measurement (right)

due to the time required for the photoreaction as well as accumulation and diffusion of CO_2 for the detection by the sensor, which is located on the cap of the chamber. The irradiation lasted for 15 min and the concentration of CO_2 in the head space increased by 1.74×10^3 ppm maximumly (Fig. 4). Prolonged irradiation did not lead to more CO_2 release. The concentration slowly decreased after the irradiation was

removed due to reabsorption of CO_2 by the solution and maybe leakage of the chamber.

The pH of the solution in an open container before CO_2 loading, after CO_2 loading, and immediately after irradiation were measured to be 7.6, 6.0, and 5.5 respectively. Please note that the pH measured immediately after irradiation, i.e. 5.5, may not represent the maximum pH drop in the process. This is because CO_2 was released during irradiation, which

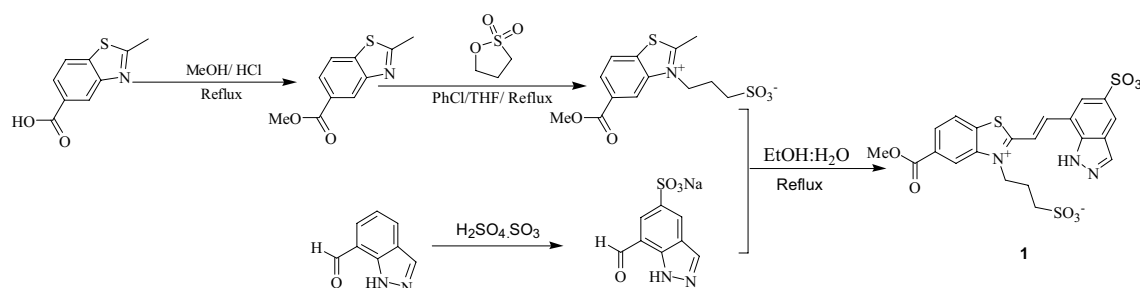


Fig. 5 Synthesis of **1**

resulted in pH increase. So, the maximum pH drop occurred during the irradiation. However, our pH meter did not allow us to follow the quick pH change during the irradiation. As described below, the pH drop is enough to release essentially all the CO₂ captured. After the irradiation, the photoacid reversed back to the less acidic *trans*-isomer, which led to pH increase and regeneration of non-protonated morpholine. In fact, the pH recovered to 7.5, which is close to the initial value before CO₂ loading, 20 min after irradiation.

The regeneration of the sorbent was demonstrated by repeatedly loading CO₂ to the sample followed by irradiation using the same procedure as in the first cycle. The release of CO₂ in the 2nd cycle (1.57×10^3 ppm) was close to that of the first cycle. The CO₂ release in the third cycle was 1.50×10^3 ppm. The decrease of CO₂ release in the 2nd and 3rd cycle is likely due to evaporation of morpholine during the CO₂ loading and equilibrating steps in each cycle.

The amount of CO₂ release was compared to that of an aqueous solution with the same amount of NaHCO₃ as that of morpholine. The decomposition of NaHCO₃ was induced by injection of a concentrated HCl solution through a septum on the chamber. Addition of a strong acid leads to complete decomposition of the bicarbonate and CO₂ release. The CO₂ released was 5.17×10^3 ppm. The less amount of CO₂ release from the mixture of morpholine and **1** is mainly due to less CO₂ captured than the amount of NaHCO₃. Morpholine can capture CO₂ by forming carbamate salt, in which case the ratio between morpholine and CO₂ is 2:1. It also reacts with CO₂ via an acid–base reaction to form bicarbonate salt. Although the ratio between morpholine and CO₂ is 1:1, the bicarbonate is less stable than the carbamate. Under ambient condition, the bicarbonate forms equilibrium with free morpholine in the solution and CO₂ in air. For the concentration (10 mM) used for this study, bicarbonate is the predominate form. The CO₂ captured was less than the amount of morpholine due to the equilibrium. To prove this, a solution of the photoacid/morpholine mixture was added HCl after it was loaded with CO₂ and equilibrated with air. The CO₂ released was 1.77×10^3 ppm. For comparison,

the CO₂ released under irradiation is 1.74×10^3 ppm. This result shows that nearly all the CO₂ captured was released by irradiation.

