

Photoinduced Carbon Dioxide Release via a Metastable Photoacid in a Nonaqueous Environment

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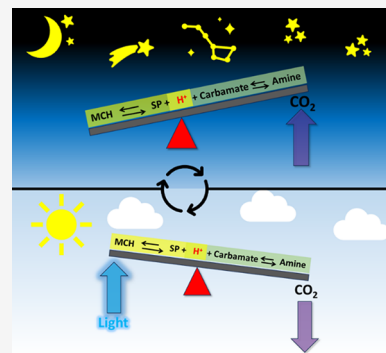


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Supporting Information

ABSTRACT: Capturing carbon dioxide (CO_2) from the atmosphere is a scientific and technological challenge. CO_2 can be captured by forming carbamate bonds with amines, most notably monoethanolamine (MEA). Regenerating MEA by releasing captured CO_2 requires that the carbamate solution be heated. Recently, photoacids were used to induce a pH change to release CO_2 from aqueous carbonate solutions. We report a merocyanine photoacid that releases CO_2 from nonaqueous carbamate solutions of MEA, which has a CO_2 loading capacity that is higher than that of water. On the basis of the absorption spectra of the photoacid in the presence of acids and CO_2 , we show that the photoacid cycle and the CO_2 capture of MEA are two separate equilibria coupled to each other via protons. We demonstrate that irradiating the sample with 405 nm light induces the release of CO_2 , which we detect using an in-line mass spectrometer. This work highlights an alternative path for optimizing a photoinduced CO_2 capture and release system.



Control over the atmospheric CO_2 concentration is an important contemporary scientific and technological challenge. A number of direct air capture (DAC) technologies have emerged recently, including some that convert CO_2 into organic or inorganic carbonates and carbamates during absorption.¹ Concurrent with DAC technologies, it is also necessary to develop methods to desorb and release a pure CO_2 stream for potential conversion to fuels or other products. This challenge is especially important when CO_2 adsorption is highly exothermic, which requires significant energy for its desorption. For example, the capture of CO_2 by the well-known reagent monoethanolamine (MEA) is highly exothermic ($\Delta H = -80$ to -100 kJ/mol);² hence, expelling CO_2 from this reagent requires that the solution be heated to temperatures of >400 K,³ which also greatly enhances water vaporization and amine degradation. Taken together, the total energetic cost to thermally regenerate an aqueous amine capturing solution is split among the heat required to increase the temperature of the solution, the heat of water vaporization, and the heat required to desorb CO_2 .³ As such, isothermal desorption methods would more precisely target CO_2 desorption to decrease the cost of regeneration.

An alternative approach takes advantage of the pH dependence of the dissolved CO_2 vapor–liquid phase equilibrium. In prototypical capture solutions, a primary or secondary amine is deprotonated by self-exchange with another amine or by a separate Brønsted base. This enables the deprotonated amine to act as a strong base and attack the Lewis acidic carbon on CO_2 , making a carbamate bond (Figure 1).^{4,5} Acidifying the solution reprotonates the amine and shifts the equilibrium to favor the release of CO_2 . Subsequently, the excess acid is removed to regenerate the starting sorbent. This

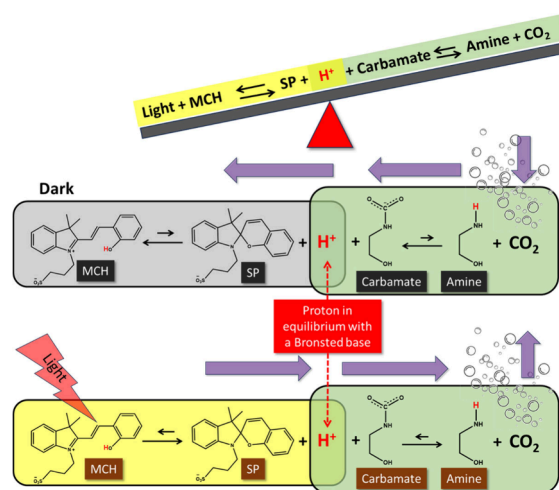


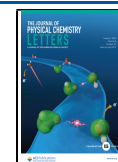
Figure 1. Concept of photodriven pH swing and its coupling to the CO_2 capture equilibrium via PA1. In the top panel, the protonated photoacid MCH is in equilibrium with its deprotonated SP form and protons. The CO_2 captured by amines also produces protons. The protons are taken from the amine by a suitable Brønsted base or proton self-exchange (not shown). Therefore, the protons couple the two equilibria. In the bottom panel, light causes the MCH to release its proton and be converted into SP. The released H^+ reprotonates the carbamate and shifts the equilibrium toward CO_2 release.

