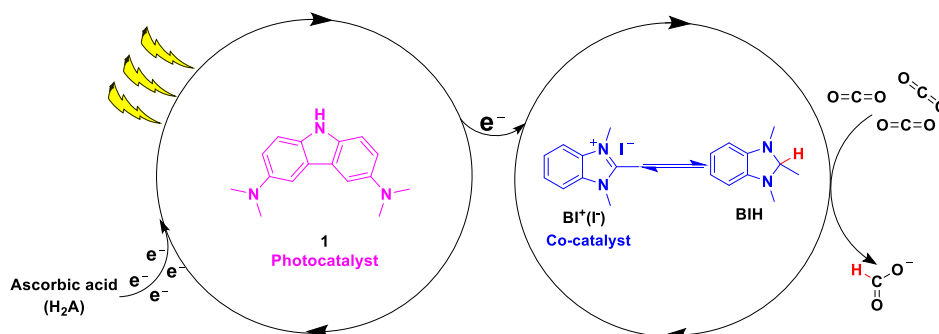


## Development of transition metal-free photochemical CO<sub>2</sub> reduction enabled by photosensitized regeneration of organohydride

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The ever-increasing demand for fossil fuels has exacerbated dramatic energy shortages and massive greenhouse gas emissions, particularly carbon dioxide.<sup>1</sup> Using renewable solar light as an energy source to convert carbon dioxide into value-added chemical fuels is an ideal approach to address the current predicament.<sup>2</sup> As a thermodynamically stable gas CO<sub>2</sub>, its reduction requires high-energy as inputs. Besides, the selectivity of the formed products deserves consideration.<sup>3</sup> Thus, developing an efficient photocatalyst system is an indispensable key to achieving photocatalytic reduction of carbon dioxide and practical solar energy storage. Herein, we utilized organic photocatalytic cycle to provide electrons for regeneration of **BIH** from **BI<sup>+</sup>(I<sup>-</sup>)** as a strategy and successfully designed and demonstrated an ideal approach that photocatalytic conversion of CO<sub>2</sub> to value-added formate comprising carbazole moiety as a visible light-driven photosensitizer, benzimidazoline-based organohydride as co-catalyst, and ascorbic acid as a sacrificial reductant using visible light irradiation at 400 nm. In this case, photocatalyst and co-catalyst show strong durability and fast rate: based on photocatalyst (TON<sub>HCOO<sup>-</sup></sub> = 8820 and TOF<sub>HCOO<sup>-</sup></sub> = 2205/h) and based on co-catalyst (TON<sub>HCOO<sup>-</sup></sub> = 6070 and TOF<sub>HCOO<sup>-</sup></sub> = 1520/h). Besides, current reaction system for photocatalytic CO<sub>2</sub> reduction reaction showed exclusive selectivity to yield formate as a sole product, while formaldehyde, oxalate, CO, and H<sub>2</sub> as potential evolved products were not detected by <sup>13</sup>C-labeling experiment and GC-based quantitative analysis of evolved gases experiment. Finally, using dehydroascorbic acid instead of ascorbic acid as sacrificial reductant in the photocatalytic reduction of CO<sub>2</sub> to fully corroborate that a two-time oxidation of ascorbic acid (four electrons provided per molecule) via intermediate dehydroascorbic acid was involved, which was consistent with more than 100% yield.<sup>4</sup>



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