Non-sensitized Selective Photochemical Reduction of CO₂ to CO under Visible Light with an Iron Molecular Catalyst

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Electronic Supplementary Information

Experimental details

Acetonitrile (ACN, 99.9% extra-dry, Acros Organics) was used as received and triethylamine (TEA, 99% pure, Acros Organics) was distilled before use. Carbon dioxide and argon (Arcal 1) were from Air Liquide.

1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) was prepared according to literature procedure.^{S1} Its NMR spectrum in DMSO-d₆ is showed in Fig. S1 and is similar to previously published data.^{S2}

The synthesis of chloro iron(III) 5,10,15,20-tetra(40-N,N,N-trimethylanilinium)porphyrin (Fe-p-TMA) has been described elsewhere.^{S3}

Continuous irradiation at right angle of CO_2 -saturated solutions in a 1 x 1 cm quartz suprasil cuvette (Hellma) equipped with a home-designed headspace glassware was ensured by a Newport LCS-100 solar simulator (1 sun irradiation). Irradiation above 420 nm was ensured thanks to a Schott GG420 longpass filter, whereas IR and low UV were cut off by a 2 cm long glass OS cell filled with deionized water.

Samples were irradiated on an area of 3.4 cm^2 , typical incident light power was ca. 15 mW cm⁻² s⁻¹ and typical absorbed light power was ca. 5 mW cm⁻² s⁻¹. The number of absorbed photons by the whole sample is then ca. 1.3×10^{20} photons per hour.

The CO₂-to-CO reduction being a two electrons process, the overall quantum yield Φ was determined using the following equation:

 $\Phi(\text{CO}) (\%) = \frac{\text{Number of CO molecules } \times 2}{\text{Number of absorbed photons}} \times 100$

Taking 101 as the highest number of catalytic cycles for CO after 102 hours, we obtain a global quantum yield Φ = 0.006%.

Gas products analysis was performed with an Agilent Technology 7820A GC system equipped with a capillary column (CarboPLOT P7, length 25 m, inner diameter 25 mm) and a thermal conductivity

detector. Calibration curves for CO and H_2 were established separately. Control experiments, with no catalyst, no CO₂ or no light were conducted in the same conditions than the full system. We also checked for the presence of liquid phase reduction products, such as formate ions, but none was detected by ion chromatography (Thermo Scientific Dionex ICS-1100).

UV-Visible absorption data were collected with an Analytik Jena Specord 600 UV/Vis spectrophotometer.

Number of catalytic cycle and turnover number (TON) were defined as the ratio of the amount of the product formed to the initial amount of introduced catalyst.



NMR spectrum of BIH



UV-Visible absorption spectra of sacrificial electron donor

Both electron donors used have no absorption in the irradiation domain, as showed in Fig. S2 below.



Fig. S2 UV-Visible absorption spectra of TEA and BIH in acetonitrile.

Additional references

- S1 E. Hasegawa, T. Seida, N. Chiba, T. Takahashi and H. Ikeda, J. Org. Chem., 2005, 70, 9632.
- S2 B. D. Naab, S. Guo, S. Olthof, E. G. B. Evans, P. Wei, G. L. Millhauser, A. Kahn, S. Barlow, S. R. Marder and Z. Bao, *J. Am. Chem. Soc.*, 2013, **135**, 15018.
- S3 C. Costentin, M. Robert, J.-M. Savéant and A. Tatin, Proc. Natl. Acad. Sci. U.S.A., 2015, 112, 6882.