Towards Energy-Efficient Direct Air Capture with Photochemically-Driven CO_2 Release and Solvent Regeneration

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Abstract

The intensive energy demands associated with solvent regeneration and CO_2 release in current direct air capture (DAC) technologies makes their deployment at the massive $GtCO_2$/year scales required to positively impact the climate economically unfeasible. This challenge underscores the critical need to develop new DAC processes with significantly reduced energy costs. Recently, we developed a new approach to photochemically drive efficient release of CO_2 through an intermolecular proton transfer reaction by exploiting the unique properties of an indazole metastable-state photoacid (mPAH), opening a new avenue towards energy efficient on-demand CO_2 release and solvent regeneration using abundant solar energy instead of heat. In this Concept Article, we will describe the principle of our photochemically-driven CO_2 release approach for solvent-based DAC systems, discuss the essential prerequisites and conditions to realize this cyclable CO_2 release chemistry under ambient conditions. We outline the key findings of our approach, discuss the latest developments from other research laboratories, detail approaches used to monitor DAC systems *in situ*, and highlight experimental procedures for validating its feasibility. We conclude with a summary and outlook into the immediate challenges that must be addressed in order to fully exploit this novel photochemically-driven approach to DAC solvent regeneration.

1. Introduction

As the name suggests, direct air capture (DAC) removes CO_2 directly from the atmosphere, and thus provides a unique opportunity to restore atmospheric levels of CO_2 to a level needed to mitigate climate change. The most significant challenge in DAC is the very low absolute atmospheric concentration of CO_2 (about 0.04%), thereby requiring solvents capable of binding CO_2 quickly, strongly, and selectively against other components in the air (nitrogen, water, etc.). This results in strong CO_2 binding leading to thermodynamically stable products that consequently require intensive energy inputs and high temperatures to release the bound CO_2 in order to regenerate the solvent.[1 2] In the case of aqueous solvents, the energy requirements are further escalated by the large heat capacity and vaporization enthalpy of water. For conventional aqueous solvents and solid sorbents, *i.e.*, strong alkaline bases and solid-supported amines, the total energy requirements range from 8.4 to 12.5 GJ/ton CO_2 and from 4 to 6 GJ/ton CO_2, respectively.[1] Furthermore, repeated heating of the sorbent/solvent at temperatures as high as 900 °C can cause significant oxidation and thermal degradation of the sorbent/solvent over time.[3] While several emerging approaches to DAC based on either aqueous amino acid (AA) solutions alone or their combination with guanidines can cycle at significantly reduced temperatures,[4 5 6] the regeneration energy still remains substantial due to prolonged heating.[7] Unless this energy demand is significantly reduced, deployment at the $GtCO_2$/year scale necessary to positively impact the climate will remain economically unfeasible. This emphasizes the critical need to develop new DAC processes with substantially reduced energy need for the release and regeneration processes.

To seek energy-efficient DAC approaches, we recently developed a new approach to photochemically drive the efficient release of CO_2 through a deliberate proton transfer reaction via an indazole metastable-state photoacid (mPAH).[8] Through measurements on simulated DAC systems and AA solutions loaded with CO_2 under DAC conditions we demonstrated the feasibility of CO_2 release under *ambient* conditions using light instead of heat. This approach can lead to significant energy savings and extended solvent lifetimes. In this Concept Article, we will describe the principle of photochemically-driven CO_2 release for solution-based DAC systems, discuss the essential prerequisites and conditions to realize this cyclable process. We outline key findings in this field of research and describe approaches to monitor the chemistry of the DAC system *in situ*, which is particularly important for its applications at a technology relevant scale, along with experimental procedures for validating feasibility. Finally, we will summarize the main advances and outline the future research focuses on this promising direction.

2. The case for photochemically driven CO_2 release

Photoacids are a class of organic molecular compounds that increase their acidity by dramatically lowering their pK_a – and therefore the solution pH – upon optical excitation with either UV or visible light.[9-11] This offers an attractive means to photochemically drive efficient release of the CO_2 through a proton transfer reaction using light under ambient conditions instead of thermal- or chemical-swing approaches that are energetically inefficient and unsustainable. This concept of photochemically driven CO_2 release was initially inspired by the observation of carbonic acid formation in aqueous solution.[12] Through optical excitation of an excited-state photoacid, 2-naphthol-6,8-disulfonate (2N68DS), and monitoring infrared-active reporter modes of the reactants and products in a D_2O solution of $NaHCO_3$, Pine, Nibbering and co-workers tracked the ultrafast protonation of various species in solution and their persistence for nanoseconds. Because this photoinduced reaction is governed by a diffusion-assisted bimolecular process and the lifetime of the deprotonated photoacid is only 12.5 ns,[13] high concentrations of bicarbonate anions (0.1 to 0.8 M) and 2N68DS (50 mM) were essential to form carbonic acid at the molecular scale. Obviously, to overcome this significant limitation and yield a *macroscopic* chemical change, reversible photoacids with an extended excited-state lifetime are needed. This need was confirmed by Bennett *et al*.[14] using a different photoacid, a metastable state photoacid (mPAH). This merocyanine mPAH with a deprotonated state lifetime of ~70 s[15] enabled a *macroscopic* pH change and therefore CO_2 removal from a CO_2-saturated aqueous NaOH solution at a concentration as low as 0.1 mM using light.

To exploit this concept for DAC conditions, where CO_2 is captured from very low absolute atmospheric concentration (~420 ppm, 0.04% of air), a sorbent system capable of readily reacting with CO_2 and releasing CO_2 by precisely regulating the solution pH using a suitable photoacid in controllable and reversible manner is needed. Among the various CO_2 solvents that have been demonstrated to date, AAs are our preferred choice owing to their attractive properties for DAC, including non-toxicity, non-volatility, environmental compatibility, and fast reactions with CO_2. Based on this system, a schematic for photochemically-driven CO_2 release and solvent regeneration is depicted in Figure 1. First, in the capture step, an aqueous solution of anionic AAs as sodium or potassium salts (glycine shown), react with CO_2 to form a mixture of carbamates, bicarbonates, carbonates and neutral AAs.[7, 16] Second, upon irradiation, the photoacid undergoes a series of photoinduced conformational changes involving *trans, cis, spiro,* etc. isomers and concomitant intermolecular proton transfer to the solvent (water).[9, 17, 18] For simplicity, only the initial *trans* and final *spiro* isomers are shown in Figure 1 for the forward photoreaction and its reverse reaction in the absence of irradiation. Finally, the subsequent proton transfer to the bicarbonate anion results in formation of carbonic acid (H_2CO_3), which is thermodynamically unstable and can readily convert to CO_2 under ambient conditions. As light irradiation ceases, the photoacid returns to its initial protonated *trans* form and the concomitant pH swing will facilitate the regeneration of anionic state of AAs required for subsequent CO_2 capture cycles. While we illustrate this concept for AAs, this principle is readily adaptable for hydroxide-based DAC solvents as well.

