A Novel Approach to Organic Liquid Co-Catalyzed Photosynthesis of CO

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Abstract:

The activation of thermodynamically stable CO2 by metal catalysts or metalloenzymes is necessary for the conversion of CO2 to chemical feedstocks, which is of major relevance. Metal-free organ catalysts for application in CO2 activation at ambient settings have been developed recently, providing new opportunities for Chemistry of carbon fixing. Here, we detail ionic liquid-mediated CO2 collection and activation coupled with photo redox catalysis for CO synthesis. It has been shown that the activation and reduction of CO2 is profoundly affected by the chemical nature of the anions and the organic functional groups on the imidazolium cations of ionic liquids, as well as the reaction media. By connecting ionic liquid-based materials with chromophore molecules, this photochemical pathway offers novel possibilities for carbon fixation by rationally designed chemical systems, allowing us to overcome the formidable obstacles in artificial photosynthesis.

INTRODUCTION

The process of turning carbon dioxide (a key component of natural photosynthesis) into value-added molecules (such as methane, methanol, carbon monoxide, and sugar) has gained great interest because to its significance in the chemical industry, geopolitics, and carbon recycling.Plants, algae, and cyanobacteria are examples of photosynthetic organisms that utilize carbon dioxide (CO2), water, and sunlight to create carbohydrates for the plant and oxygen for the atmosphere via a process termed photosynthesis (ecosystems 1-6). The artificial conversion of very inert CO2 often necessitates the activation of transition metal catalysts with many redox states, followed by integration to reduction processes through multi-electron transfer connected with protons to avoid high energy intermediates.A crucial step forward in C1 chemistry has been the discovery of metal-free organ catalysts for the binding and activation of CO2 at room temperature and atmospheric pressure (Fig. 1)7-10. These substrates include frustrated Lewis pairs (FLPs), carbenes, bicyclic amidines, and ionic liquids (ILs). FLPs were shown to be effective catalysts for the transformation of carbon dioxide into methanol and methane. Diphenyl silane is the stoichiometric reductant12 in the reductive deoxygenation of CO2, and the zwitterionic NHCNCO2 adducts produced by the N-heterocyclic carbene (NHC) are critical intermediates in this process. Rosen et al. thirteen recently shown that the electrochemical reduction of CO2 to CO may be accelerated at a low overpotential of 0.17 V by using 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid as the CO2 coordinating sub- strata in water. The weak interaction between a large organic ion and a charge-delocalized inorganic/organic anion may produce inorganic liquids (ILs), which are molten salts, at ambient temperature. The scientific and technological relevance of ionic liquids stems from their versatility as lubricants, electrolytes, catalysts, and gas capturers15–17. Given their wide range of applications, ILs' potential use as environmentally friendly solvents18-22 is of particular interest. These characteristics include high polarity, strong ionic conductivity, low volatility, and chemical compatibility. Because of their versatility and tunability, room temperature ILs (RTILs) may be used in the creation of reversible CO2 capture systems with excellent adsorption capacities. At ambient pressure, the gravimetric capacity of amine-functionalized task-specific ILs (TSILs) for CO2 collection is reported to be 7% (0.5 mol CO2 per mol of the TSIL), but kinetics23 is severely limited by viscosity. Furthermore, the manufacture of amine functionalized TSIL requires a number of synthetic and purification steps. In a recent study, Dai's team demonstrated the feasibility of rapid and reversible CO2 collection by synthesizing basic and superbase-derived ILs with an equimolar absorption capability24. In addition, by combining ILs with alkanolamines25, significant quantities of reversible CO2 collection have been produced in IL solvents. It is interesting to note that the carbon atoms in the aforementioned

