

A Fully Light-Driven Approach to Separate Carbon Dioxide from Emission Streams

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SUMMARY

Carbon capture from industrial point sources is an essential component of the global effort to mitigate climate risks. However, traditional approaches require significant energy input—often provided, counterproductively, by fossil fuel combustion. Using sunlight directly as the energy source would significantly improve the energy efficiency of carbon capture processes. Herein, we report the first fully visible light-driven CO₂ separation system, in which carbon capture is achieved via the photoenolization/cycloaddition reaction of inexpensive 2-methylbenzophenone with CO₂, and CO₂ release is realized through an intramolecular photodecarboxylation reaction. This system operates isothermally, works with natural sunlight, and facilitates CO₂ removal from natural gas flue emissions, providing a blueprint for other non-thermal chemical separations.

INTRODUCTION

The rising atmospheric levels of CO₂ represent a significant climate threat to humanity. Meeting the goals of the Paris Accords is ambitious, and, even in the best case scenario, will require the removal of CO₂ from industrial point sources such as fossil fuel-fired power plants.^{1,2} However, current temperature-swing carbon capture technologies are highly energy- and cost-intensive, prohibiting their global deployment.³ Carbon capture is fundamentally energy-demanding due to the entropic penalty associated with concentrating CO₂ from a dilute stream into a pure gas for subsequent sequestration or valorization.⁴ Currently, the bulk of the required energy is counterintuitively provided by fossil fuel combustion; in this case, energy transition efforts may be more productive towards reducing atmospheric CO₂ levels than post-combustion carbon capture.^{3,5} The use of renewable energy to power CO₂ capture would help to overcome this challenge. In particular, sunlight is attractive because it is the most abundant energy resource on Earth,⁶ leading to its rapidly growing use for electricity generation and other environmental applications.^{7–12}

In the simplest configuration, a solar panel could be employed for solar-to-electricity or solar-to-heat conversion to drive a traditional temperature-swing process. However, the inefficiency of carbon capture is exacerbated by many energy exchange and conversion steps, leading to significant energy loss.^{13–15} Current accessible, commercial solar panels can harness up to 30% of solar energy;¹⁶ however, a recent analysis of a solar direct air CO₂ capture system revealed only ~8% of the energy supply results in CO₂ removal,¹⁴ reflecting at most a 2.4% solar energy efficiency. We propose that the direct use of (sun)light to drive CO₂ capture and release could help to overcome these inefficiencies. There are scattered examples of using light to drive carbon capture/release processes, but most exhibit low capture capacities, require additional cooling, and/or rely on ultraviolet (UV) light irradiation, which is

scarce within the solar spectrum (Figure 1A).^{17–22} These drawbacks generally stem from using light to drive only the release step, with capture achieved in the dark (Figure 1B). Such systems with a thermodynamic driving force sufficient for CO₂ capture from dilute sources, such as the flue gas of power plants (4–15% CO₂),²³ typically require high-energy UV light to drive CO₂ release. In contrast, a carbon capture strategy that utilizes visible light (380–780 nm)—which is abundant within the solar light spectrum (Figure 1A)—for *both* the capture and release steps would be an energy-saving strategy with sufficient thermodynamic driving force to facilitate challenging separations (Figure 1C).

Nature provides inspiration for the design of visible light-driven pathways for both CO₂ capture and release. Photosynthetic organisms fix CO₂ on massive scale using enols generated in the active site of the enzyme RuBisCo, yet enols (and carbon-based nucleophiles in general) remain largely unstudied for chemisorptive carbon capture.²⁴ As a potential synthetic analog of this transformation, 2-alkylphenyl ketones can undergo a photoenolization/Diels-Alder (PEDA) reaction with CO₂, although this process typically requires UV light irradiation and relatively long reaction times (≥ 2 h) under an atmosphere of pure CO₂, which are not realistic conditions for large-scale carbon capture applications.^{25–27} However, PEDA has never been paired with a CO₂-releasing mechanism to produce a formal CO₂ separation system. Nonetheless, the oxidative decarboxylation of phenylacetic acids is a common pathway in both biology (Figure 1E) and photoredox catalysis,^{28–30} potentially offering a pathway for CO₂ release if an optimal photocatalyst can be identified. Through the combination of these two reactions, we report herein the first fully visible light-driven system for reversible CO₂ capture, providing a new platform for sustainable separations that do not require careful thermal management (Figure 1F).