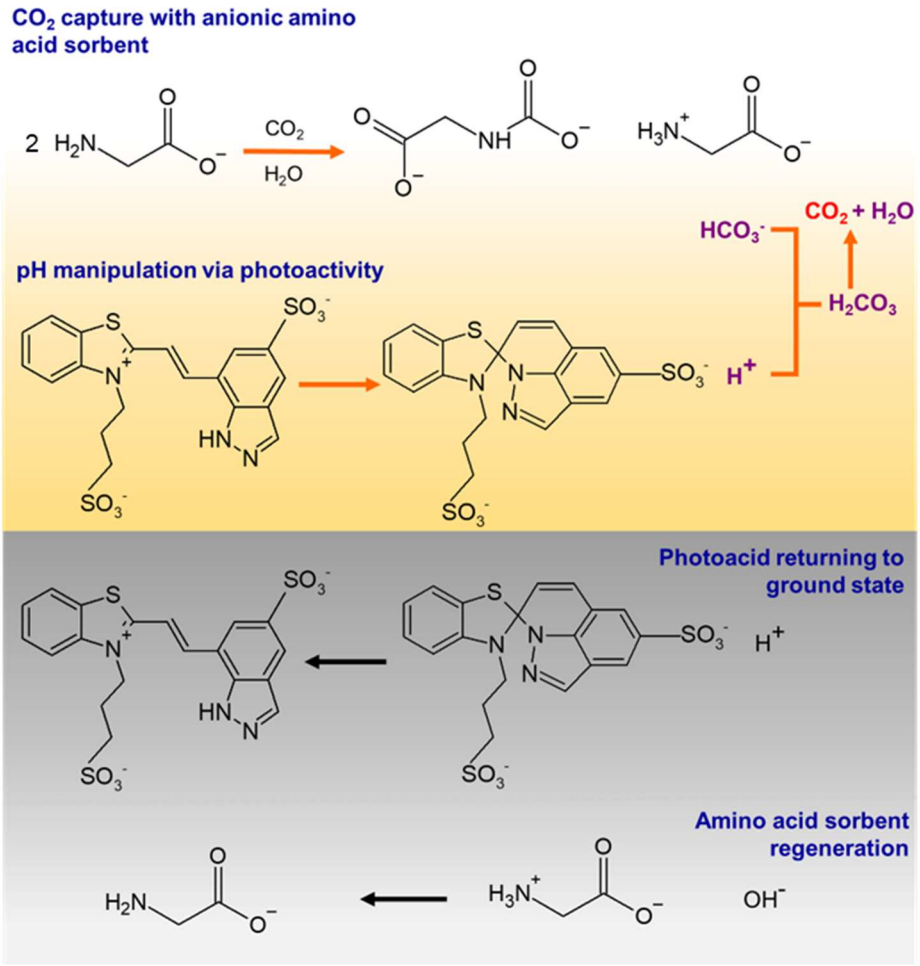

Figure 1: The concept of direct air capture (DAC) using an amino acid (AA) sorbent (glycine shown) and a mPAH for photochemically-driven CO_2 release. Only important species involved in the process are shown for simplicity.

3. Photoacid selection and reaction conditions criteria

3.1. Proton concentration requirement

To realize reversible CO_2 release at *macroscopic* level, any chosen photoacid must meet two critical prerequisites. First, the photoacid must be fully reversible by simply turning off irradiation, thus providing reproducible control of the solution pH. This requirement immediately excludes photoacid generators (PAGs) as possible candidates.[19, 20] Although PAGs can photochemically change to very strong acids and generate a high proton concentration, these changes are generally irreversible, making PAGs impractical for DAC applications. Second, the photoacid must be capable of generating a high proton concentration with high efficiency with a long-lived deprotonated state. This is essential to facilitate diffusion-assisted, intermolecular proton transfer to bicarbonate anions at low and moderate concentrations of both photoacid and bicarbonate anion. This requirement generally excludes extensively studied excited-state photoacids owing to the short lifetimes of their deprotonated states as discussed above.[10, 13, 21, 22] As a result, mPAHs are ideal candidates due to their unique ability to generate a large proton concentration with high efficiency, good reversibility, and an extremely long-lived acidic state with a half-life ranging from seconds to hours.[9,

[18, 23] Such mPAHs are typically build from a push-pull molecular structure that links an electron-accepting moiety with a weakly acidic nucleophilic moiety via a double bond. Upon optical excitation, mPAHs undergo a series of configurational and structural changes including *trans-cis* isomerization or/and cyclization reactions that result in a metastable intermediate, but can be reversed by simply turning off the irradiation and waiting long enough.[9, 23] These photoinduced structural changes offer not only long-lived acidic states but also a straightforward means to control the timescales of these states by altering aqueous solution properties or/and structural modifications to the mPAHs. On the downside, mPAHs are likely to hydolyse in aqueous environments. While the hydrolysis of merocyanines due to limited chemical stability is known,[23, 24] we note that there is no detailed study on hydrolysis of indazole mPAHs so far, in part due to the spectral overlap with the isomers formed in thermal ring-closing or *trans*→*cis* reactions.[25] Nevertheless, previous reports indicate that structural modifications such as 1) adding electron-donating substituents conjugated to the bridging double bond, [24] 2) increasing the length of the alkyl sulfonate side chain,[24] or 3) using different solvent mixtures[26] can potentially improve the hydrolytic stability necessary for prolonged DAC campaigns.