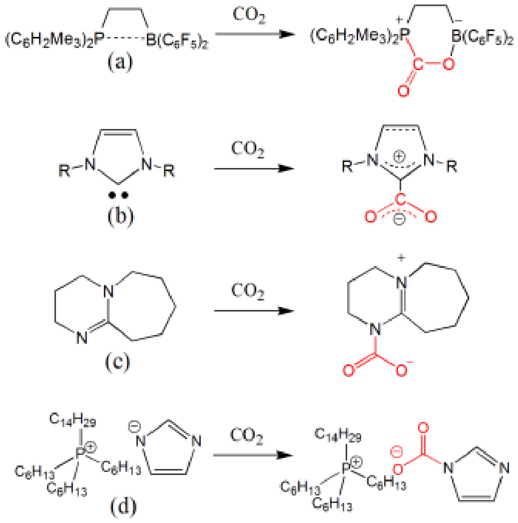


Figure 1 | Metal-free organ catalysts for CO2 activation by coordinating with frustrated Lewis's pair (a), N-heterocyclic carbene (b), bicyclic amidine (c) and ionic liquid (d).

Carbamates are generated in capture systems when CO2 binds to the amines linked to the cations (or anions) of ILs, or to the amino groups. This technique is like the first phase of photosynthesis in plants. biosynthetic cycle twenty-six in which CO2 is initially bonded to nitrogen atoms, producing reactive carbamate intermediates. As a result, we are inspired to improve synthetic photosynthesis by using the unique coordination chemistry of Erstwhile ILs have been suggested for future carbon photo-fixation in high-pressure biphasic ILs-CO2 (liquid) systems13,23-25,27,28, combining IL chemistry with photo redoxorganocatalytic to perform gas CO2 fixation with visible light under ambient circumstances is seldom explored. In this paper, we discuss the potential of ILs to facilitate CO2 collection in the wild and how this may be integrated with a conventional photo redox catalytic cycle to generate CO2. This novel IL-promoted CO2 photoconversion protocol was first tested using a photochemical tandem system consisting of a light sensitizer/electron mediator catalyst combination of [Ru(by)3] Cl2(bpy52,29-bipyridine) and CoCl2?6H2O, triethanolamine (TEOA) as an electron donor, and a visible light source. The method works in tandem with ILs to hasten CO2 photochemical reduction under mild conditions in a variety of solvents.

Results

To split CO2 into CO and [O] in an aqueous media by photocatalysis, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]) was first developed as an RTIL, accompanied by the. TEOA's oxidative dehydrogenation to produce hydrogen gas (H2). The two-electron two-proton reduction cycle was completed when some of the produced H2 (2H1 1 2e2) accepted the [O] to create H2O. Overall, CO2 2H1 2e2R CO 1 H2O is formed. Several benchmark tests were developed to highlight the significance of ILs in reactions and to improve reaction settings. Table 1 summarizes the findings. No gas is found in the system when the lights go off. When nevertheless, visible light was used to illuminate the system.

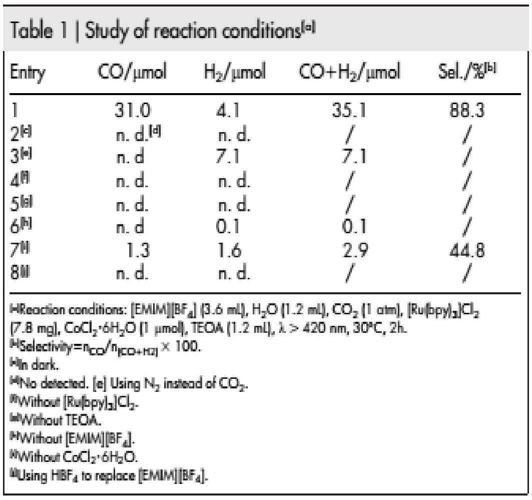


Table 1 | Study of reaction conditions[a]

Entry	CO/μmol	H_2/μmol	CO+H_2/μmol	Sel./%[b]
1	31.0	4.1	35.1	88.3
2[c]	n. d.[d]	n. d.	/	/
3[e]	n. d	7.1	7.1	/
4[f]	n. d.	n. d.	/	/
5[g]	n. d.	n. d.	/	/
6[h]	n. d	0.1	0.1	/
7[i]	1.3	1.6	2.9	44.8
8[j]	n. d.	n. d.	/	/

