# *Photo-assisted electrocatalytic reduction of CO2: A new strategy for reducing catalytic overpotentials*

Article

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# Photo-assisted Electrocatalytic Reduction of $CO_2$: A New Strategy for Reducing Catalytic Overpotentials

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**Abstract:** Electrochemical and photochemical reduction of $CO_2$ are both well-established, independent catalytic routes toward producing added-value chemicals. The potential for any cross-reactivity has, however, hardly been explored so far. In this report, we assess a system primarily using spectroelectrochemical monitoring, where photochemistry assists the cathodic activation of precursor complexes [$Mn(CO)_3$(2,2'-bipyridine)Br] and [$Mo(CO)_4$(6,6'-dimethyl-2,2'-bipyridine)] to lower the catalytic overpotential needed to trigger the electrocatalytic reduction of $CO_2$ to CO. Following the complete initial $1e^-$ reduction of the parent complexes, the key photochemical cleavage of the Mn–Mn and Mo–CO bonds in the reduction products, [$Mn(CO)_3$(2,2'-bipyridine)]$_2$ and [$Mo(CO)_4$(6,6'-dimethyl-2,2'-bipyridine)]$^{\bullet-}$, respectively, generates the $2e^-$-reduced, 5-coordinate catalysts, [$Mn(CO)_3$(2,2'-bipyridine)]$^-$ and [$Mo(CO)_3$(6,6'-dimethyl-2,2'-bipyridine)]$^{2-}$ appreciably closer to the initial cathodic wave R1. Experiments under $CO_2$ confirm the activity of both electrocatalysts under the photoirradiation with 405-nm and 365-nm light, respectively. This remarkable achievement corresponds to a *ca.* 500 mV positive shift of the catalytic onset compared to the exclusive standard electrocatalytic activation.

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## Experimental Procedures

### Materials

Tetrahydrofuran (THF, Fisher) was freshly distilled from sodium/benzophenone (soluble purple ketyl radicals). Prior to use, the solvent was bubbled with dry argon (BOC, 99.9%) on a frit. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH, >99.8%, Acros-Organics) was recrystallized twice from hot ethanol and then dried under vacuum. The supporting electrolyte was dried prior to use once more at 120 °C for 12 h. All electrochemical measurements were conducted under an atmosphere of dry argon, or $CO_2$ (BOC, 99.9%), using standard Schlenk techniques. Prior to electrocatalytic experiments, solutions were saturated with $CO_2$ by bubbling on a frit at the atmospheric pressure. [$Mn(CO)_3$(2,2'-bipyridine)Br] (**1**) (ref. [1]), [$Mn(CO)_3$(2,2'-bipyridine)(OTf)] (ref [2]) and [$Mo(CO)_4$(6,6'-dimethyl-2,2'-bipyridine)] (**2**) (ref. [3]) were synthesised in house according to the established literature procedures. $^1$H NMR spectra were measured on Bruker 400 MHz Nanobay spectrometer. The identity and purity of the studied complexes was confirmed by a combination of IR spectroscopy, $^1$H NMR spectroscopy and cyclic voltammetry. [$Mn(CO)_3$(2,2'-bipyridine)Br]: IR (THF), ν(CO) at 2023, 1934 and 1915 $cm^{-1}$. [$Mn(CO)_3$(2,2'-bipyridine)(OTf)]: IR (THF), ν(CO) at 2043 and 1943 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.28 (2H, d, $J$ = 5.2 Hz), 8.16 (4H, m, $J$ = 8 Hz), 7.32 (2H, t, $J$ = 6 Hz). [$Mo(CO)_4$(6,6'-dimethyl-2,2'-bipyridine)]: IR (THF), ν(CO) at 2014, 1899, 1879 and 1836 $cm^{-1}$; $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.84 (2H, d, $J$ = 7.6 Hz), 7.74 (2H, t, $J$ = 7.5 Hz), 7.32 (2H, d, $J$ = 7.1 Hz), 2.95 (6H, s).

### Methods

### Cyclic Voltammetry

Cyclic voltammograms were recorded on a PGSTAT302N potentiostat (Metrohm Autolab) under an atmosphere of dry argon using a standard configuration of an airtight, three-electrode, single-compartment cell. Pt, Au or Cu microdiscs (all $d$ = 0.4 mm), polished by a 0.25-μm diamond paste (Kemet), served as the working electrode; the auxiliary and pseudoreference electrodes were made of coiled Pt and Ag wires, respectively, protected by a glass mantle. Ferrocene (Fc) served as the internal potential reference for these measurements and was added just before the ultimate voltammetric scan. The solutions prepared for cyclic voltammetry contained 1 mM analyte and $10^{-1}$ M TBAH.

