Photochemical and Electrochemical Catalytic Reduction of CO_2 with NHC-Containing Dicarbonyl Rhenium(I) Bipyridine Complexes

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Supplementary Information

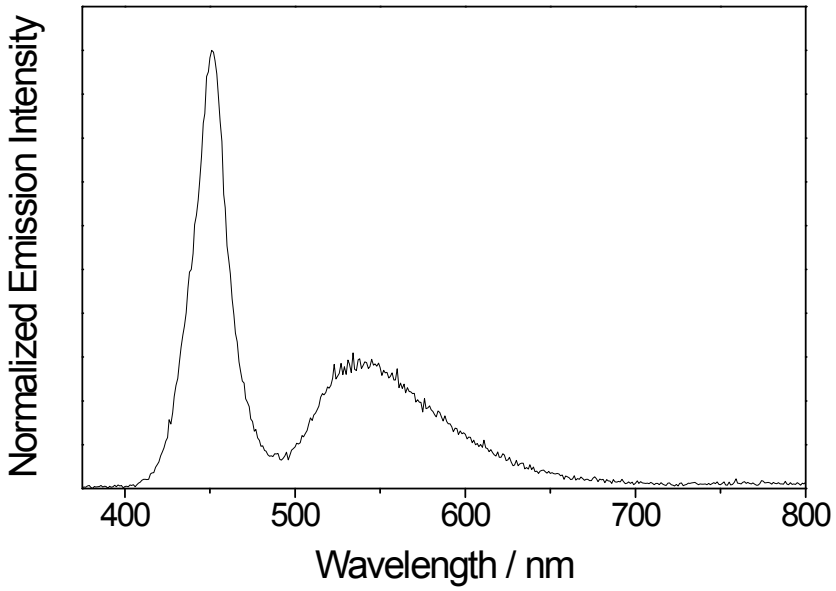

Figure S1. Lamp spectrum of Osram Parathom 13W white-light LED.

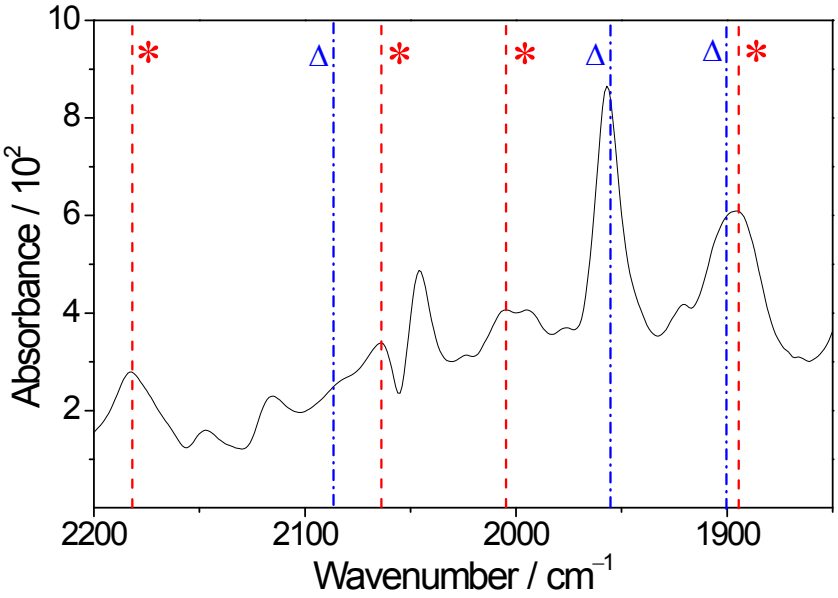

Figure S2. IR spectrum of the dichloromethane extracts of the photocatalytic reaction mixture of **2** after 30-min irradiation. (Due to the complexity, possibly resulted from various ligand dissociations and geometrical photo-isomerizations, these C≡O and C≡N stretches cannot be unambiguously assigned. The position of C≡O and C≡N stretches of **2** (▲) and $[Re(CO)(phen)(CNC_6H_4Cl\text{-}4)_3]PF_6$[†] (*) are marked for reference.)