[a] Reaction conditions: [EMIM][BF_4] (3.6 ml), H_2O (1.2 ml), CO_2 (1 atm), [Ru(bpy)$_3$]Cl_2 (7.8 mg), $CoCl_2 \cdot 6H_2O$ (1 μmol), TEOA (1.2 ml), λ > 420 nm, 30°C, 2h.
[b] Selectivity=$n_{CO}/n_{(CO+H2)}$ × 100.
[c] In dark.
[d] No detected. [e] Using N_2 instead of CO_2.
[f] Without [Ru(bpy)$_3$]Cl_2.
[g] Without TEOA.
[h] Without [EMIM][BF_4].
[i] Without $CoCl_2 \cdot 6H_2O$.
[j] Using HBF_4 to replace [EMIM][BF_4].

At a reaction rate of 15.5 mmol/h, CO2 molecules were photocatalyzed into a more reactive CO species (entry one, table 1), while H2 was released at a rate of 2.1 mmol/h. These Experiments show conclusively that the excited state of the dye is involved in the catalytic cycle. Syngas, mostly composed of carbon monoxide and hydrogen, is used as a carbon feedstock in the chemical industry to produce a wide variety of synthetic value chemicals (such as die- sell, methane, methanol, and dimethyl ether)30.In the absence of [Ru(by)3]Cl2, TEOA, or [EMIM][BF4] (entry 4-6, table 1), no response was seen in the control trials. When HBF4 was utilized in lieu of [EMIM][BF4], it was discovered that neither CO nor H2 could be created (entry eight, table 1), ruling out the possible promotional impact of the BF42 anion (note that CO2 is known to form weak complexes with BF42 anion). This strongly suggests that the imidazolium cation plays a crucial role in the CO2 to CO conversion reaction. As predicted, the quantity of CO and H2 produced in this reaction was drastically reduced when Co 21 was not present to function as an efficient electron transport carrier (entry 7, table 1).When N2 was introduced into the system in lieu of CO2, it was noted that only H2 gas was identified under the reaction conditions and no CO was found, confirming the involvement of CO2 in the process. H2 is produced when light-induced electrons decrease proton in the absence of CO2. However, the overall efficiency of the photo-chemical reduction process was enhanced in the presence of CO2 caught by the [EMIM][BF4]-TEOA system (termed as *CO2 to distinguish from inert CO2). Under these experimental circumstances, the photogenerated electrons clearly have a kinetic advantage over the proton beams used in previous attempts to reduce *CO2. Bockius and colleagues argue that the creation of a "CO22" intermediate, with a strong negative formation potential in water and in most organic solvents31, is the initial stage in the CO2 conversion process, making a large over-potential normally necessary for this reaction to occur. According to reports13,32, [EMIM][BF4] may significantly reduce the barrier to the process by lowering the free energy of CO2 production through complexation (with EMIM1). As a cocatalyst that lessens the potential for production of the CO22 species, IL is advantageous not only for CO2 capture but also for CO2 activation. There was also an examination of how the [EMIM][BF4]/H2O ratio affects CO2 removal. Increases in CO and H2 production with increasing [EMIM][BF4]/H2O ratios are shown in the inset of Fig. 2, demonstrating that a high concentration of IL plays a significant role in boosting photocatalytic activity for CO2 reduction. When H2O was taken out of the equation, however, CO and H2 production activity dropped significantly. Without water, the reaction must gradually build up its momentum.