The unique ability of mPAH in the release of captured CO_2 can be assessed quantitatively by light-driven pH changes and CO_2 release. Since the CO_2 release takes place following decomposition of H_2CO_3,[27] a gradual pH increase should accompany this process. This offers a straightforward means to monitor the CO_2 release in real time. In our previous report we demonstrated this pH change using a 1 mM $KHCO_3$ solution as a simulated aqueous DAC system in combination with 1 mM indazole mPAH (Figure 2).[9, 17] Here, we observed a substantial pH increase of ~0.4 units that corresponds to the CO_2 release from the solution. The corresponding pH change in the dark is also shown in the same plot in Figure 2. Through total inorganic carbon analysis using coulometric titration, we further found that ~55% of the total inorganic carbon available in solution was released as CO_2 upon mPAH irradiation, corresponding to ~0.5 mM of CO_2.[8] Both the pH increase and released CO_2 quantity are greater than those obtained using the commercially available, extensively studied excited-state photoacid, pyranine (also called HPTS)[28] in an aqueous bicarbonate buffer system saturated with 15% CO_2, where the photoacid and bicarbonate concentrations are 100 times higher.[29] Specifically, upon irradiation of a 5 mL aqueous solution of 100 mM pyranine and 100 mM K_2CO_3 saturated by 15% CO_2 using a blue LED (427 nm), Seo and Hatton observed a pH increase of < 0.1 unit and a release of ~0.07 mM of CO_2. It is possible that this limited CO_2 release and concomitant pH change may result from the short lifetime of the pyranine deprotonated state (5 ns), but further experimental verifications under similar experimental conditions would be needed to confirm this hypothesis. Nevertheless, these early observations clearly point to the importance of generating and maintaining high proton concentrations for a meaningful macroscopic CO_2 release. This underscores the critical need of a mPAH for the photochemically-driven CO_2 release.

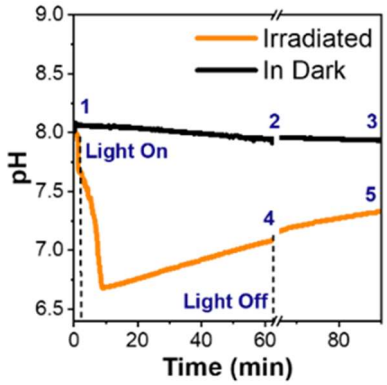

Figure 2. pH measurement as a function of time under light irradaition and in dark for 1 mM indazole mPAH and 1 mM $KHCO_3$. Data is reproduced from Ref. [8], Copyright 2023, with permission from Wiley-VCH.

3.2. pK_a match

While a mPAH is capable of generating a sufficiently high proton concentration to cause corresponding macroscopic H_2CO_3 formation at low bicarbonate concentrations (as low as 1 mM), the a proton generation and intermolecular transfer should *only* occur under irradiation. To meet this requirement, it is important that the pK_a of any chosen CO_2 capturing solvent matches the pK_a of the mPAH in the electronic ground state to avoid *chemical* deprotonation in the absence of irradiation. This requirement is also crucial to enable proton exchange from solvent back to the mPAH in the absence of irradiation to facilitate regeneration for subsequent CO_2 capture cycles. For instance, a typical AA used for CO_2 capture has a pK_a of 8-10. Thus, the pK_a match criteria requires one to use a mPAH with a dark pK_a in the same range. This requirement is readily met by the indazole mPAH.[25]

The sensitivity of this photochemically-driven CO_2 release on the solution pH can be seen by comparing two simulated aqueous DAC systems containing 1 mM indazole mPAH and 1 mM $KHCO_3$ with different initial pH conditions as shown in Figure 3. As discussed previously, for the as-prepared aqueous solution of 1 mM $KHCO_3$ without any pH adjustment, we observed a pH increase of ~0.4 units upon illumination for 60 minutes following the initial photodriven pH drop, as shown by the solid orangecurve in Figure 3. When the initial pH of such an aqueous $KHCO_3$ solution was adjusted to ~9.6 using concentrated KOH solution to closely match the basic conditions typically found in CO_2-loaded aqueous solutions of AAs,[6] we observed a greater pH increase of ~0.6 upon 60 minutes of illumination as shown by the dashed orange curve in Figure 3. This observation shows not only the importance of pK_a matching but also the sensitivity of both mPAH deprotonation and CO_2 release dynamics to the initial reaction conditions. The sufficiently broad pH range that mPAHs can operate further suggests that their applications for photochemically-driven CO_2 release are not limited to a specific CO_2 solvent system. However, we note that the overall pH vs time profiles such as those shown in Figure 3 also depend on the system, chemistry, and efficiencies of these dynamical processes. For instance, if the proton transfer to bicarbonate can take place during the the *trans* → *cis* isomerization process that causes the initial pH drop, one might not observe a dramatic pH drop in the beginning. In another scenario, if the proton transfer to bicarbonate ion is direct and not solvent mediated, the overall CO_2 release process could be faster and consequently the corresponding bulk pH swing would be minimal.

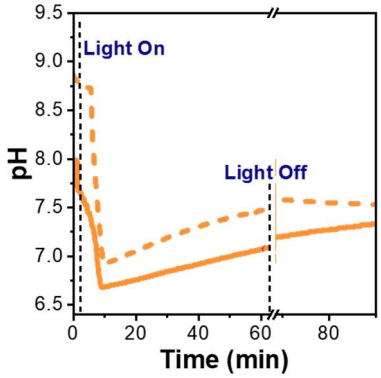

Figure 3. pH changes versus time under irradiation for aqueous solutions of 1 mM mPAH and 1 mM $KHCO_3$ with different intial pH values. Data are reproduced and replotted from Ref. [8], Copyright 2023, with permission from Wiley-VCH.

This pK_a match requirement defines the effective pH range that a CO_2 capture solvent can operate for a given photoacid, which should be between the pK_a in the dark and the pK_a under light of the mPAH.[29] For the merocyanine mPAH used by Bennett *et al.*,[14] which has a dark pK_a of ~6 and light pK_a of 2-3,[23] a CO_2 loaded solvent of low pH was needed. This was realized using 1:1 mixture of NaOH and merocyanine mPAH (10^{-4} M) saturated with CO_2. The pH of the mixture changed from 6 to 9.4 with the addition of NaOH and subsequently to 4.1 after being saturated with CO_2, which is well below the pK_a of the merocyanine mPAH in the dark. Upon irradiation, an increased CO_2 concentration of 0.467% to 0.507% was observed in the headspace. However, since the solution was saturated with CO_2 and the partial pressure of CO_2 in headspace was low, the observed difference between the pHs induced by CO_2 release upon irradiation and slow desorption in the absence of light was small, as shown in Figure 4. This is in direct contrast to the result shown in Figure 2, where the difference between the pH values in dark and under irradiation for the indazole mPAH was significantly larger.