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process is known as pH swing desorption and is typically achieved by dialysis or by modulating the pH using a spectator analyte.^{6–8}

Because sunlight is an abundant resource, methods that use light for CO₂ desorption could reduce operating costs. A connection between light excitation and pH swing is achieved by using photoacids, which are molecules that release protons upon absorbing light. It is important for the photoreleased protons to remain in solution with sufficient lifetimes to induce chemical changes in the environment and not recombine with the conjugate base. A class of photoacids, metastable photoacids, have been recently studied as the active agents for photoinduced pH swing desorption because of the long lifetime (greater than microseconds) of their conjugate base.^{9–15} A prime example of this kind of class is the merocyanine dyes (Figure 1). Upon irradiation, the protonated merocyanine form (MCH) releases H⁺ and undergoes cyclization to form spiropyran (SP). In the dark, the MCH \rightleftharpoons SP + H⁺ equilibrium is dependent on pH, with MCH favored at low pH and SP favored at high pH. When MCH absorbs light, the equilibrium is further shifted to favor the SP form and the release of a proton. A rich body of literature spanning many years has reported the synthesis, chemical modification, solvatochromism, and dynamics of this family of photoacids.^{10,16–18} A major application of this class of photoacids for controlling the CO₂ concentration in aqueous and binary dimethyl sulfoxide (DMSO)/water solutions was recently reported by Alfaraiddi and co-workers¹³ and de Vries and co-workers.¹⁴ Similar photoacids in basic aqueous solutions have also been studied for CO₂ capture and photoinduced release.^{12,19,20} These seminal studies clearly demonstrated the release of CO₂ by light and opened the path for generalizing and broadening the concept.

There are two reasons to extend the concept of light-controlled CO₂ release in nonaqueous environments. First, although water can adsorb CO₂, the loading efficiency is not remotely comparable to those of the commonly used capture agents that are based on amines. Hence, amines such as monoethanolamine (MEA) are widely used in commercial CO₂ capture. Second, the merocyanine photoacid that is the functional agent of photocontrol is known to irreversibly hydrolyze into indolium and salicylic acid derivatives^{10,14,21–23} with a half-life on the order of hours. Therefore, to make the photocontrol of CO₂ release practical, it is crucially necessary to extend the concept to nonaqueous environments.

Here, we report the use of a merocyanine photoacid for the release of CO₂ from the archetypal CO₂ capture agent MEA in the absence of water. Amine-based systems have been extensively studied^{24–26} for CO₂ capture due to their favorable thermodynamics and kinetics.^{3,26} However, the relevant equilibria and kinetics for photoacids remain understudied in these nonaqueous solvents. We tested whether a canonical merocyanine-based metastable photoacid (hereafter termed PA1), first reported by the Liao group (Figure 1),¹⁶ could successfully drive pH swing desorption in a CO₂-saturated MEA solution (see Section S1 of the Supporting Information and Figure S1 for synthetic details).

Figure 1 illustrates the coupled equilibria of PA1 and CO₂ captured by MEA. For amines to capture CO₂, a deprotonating base is necessary. In MEA, deprotonation occurs via proton self-exchange with another MEA molecule, generating ammonium. The deprotonated amine forms a carbamate bond with the CO₂, while the ammonium, which is effectively a

reservoir of protons in the solution, is in equilibrium with the photoacid. The relevant states of PA1 are the protonated MCH and the deprotonated SP forms, which are in equilibrium with each other and the proton reservoir in the solution in the dark. When MCH absorbs light, it releases its proton and is converted into the SP form. The released proton adds to the proton reservoir in the solution, which in turn shifts the CO₂ capture equilibrium by protonating the carbamates and releasing the CO₂. Note that unlike pH-jump experiments in aqueous solutions, MCH should not reform on its own without further addition of CO₂ to repeat the cycle.