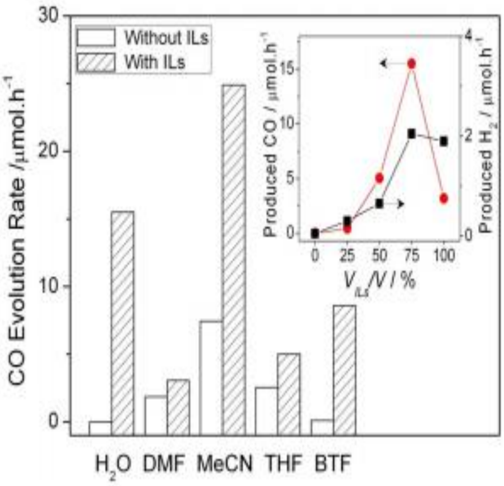


Figure 2 | The promotional effect of ILs on CO2 photo fixation in various

solvents. (DMF: N, N-dimethylformamide. Men: acetonitrile's:tetrahydrofuran.BTF: benzenyltrifluoride). The inset is the effect of [EMIM][BF4]/H2O ratio on the photocatalytic reduction of CO2.The electron and hole like to react with other charged particles. This finding suggests that IL and H2O interact mutually, with the latter serving as a pivotal part in enhancing photocatalytic activity for CO2 reduction. The IL-promoted CO2 photoreduction system was next tested in a variety of reaction media to ascertain the breadth of the ILs' promotional impact and to choose an IL-coupler as reaction medium that would allow for the most effective photo fixation of CO2. DMF, Men, THF, and BTF were only some of the solvents used in the CO2 reduction process. Resulting figures are shown in Figure 2 and Figure S1, respectively. Remarkably, the addition of [EMIM][BF4] improved the photocatalytic reactivity of all solvent systems toward CO2 reduction. The CO evolution rate (CER) in the IL-Men combination was 26.3 mmol/h, while the H2 evolution rate (HER) was 2.1 mmol/h. When IL was added to the mix, the output of CO increased far more than H2 production did, once again demonstrating the enhanced kinetics of IL for CO2 activation and conversion. Therefore, the system's selectivity towards CO was being drastically altered by the addition of IL. It is preferable for carbon fixation to take place in a reaction media containing water since the goal of artificial photosynthesis is to connect CO2 fixation with water splitting. Therefore, the impact of H2O on the IL-Men system was investigated. Addition of 15% H2O was shown to improve CER from 26.3 to 64.0 mmol/h (TOF56.4/h), whereas the optimal quantity of water for boosting HER was found to be 8% (Fig. S2). It has been observed that the potabilization of a ligand from [Ru(by)3] twenty-one has a considerable influence on the generation of the active catalytic spa- cies33, thirty-four when water is added. CER is consistent with the somewhat increased conductivities seen in water-containing substrates (Table S1). The improved activity may be attributable, in part, to the higher conductivity of the electrolyte, which enhances the fluid environment's capacity to assist the electron transport throughout the reduction operation. Under the monochromatic irradiation at l5420 nm, the calculated global apparent quantum yield of this improved IL- promoted CO2 photoreduction system was 12.3%. Researchers found a non-linear connection between the quantity of CO/H2 produced and the reaction time by studying the CO/H2 evolution as a function of reaction time (Fig. 3). Total CO2 and H2 generation peaked after 4 hours of illumination and thereafter rose. This is in keeping with the fact that Ru-based dyes are intrinsically unstable after several cycles in photochemical applications33,34. As a result.

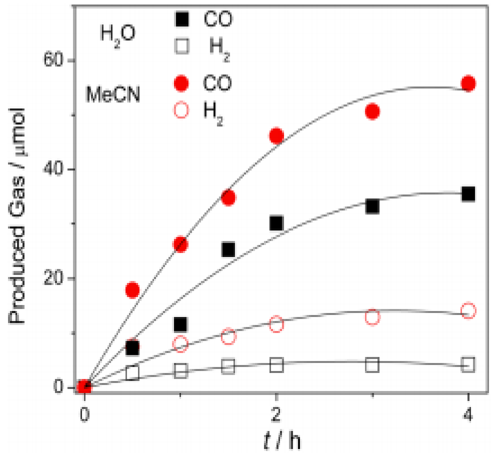


***Figure 3** | The amount of CO and H2 produced from the IL-promoted CO2 conversion system as a function of reaction time under visible light illumination.*

light energy transducers such as super-molecular and polymeric semiconductors are promoted for usage in conjunction with ILs to reduce carbon dioxide emissions. There is a current development in this area of this laboratory we have.