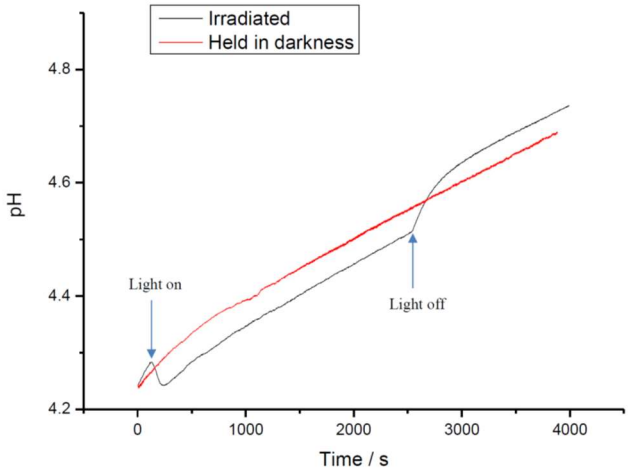

Figure 4. pH response of CO_2 loaded 10^{-4} M solution of MEH and NaOH upon exposure to light (black), with N_2 atmosphere. The difference with the non-irradiated sample (red) is the CO_2 removed from solution by light. Data are reproduced from Ref. [14], Copyright 2017, with permission from Elsevier.

The pH changes with solvents concentrations further require a suitable concentration ratio between a chosen mPAH and its corresponding CO_2 capture solvent such as bicarbonate or AA to trigger the CO_2 release. On the one hand, because the AA solution itself acts as a buffer, the deprotonation of the mPAH upon irradiation cannot significantly alter the bulk pH unless the concentration of mPAH is comparable to or greater than that of the CO_2-loaded solvent. This requirement was validated in our recent measurements on samples containing 1 mM indazole mPAH and higher concentrations of the glycine/CO_2 solutions (10 mM and 0.1 M) that showed no detectable pH change. In contrast, for an indazole mPAH/AA concentration ratio of 2:1, the pH increase was similar to the mixture with a 1:1 ratio. On the other hand, these pH changes can result in partial or even complete mPAH deprotonation prior to irradiation, which, as mentioned above, is not desirable. The concentration of protonated mPAH prior to irradiation depends on the dark pK_a of mPAH, the solvent concentration and loaded CO_2 content. A correlation between the ratio of the protonated photoacid and the total photoacid added into aqueous solutions with varying bicarbonate concentrations in water under 15% CO_2 is detailed in a very recent report by Seo and Hatton.[29]

Similarly, a recent report by Liao and coworkers demonstrated that the mPAHs are capable of retaining their protons prior to irradiation using NMR.[30] Using an aqueous solution containing 10 mM morpholine (with a pK_a 8.5) in its protonated form and an equal molar indazole mPAH with an initial pH of 6.55, the authors found that 4/9 of the photoacid molecules changed to acidic *spiro* isomers in the dark due to proton transfer to morpholines, whereas the rest 5/9 remained as the protonated *trans* isomers. Even with this

partial protonation of morpholines prior to irradiation, it was showed that the system can still repeatedly capture and release CO_2 with a high efficiency under irradiation with visible light.

A very recent study by Lukatskaya and co-workers demonstrated use of solvent mixtures (water–DMSO) to manipulate the solubility and stability of merocyanine photoacids (see Figure 5).[26] The resulting higher photoacid concentration in the presence of the DMSO cosolvent than that in neat water leads to a drastic pH swing and concomitant enhancement in CO_2 release. This approach offers an alternative means to generate high proton concentrations by simply altering the photoacid solubility instead of designing and synthesizing new photoacids.

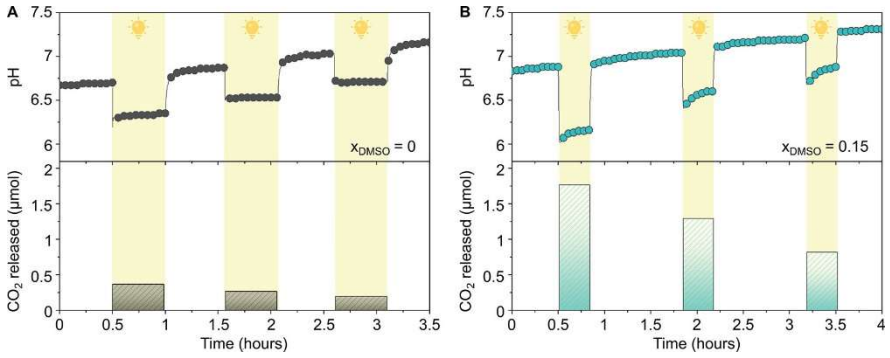

Figure 5. pH change (top) and cumulative CO_2 release (bottom) from a solution with 0.2 mM merocyanine mPAH and 0.2 mM $KHCO_3$ in pure H_2O (A), and 5.3 mM merocyanine mPAH and 5.3 mM $KHCO_3$ in x_{DMSO} = 0.15 (B) while cycling between light (yellow highlight) and dark. Data are reproduced from Ref. [26], Copyright 2024, with permission from American Chemi cal Society.

3.3. Cyclability

A photochemically driven DAC system must be capable of operating for many CO_2 capture/release cycles and solvent regeneration. This cyclability requires that the mPAH deprotonation and accompanying reactions are fully reversible so that the mPAH can be used in subsequent DAC cycles. Although the reverse reaction of an indazole mPAH itself to the initial *trans* isomer in the absence of irradiation is efficient and can be fully completed within 4-6 hours based on pH and absorption spectral measurements,[8] we found that the presence of a weak base in the mPAH solution prevents its full recovery to the *trans* form even after the solution was kept in the dark for an extended time. This partial recovery leads to a reduced pH with respect to that observed prior to irradiation for the first cycle, along with the presence of a mixture of *trans* and *spiro* forms with resolvable peaks at ~290, ~330, and ~411 nm in the absorption spectrum acquired for the solution. This incomplete recovery is likely caused by a more restricted pH change due to the presence of 1 mM $KHCO_3$ and its finite buffer capability, presumably leading to partial deprotonation in the absence of irradiation. The mPAH recovery with and without 1 mM $KHCO_3$ was further found to depend strongly on the wavelength and photon flux of the irradiation.[8] However, even with this partial reversibility, we observed that a second and a third cycles of irradiation on 1 mM indazole mPAH and 1 mM $KHCO_3$ mixture can result in pH increases of ~0.35 pH units/hour and ~0.11 pH units/hour, respectively (see Figure 6a), which are associated with the CO_2 release. Prolonged waiting times (12-24 hours) after irradiation caused a reduced pH condition as demonstrated here for the second cycle in Figure 6a. If the third cycle of CO_2 release is performed instead only 4 hours after the second cycle, a higher pH increment of ~0.31 pH units/hour was observed as shown in Figure 6c. The absorption spectra (Figure 6b,d) taken over the course of the reverse reaction process further show clearly that this extended waiting time yielded an equilibrated mixture of slightly different isomer compositions.[17 18 31] Nevertheless, our results shown in Figure 6