In summary, we have shown that the photoactivity, acidity and solubility of a photoacid can be tuned for CO₂ release from its sorbent. Photoacid **1** was paired with morpholine, which is a well-studied amine for CO₂ capture. Results showed that a mixture of **1** and morpholine in aqueous solution can repeatedly capture and release CO₂ under moderate irradiation of visible light. The CO₂ released is close to that was captured, which indicates the high efficiency of the photo-induced release.

3 Experimental section

3.1 General

Unless otherwise noted, reagents and solvents were commercially available and used as received without any further purification. UV–Vis spectra were obtained from a Varian Cary 60 Scan UV–Vis spectrophotometer. NMR spectra were determined in deuterated solvents on a Bruker av400 NMR spectrometer. Chemical shifts were reported in delta (δ) units, parts per million (ppm) downfield from TMS. A 470 nm LED array was used to irradiate the solution of the photoacid. The photon flux of irradiation was about $500 \mu\text{mol s}^{-1} \text{m}^{-2}$. For UV–Vis absorption study, irradiation was applied through the window of a typical 1-cm UV quartz cell containing the photoacid solution for about 5 min. Absorption spectra were taken quickly after irradiation. The carbon dioxide sensor (CU-1107N) was purchased from co2meter.com.

3.2 Synthesis of photoacid **1**

Photoacid **1** was synthesized following the route shown in Fig. 5

Synthesis of methyl-2-methyl-benzothiazole-5-carboxylate 2-Methyl-benzothiazole-5-carboxylic acid (1.50 g, 1.77 mmol) was dissolved in 20 mL dry MeOH and a few drops of HCl were added. The reaction was refluxed for 48 h and cooled to room temperature. Then the reaction solution was concentrated by rotary evaporation and dropped into 50 mL of 0.1 M NaHCO₃ solution. The precipitate was filtered off, washed with water and dried under vacuum to give the desired product as a white solid, yield, 1.2 g, 74%. ¹H NMR (400 MHz, d₆-DMSO δ ppm): δ = 8.42 (s, 1H), 8.19 (d, 1H, *J* = 8.4 Hz), 7.96 (d, 1H, *J* = 8.4 Hz), 3.90 (s, 3H), 2.84 (s, 3H).

Synthesis of 3-(5-(methoxycarbonyl)-2-methylbenzothiazol-3-yl)propane-1-sulfonate Methyl-2-methyl-benzothiazole-5-carboxylate (0.30 g, 1.55 mmol) and 1,3-propane sultone (0.26 g, 2.12 mmol) were dissolved in minimum amount of mixed dry THF and chlorobenzene (1:2). Then, the reaction mixture was refluxed for 48 h and cooled to room temperature. Sandy white solid was collected by filtration and washed with THF to give the product, yield 0.4 g, 84%. ¹H NMR (400 MHz, d₆-DMSO δ ppm): δ = 8.88 (s, 1H), 8.56 (d, 1H, *J* = 8.4 Hz), 8.30 (d, 1H, *J* = 8.4 Hz), 4.99 (t, 2H, *J* = 7.2 Hz), 3.97 (s, 3H), 3.22 (s, 3H), 2.62 (t, 2H, *J* = 6.80 Hz), 2.17 (m, 2H).

Synthesis of 1 The benzothiazolium sulfonate prepared in the last step (0.32 g, 1.00 mmol) and sodium 7-formyl-1-H-indazole-5-sulfonate (0.31 g, 1.25 mmol), which was synthesized as reported before [11] were dissolved in 12 mL mixed H₂O and EtOH (1:5). A catalytic amount of ammonium acetate was added and the reaction mixture was refluxed overnight. After cooling, the yellow solid precipitate was filtered and washed with cold EtOH. The crude product was purified by adding ethanol to a concentrated aqueous solution to give the orange final product, Yield, 0.4 g, 73%. ¹H NMR (400 MHz, d₆-DMSO δ ppm): δ = 14.07 (s, 1H), 8.85 (s, 1H), 8.68 (d, 1H, *J* = 16.0 Hz), 8.62 (d, 1H, *J* = 8.40 Hz), 8.42 (s, 1H), 8.37 (s, 1H), 8.31 (s, 1H), 8.29 (d, 1H, *J* = 8.8 Hz), 8.18 (d, 1H, *J* = 16.8 Hz), 5.23 (t, 2H, *J* = 7.2 Hz), 3.99 (s, 3H), 2.75 (t, 2H, *J* = 6.0 Hz), 2.29 (m, 2H, *J* = 5.3 Hz).