RESULTS AND DISCUSSION

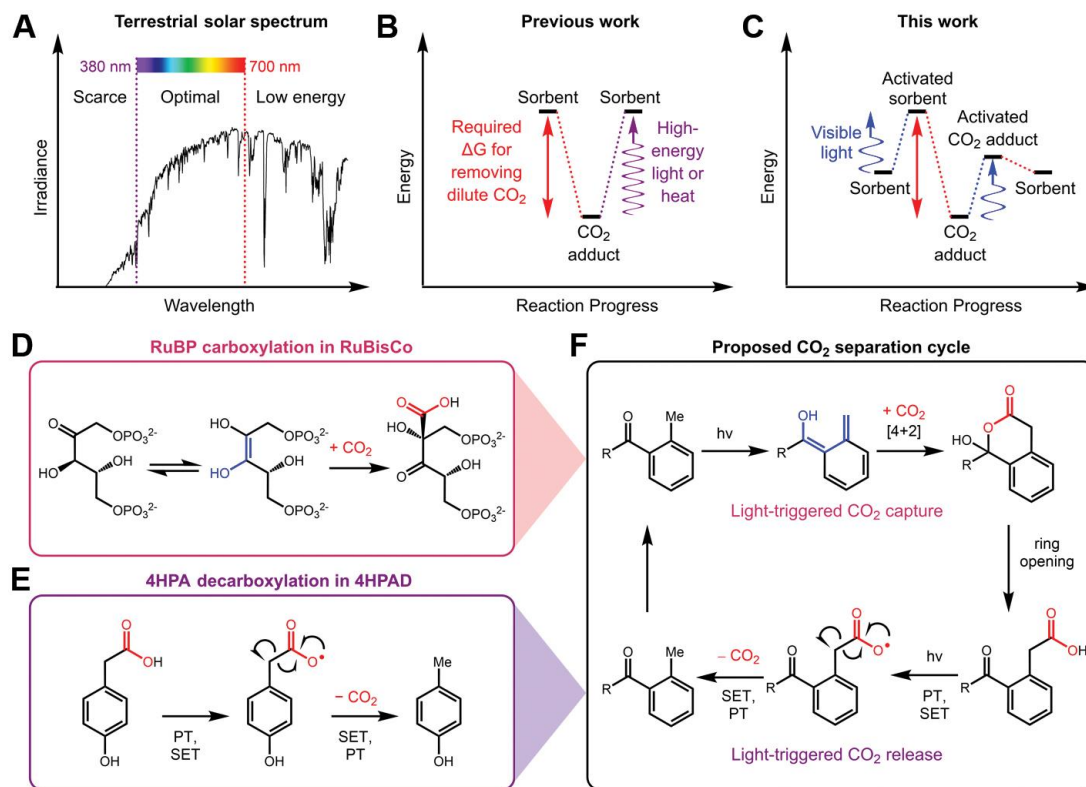


Figure 1. Design of a fully light-driven CO₂ capture system.

(A) Terrestrial solar spectrum.

(B and C) Illustrative energy diagrams of (B) traditional and (C) proposed carbon capture technologies.

(D) CO₂ fixation by a reactive enol catalyzed by RuBisCo as an inspiration for the CO₂ capture mechanism.

(E) Radical decarboxylation catalyzed by 4-hydroxyphenylacetate decarboxylase (4HPAD) as an inspiration for the CO₂ release mechanism.

(F) Mechanistic pathways for light-triggered CO₂ capture and release using 2-methylphenyl ketones.

PT = proton transfer, SET = single electron transfer.

CO₂ capture using visible light

We first evaluated whether PEDAs can be conducted with shorter reaction times and visible light irradiation. Among 2-alkylphenyl ketones, 2-methylbenzophenone (**1**) was chosen as a model sorbent because of its low cost and absorbance in the high-energy portion of the visible light region (Figure S27).^{31,32} CO₂ capture was first evaluated using varying concentrations of **1** dissolved in the green solvent dimethyl sulfoxide (DMSO) under purple light (390 nm) irradiation (Figure 2A, see Supplemental Information for details). No effort was made to exclude H₂O or O₂ from these experiments. At lower concentrations (0.1 M), a high conversion to **2** (59%) could be achieved in only 30 min. This amount represents more than half of the theoretical uptake capacity (5.5 mmol g⁻¹ of **1**), comparable to other carbon capture technologies.^{18–22,33} Higher overall concentrations of **2** (reflecting more CO₂ capture) could be achieved using higher initial concentrations of **1** (up to 2 M); thus, a concentration of 2 M was employed for subsequent experiments. Similar performance was observed for CO₂ capture with or without fan-cooling (Figure S17), indicating that careful thermal management is not necessary for this approach. This represents a significant advantage over systems in which only the carbon release step is driven via