In Figure 2, we provide evidence that the CO₂–PA1 equilibria, as shown in Figure 1, are linked via protons. Because

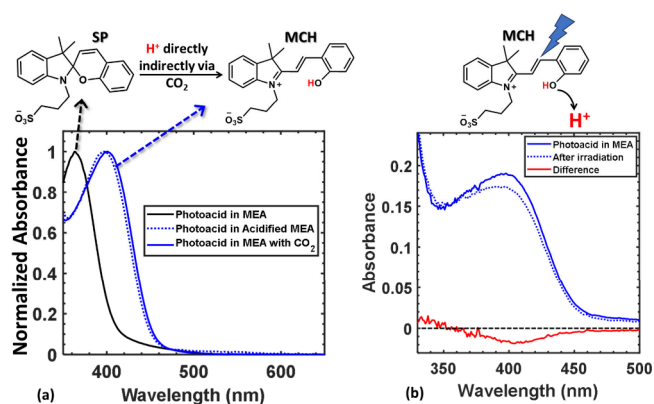


Figure 2. (a) Evidence of the influence of the CO₂ equilibrium on PA1. The black line shows the SP form of PA1 in MEA prior to exposure to the aqueous CO₂. The blue solid line shows the spectrum after the introduction of CO₂. The blue dashed line shows that this effect is identical to that of acidifying the solution. (b) Spectra of an acidified MEA solution containing PA1 before (solid blue line) and after irradiation for 20 min (dotted blue line). The difference between the spectra (red line) shows the bleaching of this band by light.

MEA is a base, the photoacid MCH is deprotonated in MEA, making the SP form the dominant species. This is identified by the known ultraviolet absorption of the SP form, with a peak at 370 nm (black line, Figure 2a). When CO₂ is added to the solution, carbamate is formed and the solution is acidified according to the equilibrium illustrated in Figure 1. The released protons shift the PA1 equilibrium toward MCH, as evidenced by the characteristic absorption peak near 400 nm (blue line, Figure 2a). To ensure that the observed absorption is truly caused by the addition of free protons, we acidified a solution of MEA containing PA1 without adding any CO₂ and obtained a similar absorption spectrum (dashed blue line, Figure 2a). The acidification was done with glacial acetic acid to avoid the introduction of large quantities of water. Similar effects were observed with concentrated HCl (see Figure S2). The slight shift between the spectra of MCH created by acidification and the introduction of CO₂ is likely solvatochromic. Therefore, we show that CO₂ capture does influence the photoacid equilibrium as illustrated in Figure 1. We note that MEA has its own modest absorption feature from 250 to 350 nm (Figure S3). Upon acidification, the intensity of this feature increases, complicating the spectral analysis in this region. Thus, we focus on the 400 nm feature hereafter.

Next, we show evidence that irradiating the sample can release protons from the MCH (Figure 2b). First, we acidified