Discussion

CO production trends were found to be in good agreement with the antenna molecule's optical absorption spectrum, as shown by the wavelength dependency of CO evolution (Fig. 4). This study contributes new verification that charge photo-generation, separation, and subsequent tandem electron transfer were crucial steps in the CO2 reduction process.Different ILs were used in the reaction system (as seen in Fig. 5) to learn more about how the counterions, and substituents of the organic components affected the photochemical reduction of CO2. As can be seen in Table 2, the various counterions tested had a significant impact on the CO2 photo-reduction efficiency. The photocatalytic generation of CO and H2 was enhanced by the Tf2N2 anion, which outperformed other anions such L-L2, TfO2, Ac2, DCA2, and BF42. It is well known that the low viscosity given by the Tf2N2 anion's excellent structural symmetry is beneficial for reaction kinetics35. Both

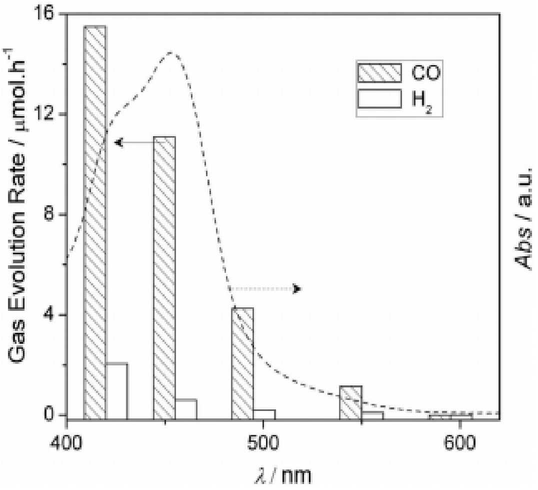


***Figure 4** | The dependence of the wavelength of incident light on the gas evolution rate of CO and H2 from the CO2 photoreduction system in [EMIM][BF4]-H2O medium*

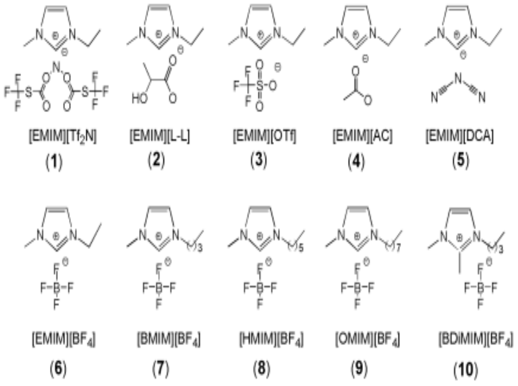
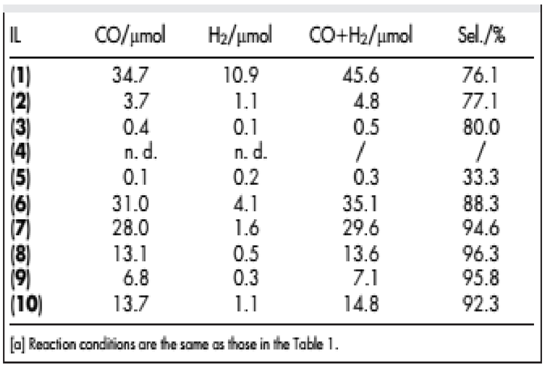


Figure 5 | Chemical structures of various ionic liquids corresponded to those in Table 2 for the photocatalytic conversion of CO2 to CO under mild conditions.

The interaction between the ILs and CO236 is known to be enhanced by the presence of a fluoroalkyl group and by the presence of Tf2N2 with a high ionic size. When the 1-position imidazolium ring's substituted alkyl chain was lengthened from activity for the generation of CO reduced successively from ethyl to octyl. The activity also dropped when a methyl group (10) replaced the hydrogen (H) at position C (2) of seven. The longer the carbon chain, the more van der Waals interactions and the heavier the molecule, both of which contributed to the lower yields. Low reactivities36 result from the limited catalytic kinetics caused by these factors and the higher solvent viscosity. These findings highlight the fact that the counterions and the organic functional groups on ILs, which determine properties of ILs like viscosity, conductivity, polarity, dielectric constant, and acid-base chemistry, are closely related to the promotional effect of ILs in the photochemical reduction of CO2. Because of this, ionic liquids are a viable option for supporting CO2 photochemical reduction because of the large variety of cations and anions that may be combined infinitely. In conclusion, the conversion of CO2 to CO under moderate, ambient conditions has been achieved by combining CO2 binding and activation by ILs with photo redox catalysis. The organic functional groups on the imidazolium cation and the chemical characteristics of the counterions play a significant role in the ILs' pro- emotional impact in CO2 photochemical reduction. As a result, IL chemistry is opening the door to novel approaches to organocatalytic synthesis of important compounds from CO2. Under moderate circumstances, photocatalytic conversion of CO2 to CO is shown in Table 2 below.