light irradiation, which typically causes warming of the solution that can interfere with subsequent capture steps.^{21,22}

The performance of **1** was next interrogated for CO₂ capture from dilute streams (Figure 2A). Although the capture capacity expectedly decreased for streams with lower partial pressures of CO₂, the capture rate was still satisfactory even for a 10% CO₂ in N₂ stream after 30 min (26% of the pure CO₂ capacity).³⁴ The presence of O₂ in flue gas often presents a challenge for traditional sorbents, which are prone to oxidative degradation.^{35–37} In contrast, the addition of 3% O₂ to a 10% CO₂ in N₂ stream, simulating the composition of a natural gas-fired power plant emission stream²³, only results in a slight decrease in the yield of **2** after 30 min (Figure 2A). This decrease is likely due to triplet quenching of photoexcited **1** by O₂,^{38–40} as degradation of **1** or **2** was not observed by ¹H nuclear magnetic resonance (NMR) spectroscopy. The need for constant light irradiation—supporting that this is a photo-driven and not photo-initiated process—was also confirmed by turning the light source on and off during the capture process (Figure 2B). No formation of **2** was observed in the dark. Overall, these studies support that the PEDAs reaction possesses fast kinetics, tolerance of contaminants like O₂ and H₂O,

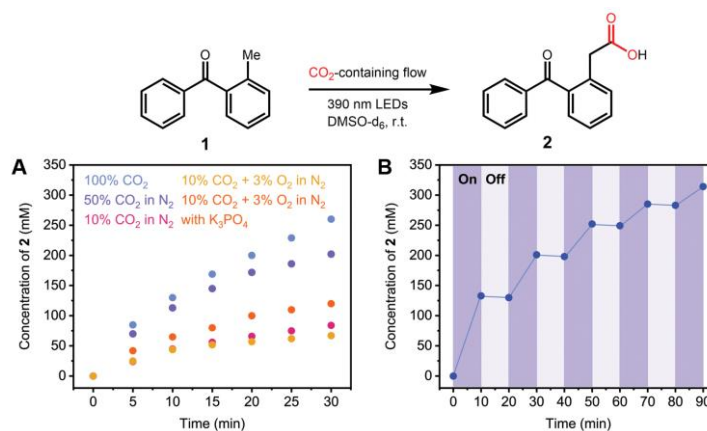


Figure 2. Optimization of CO₂ capture with 1.

(A) CO₂ capture using 2 M of **1** in DMSO-d₆ from various CO₂-containing streams. For the “with base” experiment, 15 mol% of K₃PO₄ was added.

(B) CO₂ capture using 2 M of **1** in DMSO-d₆ from a pure CO₂ stream with light switching on-and-off every 10 min.

The concentration of the CO₂-adduct **2** was determined by ¹H NMR spectroscopy against 1,3,5-trimethoxybenzene as an internal standard.

and compatibility with visible light irradiation, all of which are required for operation under realistic conditions.

Enhancing light-driven CO₂ release

Achieving efficient light-driven carbon capture is only half of the story, as a visible light-driven process to drive CO₂ release from **2** is also necessary. The direct, light-driven decarboxylation of **2** has been reported, but it requires prolonged irradiation with UV light.³⁰ This is because carboxylic acids such as **2** are resistant to photooxidative decarboxylation due to their large-magnitude redox potentials ($\geq +2.0$ V vs. SCE).^{29,41} In contrast, the corresponding carboxylates such as **3** (Figure 3) are much easier to photooxidize (+0.9–1.4 V vs. SCE).²⁹ The resulting carboxy radicals can undergo rapid decarboxylation via β -scission to produce alkyl radicals, followed by single-electron transfer (SET) and proton transfer (PT) to return the corresponding alkane (Figure 1F). Unlocking this mechanistic pathway for CO₂ release would require the addition of catalytic base to deprotonate **2** and form **3** as well as the potential addition of a photoredox catalyst capable of photooxidizing **3**. However, the presence of acids and bases has been shown to accelerate the decay of photoenols, which could potentially disrupt the CO₂ capture step.⁴² Remarkably, the addition of catalytic amounts (15% relative to **1**) of K₃PO₄ under PEDTA conditions with a simulated natural gas power plant emission stream (10% CO₂/3% O₂/remainder N₂) doubled the amount of CO₂ adduct that formed after 30 min relative to the base-free conditions (Figure 2A). This finding eliminates the need to separate the base between the prospective capture and release steps, keeping the setup simple.