confirm that recovery of the *trans* state takes place simply by turning off irradiation and this cyclability is sufficient to allow subsequent CO_2 release cycles after short periods of equilibration time. We further found that for solutions containing high bicarbonate concentrations as well; for instance, a simulated system with an indazole mPAH: bicarbonate ratio of 1:10, the weakly acidic *trans* form can still be recovered in the dark and is thus usable in subsequent release cycles.

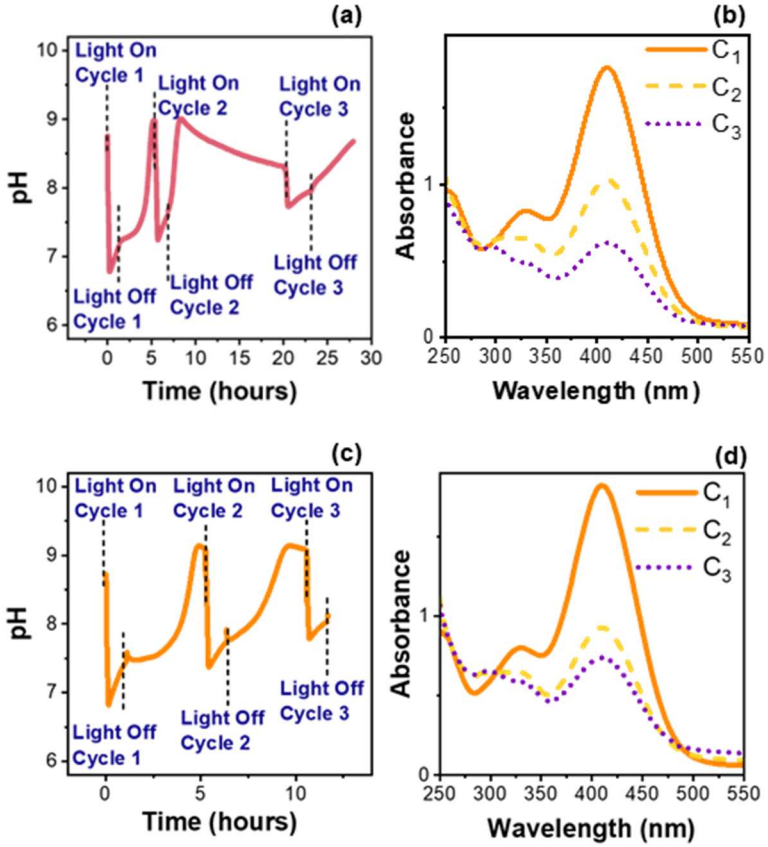

Figure 6. pH curve for subsequent cycles of irradiation of a solution containing 1 mM mPAH and 1 mM $KHCO_3$ (a,c) with the corresponding absorption spectra taken right before irradiation of each cycle (b,d). C_1, C_2, and C_3 refer to first, second, and third cycles of irradiation, respectively. Data are reproduced from Ref. [8], Copyright 2023, with permission from Wiley-VCH.

The cyclability of CO_2 release has been observed for different reaction mixtures loaded with CO_2 through purging with either pure gas or its mixture with other atmospheric components such as N_2. First, Liao and coworkers found that an aqueous solution of morpholine and a different indazole mPAH at an equal 10 mM concentration[30] can repeatedly capture and release CO_2 under moderate irradiation with visible light. The concentration of the released CO_2 over three cycles varied from 1.74×10^3 to 1.50×10^3 ppm, which is close to the total amount captured. Representative data for one cycle is shown in Figure 7. Second, Liu and coworkers demonstrated that a photoswitchable organic molecule can effectively and repeatedly capture CO_2 from the gas phase and release a near-stoichiometric quantity of CO_2 over several dark–light cycles.[32] This single-component solute based approach was accomplished by precisely tuning the pH range of spiropyran photochromic dyes using different substituents to achieve a moderate acidity. The cyclability of the CO_2 release was validated through measurements of both pH and the gaseous CO_2 content using gas chromatography for three capture and release cycles. An equal gaseous content of 46–51 μmol was

determined, corresponding to, on average, 81% of the theoretical capture capability. However, due to the limited solubility of this molecule, a 4:1 DMSO/water mixture was used instead of water. Third, Seo and Hatton demonstrated through gaseous CO_2 detection that cyclable CO_2 release is possible for an excited-state photoacid with a short deprotonated state lifetime[28] and a mPAH with extremely low water solubility.[15, 33] However, the CO_2 release capability was found to be rather limited in both cases. While this may arise from the short lifetime of the pyranine deprotonated state, it is unclear why the CO_2 release capability also remains limited for the merocyanine-mPAH given its long half-life of the proton-dissociation state (~70 s).[15]

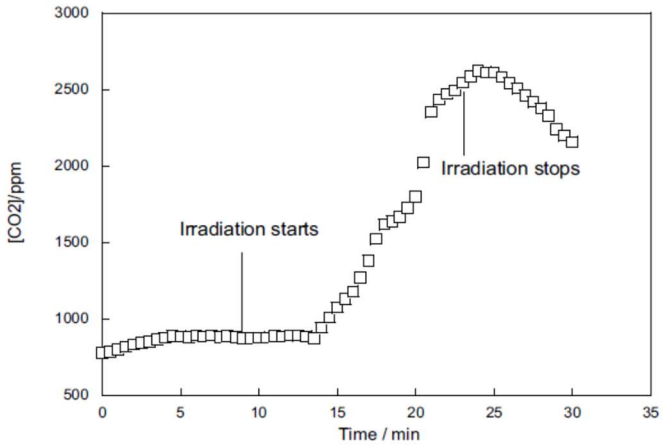

Figure 7. Head space CO_2 concentration change upon irradiation to the photoacid morpholine solution. Data are reproduced from Ref. [30], Copyright 2023, with permission from Springer.