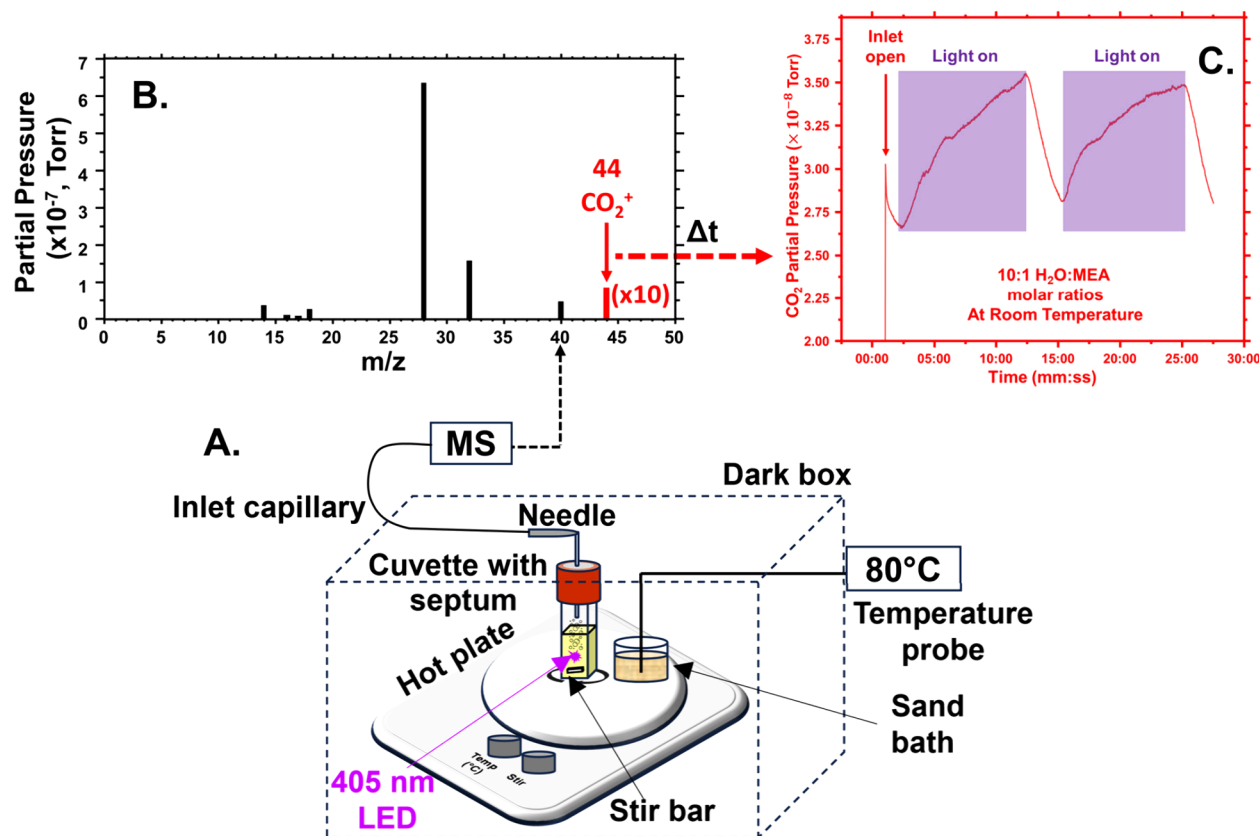


Figure 3. (A) Experimental setup. (B) Representative mass spectrum. The CO_2^+ peak (m/z 44, colored red) is monitored over the time scale of this experiment. (C) Photoinduced release of CO_2 from a 2.6 mM PA1 solution in a 10:1 (molar ratio) $\text{H}_2\text{O}/\text{MEA}$ mixture.

a solution of PA1 in MEA to generate the MCH form (solid blue line, Figure 2b). Then, we continuously irradiated the sample with a blue light-emitting diode (LED) (Thorlabs M405LP1; $\lambda_{\text{max}} = 405 \text{ nm}$) at 40 mW for 20 min, resulting in a spectrum (dotted blue line, Figure 2b) that shows a clear bleaching at 400 nm (solid red line, Figure 2b), implying depletion of the MCH population. The data show that $\sim 8\%$ of the MCH is bleached. We observe a zero-point crossing in our difference spectrum at $\sim 375 \text{ nm}$, which is near the isosbestic point between SP and MCH. However, MEA also has absorption in this spectral range, and because the quantity of MEA is also changing during the process, it is difficult to unambiguously quantify the increase in the level of the SP species (Figure S3).

As discussed below, this yield is enough to perturb the CO_2 equilibrium. At increased temperatures and powers (Figure S4), the ratio of bleached MCH is higher. Note that, upon depletion of CO_2 , the solution should return to being largely SP dominant (black line, Figure 2). While there are spectral changes at shorter wavelengths hinting at the recovery of SP, due to overlapping changes in background MEA absorption after the addition of CO_2 substitution, we were unable to quantify the recovery. While the mechanism of recovery upon irradiation has been extensively studied in aqueous solutions, information about its behavior in organic solvents is lacking and is being actively sought.

In Figure 2a, we provide evidence that introducing CO_2 shifts the photoacid equilibrium. Next, we show that irradiating PA1 shifts the CO_2 equilibrium toward desorption. For this purpose, we used a mass spectrometer (MS) with an ambient gas sampler (Hidden Analytical, HPR-20 R&D) that sampled

the gas in the headspace of a cuvette (Figure 3a). The cuvette was exposed to the 405 nm LED, and the instantaneous CO_2 partial pressure was recorded. A representative mass spectrum is shown in Figure 3b.