Typically, photooxidation reactions are conducted using expensive transition metal photocatalysts, such as Ir-based complexes.⁴³ However, both inter- and intramolecular photodecarboxylation reactions catalyzed by benzophenones have been reported,^{25,30,44} suggesting that **1**, **2**, or **3** could be capable of mediating the decarboxylation

of **3** without the need for an added photocatalyst. Strikingly, simply irradiating **3** with purple light under N₂ flow at room temperature was sufficient to induce near-complete decarboxylation and formation of **1** (after protonation) after only 30 min (Figure 3A, Figure S18). Similarly, rapid decarboxylation can be achieved by pulling slight vacuum (0.2 atm) on the solution, taking advantage of the low volatility of **3** and DMSO. As control experiments, irradiating **2** with light or heating **3** at 60 °C in the dark did not result in detectable decarboxylation, supporting the need for both base and light to trigger CO₂ release (Figure 3A). Consistently, on/off experiments support that the decarboxylation of **3** largely occurs only with the light on (Figure S20). Overall, these findings support that **3** is able to undergo spontaneous light-driven decarboxylation without the need for an added photocatalyst.

Further experiments were conducted to elucidate the photophysical pathway by which **3** undergoes photodecarboxylation. Cyclic voltammetry (CV) measurements confirm that **3** undergoes oxidation at a relatively moderate potential ($E_{1/2} = +1.15$ V vs. SCE, Figure S26), similar to other benzylic carboxylates.²⁹ By combining reductive CV (Figure S25) and photoluminescence (PL) measurements (Figure S30), the excited state redox potential of **2** ($E_{1/2}^{\text{red}*}$, as a surrogate for **3**) was estimated to be +1.06 V vs. SCE, which is close to that required to photooxidize **3** via an intermolecular pathway. Attempts to collect PL spectra of **3** resulted in multiple emission bands, as irradiation with a 355 nm pump was sufficient to induce decarboxylation and form carbanion **4**, identified by a new emission band peaked at 548 nm (Figure S30). The appearance of the new peak within the time-resolved PL instrument response function (1 ns) led us to interrogate intramolecular photodecarboxylation of **3** as an alternative pathway for CO₂ release.

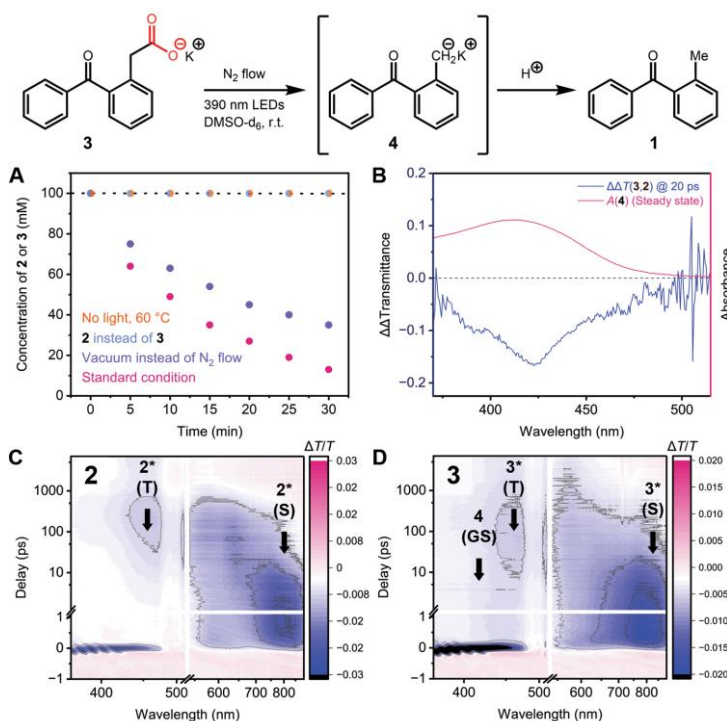


Figure 3. Optimization and spectroscopic investigation of the oxidative decarboxylation of CO₂-adduct 2 or 3.