3.4. In situ monitoring of the reaction progress

Since pH measurements are commonly used for monitoring the reaction progress in such a photochemically-driven process, the variation of pH during irradiation and recovery cycles warrants further discussion. From Figures 2, 3 and 6, one can see that the pH increase is observed both during irradiation ($\Delta pH_{Irradiated}$) and after ceasing irradiation (ΔpH_{Dark}), but the underlying mechanisms are fundamentally different. The pH increase in the presence of irradiation corresponds to decomposition of H_2CO_3 leading to CO_2 release, whereas the pH increase in the dark arises from mPAH reverse reaction. The latter was observed not only in the simulated and CO_2-loaded AA-based DAC systems but also in indazole mPAH alone and the indazole mPAH + imidazole systems as described in our previous work.[8] A simple way to distinguish these two processes in bicarbonate containing system is to measure absorption spectra during different reaction stages, which should exhibit decrease or increase of the absorption band peaking at ~411 nm as shown in Figure 8, respectively. As this absorption band is representative of the *trans* isomer (discussed further later), such that changes serve as a direct signature of the forward or reverse reaction of the mPAH in light or dark stages of the cycle. Specifically, we found that the $\Delta pH_{Irradiated}$ does not result from the reverse reaction of mPAH to its initial *trans* form as clearly evident from the absorption spectra in Figure 8a, which should be characterized by a dominant peak at ~411 nm as observed prior to irradiation. Instead, these spectra resemble more closely to the one associated with the *spiro* isomer. More importantly, this $\Delta pH_{Irradiated}$ is only observed for HCO_3^-/CO_2 containing systems and is absent for both mPAH alone and mPAH + imidazole solutions as described in our recent study.[8] Thus, the pH increase observed under irradiation results exclusively from the CO_2 release. Once irradiation ceases, the pH increase, *i.e.,* ΔpH_{Dark} describes solely the mPAH reverse reaction to its initial *trans* form as manifested by the growth of the ~411 nm absorption peak shown in Figure 8b. In contrast to the case with irradiation, ΔpH_{Dark} is found for the simulated and CO_2-loaded AA-based DAC systems, mPAH alone, and mPAH + imidazole systems. This

distinct spectral behavior provides a straightforward means to monitor the state of the DAC system *in situ*, which is important to monitoring the system in real world applications at scale.

To further highlight the fundamental difference underlying the pH increase with and without irradiation, we examined if CO_2 can still be released under the dark conditions immediately after irradiation.[8] When an aqueous solution of 2 mM indazole mPAH alone was first irradiated for 30 minutes to reach a pH value of 5.2 and then immediately mixed with an equivalent volume of aqueous solution of 2 mM $KHCO_3$ in darkness, we observed both pH increase and ~411 nm absorption peak growth in a similar manner as shown in Figure 8b, which are the characteristics of the mPAH reverse reaction. However, only ~3% of the total bicarbonate was converted to CO_2 during the subsequent reaction in the dark. In contrast, when the same experiment was repeated under continuous irradiation, we found conversion of ~50 % of the total bicarbonate in the mixture to CO_2. This observation confirms that continuous irradiation is a requisite for CO_2 release with mPAHs, simply because protonation of mPAHs would otherwise reduce or even eliminate the protons available for H_2CO_3 formation and subsequent CO_2 release. It also points to a potential means for enabling *on-demand* CO_2 release by simply turning the irradiation on or off, which would be beneficial in the context of CO_2 storage and conversion into value-added products.

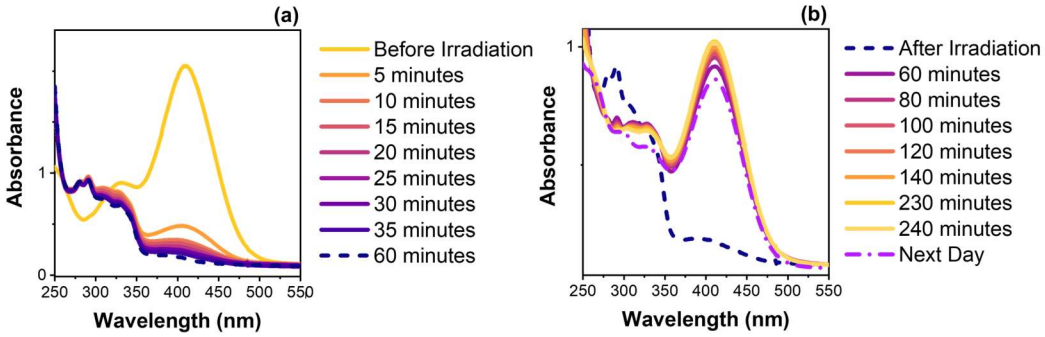

Figure 8. Absorption spectra acquired for a solution of 1 mM mPAH and 1 mM $KHCO_3$ during irradiation (a) and regeneration in dark (b). Data are reproduced from Ref. [8], Copyright 2023, with permission from Wiley-VCH.

3.5. Validation of CO_2 release

Although pH measurements in real time can provide a straightforward means to monitor CO_2 release, the results offer only indirect evidence for the feasibility of this photochemically-driven CO_2 release. Direct validation of these results must be made to quantify the release of CO_2 from both the simulated and AA based DAC systems. Several approaches can be used for this validation, including NMR spectroscopy, total inorganic carbon analysis, gas chromatography,[32] mass spectrometry based technques, optical spectroscopic approaches such as Raman, FTIR gas analysis, and gaseous CO_2 detection using CO_2 monitors,[8, 29, 30] etc. Similar to Liao's measurments (Figure 7), here we show the evidence for CO_2 release using a CO_2 meter (Figure 9) by measuring the amount of gaseous CO_2 present in the headspace of a reactor containing either a mixture of 1 mM $KHCO_3$ and 1 mM indazole mPAH or 1 mM glycine loaded with CO_2 and 1 mM indazole mPAH. A clear increase in the CO_2 content upon irradiation was observed in both cases for one and three repeated cycles, respectively. In our recent proof-of-principle study,[8] we also utilized NMR spectroscopy, thermogravimetric analysis-mass spectrometry, and total inorganic carbon analysis to obtain a more quantitative validation of the CO_2 release. For instance, total inorganic carbon analysis shows that irradiation of 1 mM and 20 mM aqueous solutions of CO_2-loaded glycine solutions with equal concentrations of mPAH resulted in approximately 68% and 78% reduction in the inorganic carbon content,

respectively. As mentioned earlier, for the simulated DAC systems containing aqueous solution of 1 mM mPAH and 1 mM $KHCO_3$, we found that ~55% of the total inorganic carbon available in the solution was converted to CO_2 upon irradiation.