[†]A. W.-Y. Cheung, L. T. L. Lo, C.-C. Ko and S.-M. Yiu, *Inorg. Chem.*, 2011, **50**, 4798

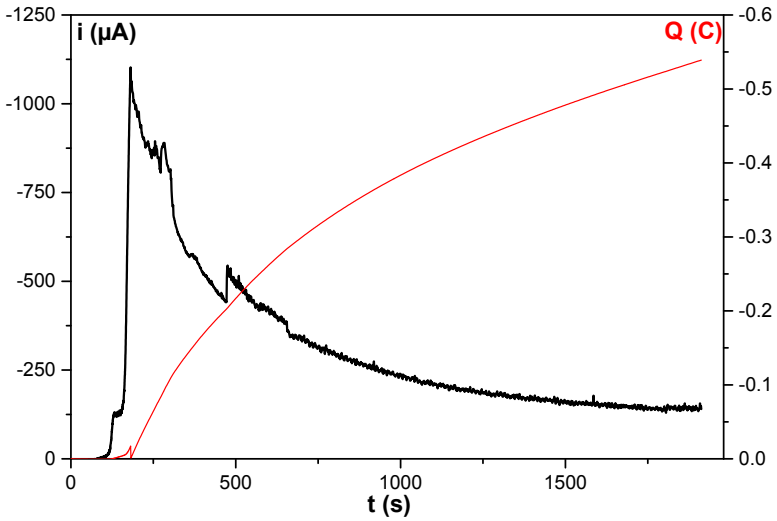

Figure S3. Controlled potential electrolysis (E = -1.8 V vs. SCE at a glassy carbon plate S = 1 cm^2) with **2** 0.5 mM (in DMF, $LiClO_4$ 0.5 M, NBu_4PF_6 0.1 M): current (black trace) and charge (red trace) *vs*. time.

Procedure for the extracting the rate constant k_{cat} for catalysis for **2** from CV analysis and from electrolysis current.

a. *Determination of* k_{cat} *from the foot-of-the wave analysis*. The foot of the wave analysis was performed as follows. The current was normalized toward the peak current of the ligand centred wave :

$$i_p^0 = 0.446\, F\, S\, C_{cat}^{\ 0} \sqrt{D_{cat}} \sqrt{\frac{Fv}{RT}}$$

using the following values for the various parameters and constants :

F = 96485 C mol^{-1} ; S = 1 cm^2 ; $C_{cat}^{\ 0} = 0.5$ x 10^{-6} mol cm^{-3}; $D_{cat} = 2.26$ x 10^{-6} mol cm^{-2} ; v = 0.1 V s^{-1} ; R = 8.314 J mol^{-1} K^{-1} ; T = 298 K

$E_{cat}^{\ 0}$ = -1.735 V vs SCE (note that the catalyst wave is not fully reversible, leading to an uncertainty of 10 to 20 mV on the $E_{cat}^{\ 0}$ value).

$k_{cat} = k\,[CO_2]$ was then determined by plotting $\frac{i}{i_p^0}$ as a function of $\left\{1 + exp\left[\frac{F\left(E - E_{cat}^{\ 0}\right)}{RT}\right]\right\}^{-1}$, from the slope of the linear part of the curve ($2.24\sqrt{\frac{2k[CO_2]\,RT}{Fv}}$), that corresponds to low current values for which secondary phenomena are minimized.[S1]

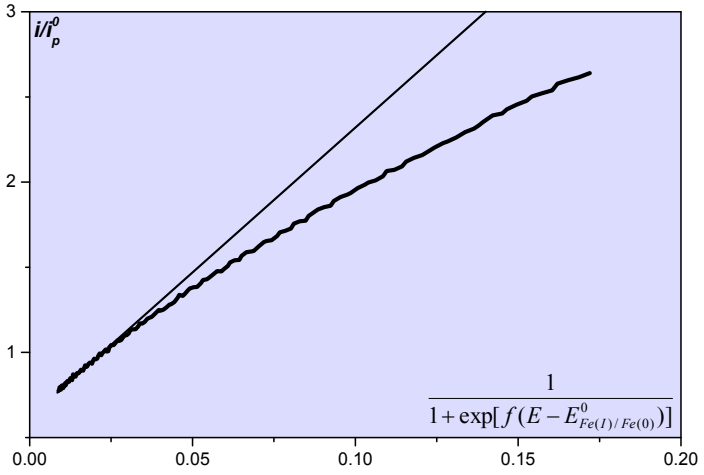

Figure S4. Foot-of-the wave analysis for **2** (0.5 mM) from CV in DMF (v = 0.1 V/s, glassy carbon electrode 0.071 cm^2, 0.23 M CO_2 + 0.5 M MeOH).

b. Determination of k_{cat} *from controlled potential electrolysis.* k_{cat} was derived from the

electrolysis current *i*, by applying the following equation:[S1]

$$\frac{i}{FS} = \frac{\sqrt{2k[\mathrm{CO_2}]D_{cat}}C_{cat}^{0}}{1 + exp\left[\frac{F\left(E - E_{cat}^{0}\right)}{RT}\right]}$$

Reference

S1. C. Costentin, M. Robert and J.-M. Savéant, *Chem. Soc. Rev.*, 2013, **42**, 423.