IL	CO/μmol	H_2/μmol	CO+H_2/μmol	Sel./%
(1)	34.7	10.9	45.6	76.1
(2)	3.7	1.1	4.8	77.1
(3)	0.4	0.1	0.5	80.0
(4)	n. d.	n. d.	/	/
(5)	0.1	0.2	0.3	33.3
(6)	31.0	4.1	35.1	88.3
(7)	28.0	1.6	29.6	94.6
(8)	13.1	0.5	13.6	96.3
(9)	6.8	0.3	7.1	95.8
(10)	13.7	1.1	14.8	92.3

[a] Reaction conditions are the same as those in the Table 1.

reaction of an organ catalyst to light, sometimes called photo redox. This new photochemical cascade reaction extends IL chemistry to artificial photosynthesis, providing a novel methodology for the splitting and conversion of chemically inert CO2.

Methods

Chemicals. Anhydrous N, N-dimethylformamide (DMF, 99.8%), Tetrahydrofuran (THF, 99.9%), Acetonitrile (Men, 99.8%), and Benzenyltrifluoride (BTF, 99%) are all imported from China. The chemicals were purchased from Sinopharm Chemical reagent Co. and kept in containers lined with molecular sieve before being use.

Obtainable from Tokyo Chemical Industry Co. is hexahydrate tris(2,29-bipyridyl) ruthenium (II) chloride (TBR, 98.0%). The commercial supply of ionic liquids accounts for 98% of Shieh Co.'s revenue. All the other reagents employed did not need any further purification for analysis. Research on CO2 photolysis. All tests were conducted in an 80-ml Schlenk flask with one atm of CO2 pressure. Six milliliters of solvent/ILs/TEOA (3 mixture system was subjected to vacuum degassing and backfilling with pure CO 5151 by volume) were added to a Schlenk flask containing ten milligrams of tris (2, 29-bipyridyl) ruthenium (II) chloride hexahydrate and one milligram of cobalt (II) chloride. These are the twogases. This is done three times, and then the CO2 is reintroduced into the flask. The system was then subjected to rapid swirling at 30uC as regulated by a water-cooling system and irradiated with a non-focus 300 W Xe-lamp with a 420 nm cut-off filter.

Gas chromatography (Shimadzu 8A) fitted with a packed molecular sieve column (TDX-1 mesh 42/10) was used to identify the generated gases (CO, H2). The GC employed AR as its carrier gas.

Analysis using infrared light. By completely dissolving [EMIM][BF4] in CO2, we were able to generate the solution that was measured. Thin films of the solution were sandwiched between two CaF2 substrates and IR spectra were taken using a Nicolet Magna 670 FT-IR spectrometer. The standard is a sample of pure [EMIM][BF4]. Tests for electrical conductivity. Conductivity was measured using DJS-1C conducting electrodes and a conductivity meter (DDSJ-318) from Shanghai Precision & Scientific Instrument Co. The Kill solution was used to calibrate the device. The electrode and solution were contained in a sealed glass tube and kept in a water bath maintained at a constant temperature of 29860.05 K. Three separate passes through each measurement allowed for the calculation of an average. Evaluations of the quantum yield. The same photochemical experimental setup was used to assess the apparent quantum yield (AQY) for CO/H2 production using an LED lamp (low-power 420 nm-LED, 3 W, Shenzhen LAMPLIC Science Co. China). LED irradiation was measured to have an intensity of 20.6 mow/cm2 (Newport 842-PE), with a regulated irradiated area of 1.0 cm2.

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