(A) CO₂ release of 0.1 M of **3** in DMSO-d₆. 0.1 M of **2** in DMSO-d₆ was used for the “**2** instead of **3**” experiment. The “no light” experiment was conducted in the dark with heating in a silicone oil bath at 60 °C.

(B) Difference spectrum obtained from the subtraction of transient absorption spectral slices of **3** by that of **2** at 20 ps (ΔT) compared to the steady state absorption spectrum of **4**. The solution of **4** was prepared *in situ* by mixing 40 mM DMSO solution of **1** and 40 mM DMSO solution of KOTBu.

(C and D) Transient absorption heat map of 20 mM of (C) **2** and (D) **3** in DMSO obtained with 355 nm excitation pulses. In parentheses, S, T, and GS refer to singlet, triplet, and ground state, respectively.

Although various intramolecular photodecarboxylation pathways of arylacetic acids have been proposed,^{30,45,46} we hypothesized that carboxylate **3** may decarboxylate through intramolecular electron transfer via a biradical intermediate, similar to ketoprofen.^{47,48} Using transient absorbance spectroscopy with 200 fs resolution, we sought to capture the formation dynamics of **4** through its unique, red-shifted absorbance spectrum (Figure 3B). Considering first unreactive **2** in DMSO, characteristic signatures of benzophenone intersystem crossing upon photoexcitation were identified: a rapid conversion from a broad, weakly absorbing photoinduced absorption to the stronger, long-lived triplet fingerprint in the >500 nm region (Figure 3C). In photoexcited **3**, we detect the same primary features on the same timescales (Figure 3D), but superimposed upon these is an additional photoinduced absorption band. Subtracting the spectral slices of **3** at 20 ps from those of **2** (ΔT in Figure 3B) to extract the spectrum of the additional species yields an excellent match to the steady-state absorption profile of **4**. This photoproduct signature is evident immediately following the 200 fs instrument response, orders of magnitude faster than would be expected for a bimolecular process dependent on the rate constant of diffusion ($k_{\text{diff}} \sim 1 \times 10^{10} \text{ s}^{-1}$).⁴⁴ We accordingly conclude that the photoinduced CO₂ release process likely follows an

intramolecular pathway. This observation suggests that the addition of base effectively enhances the photodecarboxylation by bypassing the proton transfer step.³⁰

Supported by density functional theory (DFT) calculations, we propose the following mechanism for the fully light-driven CO₂ separation process (Figure 4, see Supplemental Information for details). First, photoexcitation of **1** to **B** ultimately yields (Z)-enol **D** via hydrogen atom transfer to **C** followed by a conical intersection. At this point, two pathways are possible: the photoenol can undergo a DA reaction with CO₂^{25–27} to yield cycloadduct **G'** followed by ring-opening (RO) and PT to form **3**, or it can be deprotonated to yield photoenolate **E**. DFT calculations support that the reaction of photoenolate **E** with CO₂ is significantly faster ($\Delta G^\ddagger = 29.7 \text{ kJ/mol}$) than the reaction of photoenol **D** with CO₂ ($\Delta G^\ddagger = 80.8 \text{ kJ/mol}$). This finding is consistent with the observed enhancement in CO₂ capture observed in the presence of base (Figure 2A) and indicates that the photoenolate pathway likely dominates under basic conditions. Photoenolate **E** can in turn undergo a DA reaction with CO₂ to form a cycloadduct (akin to **G'**, see Supplemental Information) or simply attack it to form **3** directly.^{49,50} Efforts to locate any potential cycloadduct structures were unsuccessful; as such, we favor a mechanistic pathway in which photoenolate **E** directly