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Declarations

Conflict of interest There are no conflicts to declare.

References

- Erans, M., Sanz-Pérez, E. S., Hanak, D. P., Clulow, Z., Reiner, D. M., & Mutch, G. A. (2022). Direct air capture: process technology, techno-economic and socio-political challenges. *Energy & Environmental Science*, 15, 1360–1405.
- Keith, D. W., Holmes, G., St. Angelo, D., & Heidel, K. (2018). A process for capturing CO₂ from the atmosphere. *Joule*, 2, 1573–1594.
- Custelcean, R. (2022). Direct air capture of CO₂ using solvents. *Annual Review of Chemical and Biomolecular Engineering*, 13, 217–234.
- Shi, X. Y., Xiao, H., Azarabadi, H., Song, J. Z., Wu, X. L., Chen, X., & Lackner, K. S. (2020). Sorbents for the direct capture of CO₂ from ambient air. *Angewandte Chemie International Edition*, 59, 6984–7006.
- National Academies of Sciences, and Medicine. (2019). *Negative emissions technologies and reliable sequestration: A research agenda*. The National Academies Press.
- Fasihi, M., Efimova, O., & Breyer, C. (2019). Techno-economic assessment of CO₂ direct air capture plants. *Journal of Cleaner Production*, 224, 957–980.
- Liao, Y. (2017). Design and applications of metastable-state photoacids. *Accounts of Chemical Research*, 50, 1956–1964.
- Liao, Y. (2022). Reversible photo control of proton chemistry. *Physical Chemistry Chemical Physics: PCCP*, 24, 4116–4124.
- Bennett, R., Clifforda, S., Andersona, K., & Puxtya, G. (2017). Carbon capture powered by solar energy. *Energy Procedia*, 114, 1–6.
- Premadasa, U. I., Bocharova, V., Miles, A. R., Stamberg, D., Belony, S., Bryantsev, V. S., Elgattar, A., Liao, Y., Damron, J. T., Kidder, M. K., Doughty, B., Custelcean, R., & Ma, Y. (2023). Photochemically-driven CO₂ release using a metastable-state photoacid for energy efficient direct air capture. *Angewandte Chemie International Edition*, 2023, e202304957.
- Elgattar, A., Alghazwat, O., Brown, A. B., Bryantsev, V. S., Bocharova, V., & Liao, Y. (2023). Photoreaction of indazole metastable-state photoacid. *Journal of Photochemistry and Photobiology A: Chemistry*, 439, 114599.
- Abeyrathna, N., & Liao, Y. (2015). A reversible photoacid functioning in PBS buffer under visible light. *Journal of the American Chemical Society*, 137, 11282–11284.
- Berton, C., Busiello, D. M., Zamuner, S., Solari, E., Scopelliti, R., Fadaei-Tirani, F., Severin, K., & Pezzato, C. (2020). Thermodynamics and kinetics of protonated merocyanine photoacids in water. *Chemical Science*, 11, 8457–8468.
- Mazari, S. A., Abro, R., Bhutto, A. W., Saeed, I. M., Ali, B. S., Jan, B. M., Ghalib, L., Ahmed, M., & Mubarak, N. M. (2020). Thermal degradation kinetics of morpholine for carbon dioxide capture. *Journal of Environmental Chemical Engineering*, 8, 103814.
- Liu, K., Jinka, K. M., Remias, J. E., & Liu, K. (2013). Absorption of carbon dioxide in aqueous morpholine solutions. *Industrial and Engineering Chemistry Research*, 52, 15932–15938.
- Matin, N. S., Remias, J. E., Neathery, J. K., & Liu, K. (2013). The equilibrium solubility of carbon dioxide in aqueous solutions of morpholine: experimental data and thermodynamic modeling. *Industrial and Engineering Chemistry Research*, 52, 5221–5229.

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