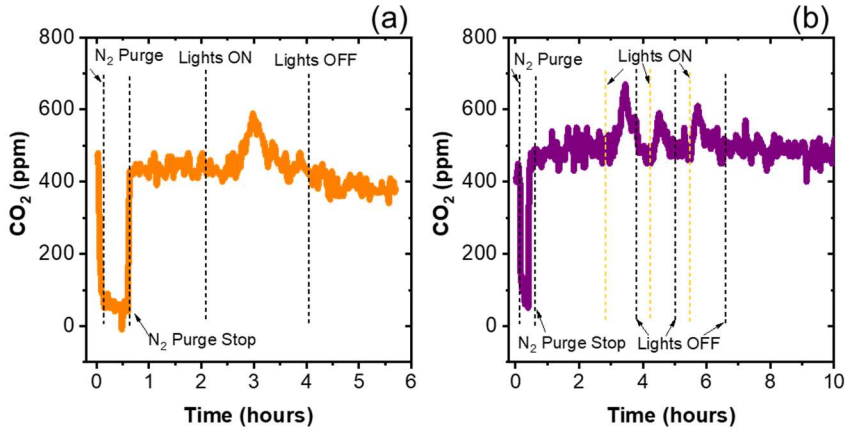

Figure 9. CO_2 sampled from the headspace of a reactor containing a mixture of 1 mM mPAH and 1 mM $KHCO_3$ (a), 1 mM CO_2 loaded glycine and 1 mM mPAH (b). Initially nitrogen was purged into the headspace to ensure calibration of the CO_2 sampling data logger, and a clear increase in the CO_2 content was found upon irradiation. Data are reproduced from Ref. [8], Copyright 2023, with permission from Wiley-VCH.

4. Summary and Outlook

In our recent proof-of-principle study,[8] we have demonstrated the feasibility of photochemically-driven CO_2 release using an indazole mPAH for DAC through pH measurements under various conditions and validation using a suite of spectroscopic, mass spectrometric, and titration methods. The chemical reversibility of mPAH in response to irradiation variations and the involvement of different mPAH isomers with distinct spectroscopic features enable not only cyclability for subsequent CO_2 releases, but also a straightforward means to monitor the progression of this complex photochemical reaction that is crucial for practical implementation of this technology. The distinct spectroscopic features further provide a valuable means to probe and understand the mechanistic steps of efficient CO_2 release, and the information gained would in turn guide the design and synthesis of new photoacids for DAC applications. Of particular interest is the generation of long-lived deprotonated states using such a mPAH, which enable realization of macroscopic CO_2 release at a relatively low concentration of mPAH. These findings open a new route towards developing photochemical approaches for CO_2 release and solvent regeneration processes through designing molecular systems suitable for a wide variety of capture solvents.

To explore full potential of this novel photochemically-driven approach, several immediate challenges must be addressed. First, most of the studies reported so far are relied on gaseous CO_2 purging in the capture process.[14, 29, 30, 32] The much greater concentrations used in these studies than the atmospheric concentration of CO_2 (about 0.04%) raises a crucial question about the feasibility of these systems to operate under actual DAC conditions. Obviously, direct validation of this feasibility would be highly desirable. Second, while we have demonstrated that it is possible to photochemically drive CO_2 release under the basic condition of a *real* DAC system composed of AAs and mPAHs, solvent regeneration in the absence of irradiation remains underexplored. Specifically, identification of the precise experimental conditions for AA regeneration such as the optimal pK_a needed for both AA and mPAH solutions, their concentration ratios,

durations for light on/off, and detailed chemistry of the system is still needed. Such experimental conditions should enable realization of both efficient proton exchange between the mPAHs and the AAs in the absence of irradiation to achieve solvent regeneration for subsequent cycles and macroscopic CO_2 release with high efficiency and satisfactory cyclability for any chosen photoacid. Third, although our recent work has uncovered a profound effect of light intensity and wavelength on the CO_2 release,[8] further detailed studies are needed to examine how one can use this parameter space to control and optimize the CO_2 release and solvent regeneration. Of particular interest is to identify a suitable irradiation photon flux and duration for optimal DAC performance based on this photochemical approach. Similarly, determination of the quantum yield of this photochemically-driven approach, *i.e.*, the number of photons absorbed per released CO_2 molecule, and its potential variation with irradiation wavelength is also important. To our knowledge, the only quantum yield of 1.3 % was reported by Liu and coworkers[32] using actinometry based on nanosecond transient absorption spectroscopy. The determination was made indirectly by monitoring proton escape kinetics from a protonated merocyanine using an aqueous $Ru(bpy)_3^{2+}$ solution as standard. Direct determination can be accomplished using a suitable chemical actinometer[34] to determine the number of photons being absorbed in combination with total inorganic carbon analysis to estimate the amount of released CO_2 molecules.[8] Fourth, the photochemically-driven CO_2 release in the DAC system containing a CO_2 capture solvent and a photoacid involves intermolecular proton transfer and slow diffusion of both protons and bicarbonate anions. To minimize this diffusion process and accelerate the CO_2 release and solvent regeneration, the single-component solute based approach reported by Liu and coworkers[32] holds promises for more rapid capture and release. Similar, chemically linking one or more solvent molecules with a photoacid molecule should also enable to speed up the proton transfer to bicarbonate anions and thus accelerate the CO_2 release. Finally, design and synthesis of new mPAHs with significantly improved solubility in water and enhanced overlap with the solar spectrum is highly desirable, which will help to push this novel approach to a concentration regime relevant to DAC technologies driven by abundant and sustainable sunlight. Wavelength tuning can be further employed to achieve specific and reversible pH changes using reversible photoacids as demonstrated by Wimberger *et al*.[35] Similarly, Liao and coworkers also reported a reversible photoacid that switches between high- and low-acidity states when irradiated with different wavelengths of light.[36] These reports suggest a promising route towards light stimulated control for CO_2 release, photoacid recovery, and CO_2 absorbent regeneration by manipulating various parameters such as wavelength, bandwidth, and photon flux. In the meantime, fundamental understanding of the mPAH chemistry and isomerization equilibria by combining theory and experiment, especially ultrafast optical spectroscopy to follow the complex photo-driven reaction in real time and identify the various reaction intermediates will be crucial for optimization of the CO_2 release and solvent regeneration towards a practical photochemically-controlled DAC process.[31, 32, 37] These results will provide new avenues to understand light-driven acid-base chemistry that is the key to CO_2 release in the absence of external heating.