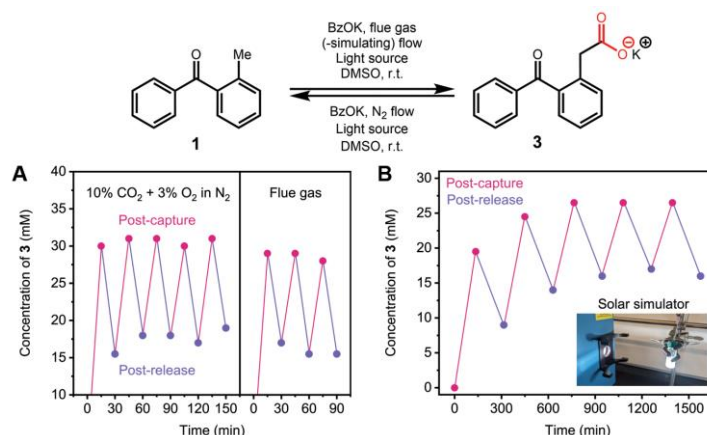


Figure 5. Realistic application of the fully visible light-driven CO₂ separation system.

(A) CO₂ capture and release of 0.1 M of **1** and 3.0 equiv. of BzOK in DMSO from simulated (left) and actual (right) flue gas using 390 nm LED lamps as the light source.

(B) CO₂ capture and release of 0.1 M of **1** and 3.0 equiv. of BzOK in DMSO from a simulated flue gas using a solar simulator as the light source.

Concentration of the CO₂-adduct **3** was determined by ¹H NMR spectroscopy against tetra-*n*-butylammonium hexafluorophosphate as internal standard.

overlaps with the UV-vis absorbance profiles of **1** and **3** (Figure S28). However, solar light represents a more ideal light source for driving carbon capture and release processes. To evaluate the performance of **1** under solar light irradiation, its CO₂ capture cycling performance from a simulated flue gas stream was evaluated using a solar simulator with 2000 W/m² irradiance (2 Suns). Using longer absorption/desorption cycling times to adjust for the decrease in photon flux (Figure S24), an average cycling capacity of 10 mM per cycle was successfully achieved (Figure 5B), which is comparable to that obtained using 390 nm LED lamps (13 mM per cycle). Further, the capture of CO₂ using **1** was conducted on the windowsill on a summer day in Ithaca, New York, United States, and, within an hour, a similar amount of CO₂ was captured from the simulated flue gas stream as achieved using the solar simulator (Figure S22). Similarly, the solar-driven release of CO₂ from **2** was accomplished with reasonable kinetics as well (Figure S23). Overall, these experiments showcase the compatibility of this system for realistic solar-driven applications.

Conclusion

The findings reported herein represent a novel strategy to separate CO₂ from emission streams by harnessing light to drive both the capture and release steps. Application of this system under realistic conditions was demonstrated by capturing CO₂ from an actual flue gas stream as well as by using sunlight as the light source, emphasizing the potential of this system for utility beyond the laboratory. Future work will focus on improving the visible light absorption features of this system to achieve solar light-driven carbon capture with improved efficiency. More broadly, our system operates through a novel photoenolate reactivity mode for CO₂ capture, representing a significant departure from traditional chemistry. Pairing this pathway with

photodecarboxylation enables a fully visible light-driven CO₂ separation that does not require thermal management. Such a combination could provide a blueprint for a new class of chemisorptive chemical separations that employ (sun)light as the only energy input.

EXPERIMENTAL PROCEDURES

Details regarding the experimental procedures can be found in the supplemental experimental procedures.

Resource availability

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Phillip J. Milner (pjm347@cornell.edu).

Materials availability

This study did not generate new unique materials.

Data and code availability

This study did not generate datasets or code.

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AUTHOR CONTRIBUTIONS

Conceptualization: B.I.Z.A., P.J.M.; Methodology: B.I.Z.A.; Investigation: B.I.Z.A., K.Z.C.; Visualization: B.I.Z.A., P.J.M., K.Z.C.; Funding acquisition: P.J.M., B.I.Z.A., A.J.M.; Project administration: P.J.M., A.J.M.; Supervision: P.J.M., A.J.M.; Writing – original draft: B.I.Z.A.; Writing – review and editing: B.I.Z.A., K.Z.C., A.J.M., P.J.M.

DECLARATION OF INTERESTS

P.J.M. and B.I.Z.A. are listed as inventors on a patent that includes a fully light-driven carbon capture process using photoenols (Cornell University, international patent application no. PCT/US24/42589, filed 15 August 2024).

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