We first performed experiments in aqueous systems to establish our experimental protocols and limitations. Figure 3c shows the typical amount of CO_2 gas detected by the MS at room temperature in the headspace of a 10:1 (molar ratio) $\text{H}_2\text{O}/\text{MEA}$ solution containing 2.6 mM PA1 after CO_2 was bubbled in the solution for 5 min. Before measurement, the CO_2 in solution is allowed to equilibrate with the headspace gas for 10 min in the dark. Once the inlet is opened, the CO_2 gas in the headspace is rapidly pulled into the MS, resulting in a lower steady-state partial pressure. When the 405 nm LED is turned on, the amount of CO_2 detected increases (purple rectangles in Figure 3c). When the light is turned off, the amount of CO_2 detected in the headspace decreases. This light on/off cycle is repeated once more to show similar results, confirming that the release of CO_2 can indeed be controlled by the photoinduced pH swing of PA1 used in this study.

We note that in a recent study of the same photoacid scaffold with various substituents,¹³ the photoacid derivative most similar to PA1 did not release detectable amounts of CO_2 upon photoexcitation in water. The authors of that study ascribed this observation to the high pK_a of the photoacid not matching the carbonate equilibrium in water. The fact that we observed photoinduced release of CO_2 in this aqueous system with PA1 could be ascribed to the sensitivity of our *in situ* detection. While the previous study obtained aliquots of the headspace after a period of irradiation and quantified the amount of CO_2 released using gas chromatography, we directly

sample the headspace as CO₂ is released. Additionally, the two experiments were quite different in the composition of the solvent. Most notably, their solution relied on adsorption of CO₂ by water while we always had MEA present, either in pure form or mixed with water, which supports a larger CO₂ loading, therefore changing the thermodynamics and kinetics of the process.

Next, we investigated photoinduced CO₂ release in the nonaqueous MEA/CO₂ mixtures, which are quite viscous due to their ionic liquid nature. Therefore, to ensure that the released CO₂ gas could escape, it was necessary to stir and heat the solution to ~80 °C, below the typical temperature used for CO₂ thermal release (~120 °C).³ First, the sample was heated and stirred for 30 min to relax the system into equilibrium at the desired temperature. Then, the sample was irradiated in an alternating pattern of dark and light for 15 min each. Figure 4a

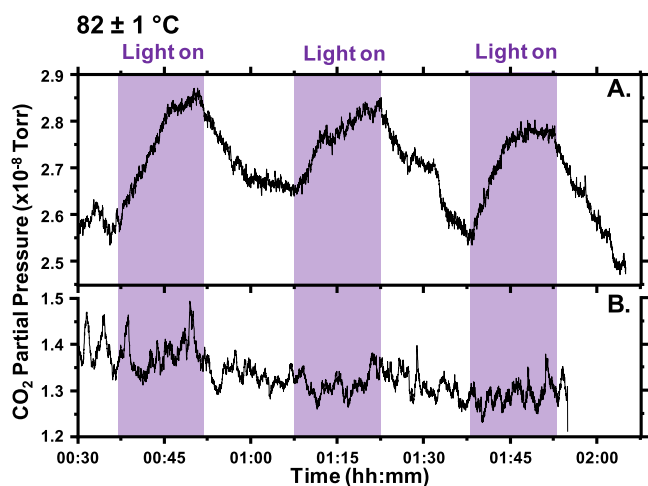


Figure 4. CO₂ partial pressure detected in the headspace of a cuvette with (A) a 13 mM solution of PA1 and (B) a 7.8 mM solution of the Reichardt dye in MEA/CO₂. Both samples were heated to 82 ± 1 °C and stirred for 30 min before 15 min light on/off cycles (highlighted in purple).