Furthermore, it is also equally important to forecast on the practicality of this photo-driven approach. While using this approach can sidestep the substantial energy and cost needs in the existing DAC technologies for CO_2 release and sorbent regeneration, future research on large scale production of photoactive materials, along with structural modifications to improve their solubility, stability, fast recovery and cyclability will be necessary to enable this novel approach economically feasible. Once the photoacid properties are improved to be highly soluble with faster recovery timescales, this photochemical approach could potentially be used in point-source applications as well. Because the main limitation in implementing this photochemical approach with concentrated CO_2 streams is related to their low solubility and time taken for the regeneration of the photoacid. In addition, development of new photoacids with extended absorption spectral range, enhanced working pK_a range, and high quantum yield will also benefit practical applications.

Although this photochemically-driven CO_2 release for energy-efficient DAC is still in its infancy, we are confident that it holds enormous potential to substantially decrease the energy demand of existing DAC technologies. Given that the photon flux density used for our proof-of-principle study (500 μmol/m^{2}s) is identical to the maximum solar radiation under the short-day condition (8 h light/16 h dark) in

photosynthesis,[38] we envision that through turning the absorption spectrum of mPAH to enhance its the spectral overlap with solar spectrum it would be entirely possible to realize CO_2 release using abundant solar light during daytime and to regenerate the AA sorbent in the nighttime. Successful development of this novel approach will create a new generation of sun-driven DAC technologies.

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Keywords

Absorption, Amino acids, Carbon capture, CO_2 release, Metastable compounds, Photochemistry, Protonation/Proton transport

Conflict of Interest Statement

There are no conflicts of interest to declare.

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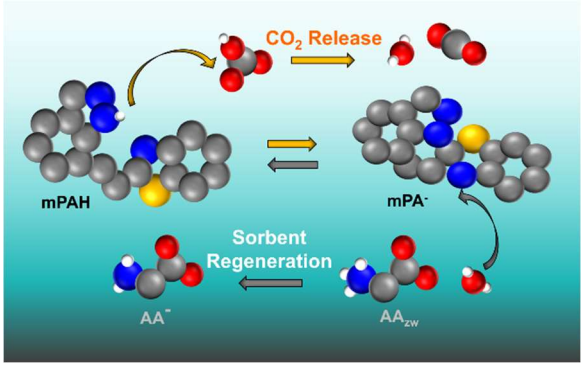
Table of Contents

An ideal direct air capture process using solvents must include means to release captured CO_2 in parallel to solvent regeneration in an energy efficient way. A potential solution is to use light-driven solution chemistry. Herein a metastable-state photoacid can alter the solution pH to convert captured CO_2 in the form of bicarbonate ions to CO_2 under ambient conditions.



Biographical Information

Uvinduni I. Premadasa: Uvinduni is a Research and Development Associate in the Chemical Sciences Division at Oak Ridge National Laboratory. After completing her B.S from University of Peradeniya, Sri Lanka, she entered Ohio University, Athens, USA for graduate studies under the supervision of Prof. Katherine Cimatu. Uvinduni's Ph.D dissertation was focused on understanding structures and molecular interactions at liquid interfaces using vibrational sum frequency generation spectroscopy. She then joined Oak Ridge National Laboratory in 2020 as a postdoctoral researcher and worked with Dr. Benjamin Doughty and Dr. Yingzhong Ma to investigate complex biosystems and chemistries using new nonlinear microscopy tools, while continuing her research on interfacial chemistry, photochemistry using nonlinear spectroscopic tools. Her research evolves around the concept of using light to drive reactions and understand chemistry in solutions and at interfaces.

Benjamin Doughty: Ben received his Ph.D. in 2010 from the University of California, Berkeley where he probed ultrafast electronic dynamics in atoms and small molecules using femtosecond soft light sources. From there, he worked as a postdoc at Columbia University where he developed new approaches to probe reaction kinetics, equilibrium structure, and binding affinities of biological molecules at interfaces. In 2013 Ben joined ORNL as a Wigner fellow and has since become a Senior R&D staff member. His current research interests include understanding complex chemistries away from equilibrium in the context of carbon capture, ion separations, and field-driven assembly.

Radu Custelcean: Radu was born and grew up in Transylvania, Romania. After completing his undergraduate and master education from Babeş-Bolyai University, Romania, in 1996, he continued his studies in Chemistry at Michigan State University in the US, where he received his Ph.D. in 2000 for work with James E. Jackson on structure and reactivity of dihydrogen-bonded crystals. After a postdoctoral training in crystal engineering at the University of Minnesota with Michael D. Ward, and a short research stint at Washington State University where he studied molecular crystals under high pressure, he started his independent career in 2003 as a research scientist at Oak Ridge National Laboratory.

Radu's research interests are in the areas of self-assembled molecules and materials for environmental and energy applications, separation science and technology, supramolecular chemistry, and crystal engineering. Over the past 7 years, Radu has been involved in basic and applied research directed toward atmospheric CO_2 capture, aka direct air capture (DAC) using aqueous organic bases such as amino acids or guanidines and employing principles of physical organic chemistry and crystal engineering. His ultimate goal is to develop energy-efficient, cost-effective DAC technologies that will help address climate change.

Ying-Zhong Ma: Ying-Zhong Ma is a Senior Scientist in the Chemical Sciences Division at Oak Ridge National Laboratory. He earned his B.S. and M.S. at Harbin University of Science and Technology and Changchun Institute of Physics, Chinese Academy of Science, respectively. After completing his Ph.D. in Umeå University under the supervision of Prof. Tomas Gillbro, Yingzhong conducted research first in Prof. Alfred Holzwarth's group at the Max-Planck Institute for Radiation Chemistry, and subsequently in Prof. Graham Fleming's lab at the University of California, Berkeley. His current research interests include ultrafast electronic excited-state phenomena in spatially

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