clearly shows that during the light cycle (purple shaded rectangles), the level of CO₂ detected is increased. To ensure that the response does not arise from a photothermal effect, i.e. the light heating the sample and favoring CO₂ release, we performed a control experiment with the Reichardt dye,²⁷ which has a significant absorption at 405 nm when in MEA (see Figure S6). The Reichardt dye has no known influence on the protonic equilibrium in MEA. We introduced this dye at a concentration of 7.8 mM into the MEA/CO₂ solution, irradiated it in the same way as PA1, and observed no correlation between the illumination and the emitted CO₂ (Figure 4b). As such, the results in Figure 4a show that the photoinduced release of CO₂ is due to increased proton activity in solution. Note that the differential change in CO₂ concentration in the nonaqueous case (Figure 4b) is smaller than in the aqueous case (Figure 3c). This is likely due to the faster kinetics of proton transfer in water. Because many CO₂ capture agents are amines in nonaqueous environments, for the photorelease concept to be widely applicable, the scope of the solvents must be extended to nonaqueous environments. Further work is needed to understand the influence of the solvent environment on the thermodynamics and kinetics of photorelease.

To further support the effect of CO₂ release caused by irradiation, we performed a photogravimetric analysis in which two identical samples of PA1 in a MEA/CO₂ mixture were prepared. Both samples were heated to 80 °C, but only one was exposed to light. We weighed the samples every hour and observed that the irradiated sample decreases in mass twice as fast as the sample kept in the dark (Figure S7). More details about this experiment are discussed in Section S3.

While we have demonstrated photoinduced release of CO₂ from a nonaqueous sorbent, it is important to note that the behavior of the photoacid in the highly viscous and ionic nonaqueous MEA environment is quite different from its behavior in water. As mentioned earlier, MCH should not recover without further addition of CO₂, as shown in Figure 1. To extend the scope of using photoacid for CO₂ desorption in organic solvents, PA1's behavior in pure MEA is of interest. To that end, we attempted to measure MCH recovery after irradiation, analogous to a pH-jump experiment. Unlike what is observed in water, we did not observe MCH recovery within the time scale of our measurement (see Figures S4b and S5). Liao,⁹ Beves,¹⁸ and de Vries¹⁴ all reported that the ring closure and ring opening kinetics are strongly affected by molecular substitutions and the choice of solvent. Liao and co-workers showed that the PA1 recovery spans orders of magnitude in different solvents: $76 \text{ M}^{-1} \text{ s}^{-1}$ in water, $1.6 \text{ M}^{-1} \text{ s}^{-1}$ in ethanol, and $0.034 \text{ M}^{-1} \text{ s}^{-1}$ in DMSO.⁹

There are two general hypotheses for why the ring opening kinetics are strongly impacted by the choice of solvent. The first assumes that protonation initiates the ring opening reaction; in this case, fewer mobile protons around the SP would hinder the ring from opening. Because of the change in the hydrogen bonding environment and more basic ammonium moieties, protons in MEA likely exhibit dynamics that are slower than those in aqueous systems. Changes in the ultrafast relaxation rate for excited-state photoacids have been ascribed to changes in the hydrogen bonding landscape around the parent photoacid.^{28,29} Furthermore, organic solvents like DMSO are known to preferentially solvate the region around the photolabile double bond for PA1.¹⁴ This preferential solvation might crowd out acidic protons from the SP site and delay the recovery of MCH.

Another plausible explanation is that increases in the solution viscosity disrupt the ring opening reaction. To test this hypothesis, we attempted to study the recovery kinetics of MCH after irradiation for 20 min in a solution with a small amount of HCl to ensure a lower viscosity. Despite the samples being much less viscous than CO₂-saturated solutions, we did not observe recovery of MCH after 20 min in the dark (Figure S5). A combination of solvent effects, including viscosity, protonation, and hydrogen bonding, and dielectric environment likely disrupts the photocycle. Analyzing the dynamics of the recovery and optimizing the photocycle efficiency will be the subject of future studies.

The purpose of this work is to report that metastable photoacids can be used to induce CO₂ release even in strongly basic nonaqueous media. Despite its initial basicity, a MEA solution that is sufficiently carbonated will reprotonate a canonical merocyanine photoacid. Similarly, irradiating the population of MCH conclusively releases CO₂ from this solution. Our results extended the utility of photoinduced pH swing to a wider range of capture agents and environments.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.4c01577>.

Additional experimental details, including the synthetic procedure, and additional figures as mentioned in the text (PDF)

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Notes

The authors declare no competing financial interest.

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