### Infrared and UV-vis Spectroelectrochemistry

Infrared spectroelectrochemical experiments were performed on a Bruker Vertex 70v FTIR spectrometer, equipped with a DTLaGS detector. UV−vis spectroelectrochemical experiments were conducted on a Scinco S-3100 diode array spectrophotometer. The electrochemical response in the form of a thin-layer cyclic voltammogram (TL-CV) at $v$ = 2 mV $s^{-1}$ was recorded during both IR and UV-vis monitoring of the controlled-potential electrolyses with an EmStat3 potentiostat (PalmSens). The spectroelectrochemical measurements were conducted with an optically transparent thin-layer electrochemical (OTTLE) cell (Spectroelectrochemistry Reading)[4]. The cell was equipped with either a Pt, Au or Cu minigrid working electrode, a Pt minigrid auxiliary electrode, an Ag microwire pseudoreference electrode and $CaF_2$ optical windows. The solutions prepared for spectroelectrochemistry contained 3 mM analyte and $3\times10^{-1}$ M TBAH.

### Photochemistry

In situ irradiation of the masked active cathodic space of the OTTLE cell during the cathodic electrolyses was accomplished using a light-emitting diode (LED) driver (ThorLabs). A 405-nm LED (M405L4) was used for [$Mn(CO)_3$(bipy)Br] and a 365-nm LED (M365L2) for [$Mo(CO)_4$(6,6'-dmbipy)] experiments, both equipped with a collimating lens. The LED was placed in front of the cell window and switched on to a maximum power once the initial 1$e^-$ electrochemical reduction of the parent complex was complete. Samples were irradiated and spectra recorded at 5 min or 10 min intervals, up to a maximum of 45 min total irradiation time; this was sufficient in most cases to convert 60-70% of the starting material to the further reducible photoproduct, as revealed by IR spectral monitoring.

## Spectro-Electrochemical Figures

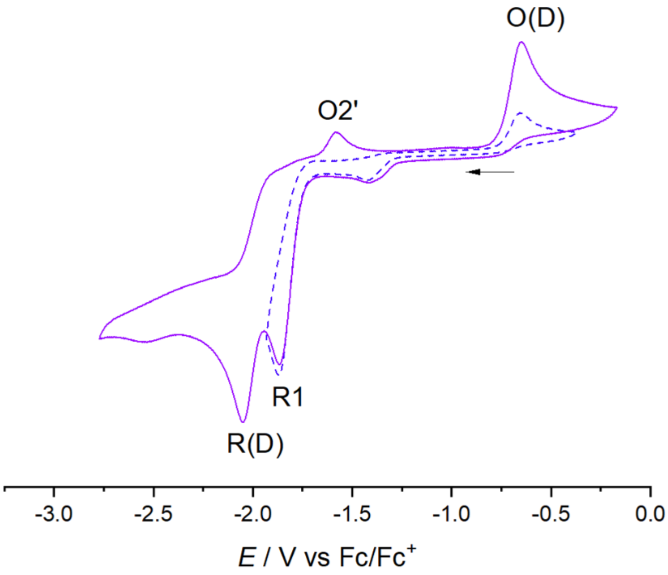

**Figure SI-1.** Cyclic voltammogram of [$Mn(CO)_3(bipy)Br$]. Conditions: Ar-saturated THF/TBAH, Pt microdisc electrode, $v$ = 100 mV $s^{-1}$, $T$ = 298 K. Legend: R1 – reduction of the parent complex; R(D) and O(D) – reduction and oxidation of [$Mn(CO)_3(bipy)$]$_2$; O2' – oxidation of [$Mn(CO)_3(bipy)$]$^-$.

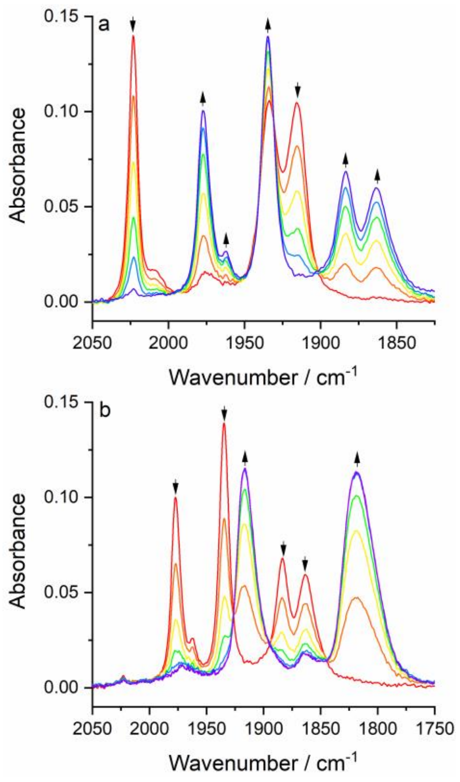

**Figure SI-2.** IR SEC monitoring of [$Mn(CO)_3(bipy)Br$] during (a) the initial reduction at R1 producing the dimer [$Mn(CO)_3(bipy)$]$_2$, and (b) the subsequent dimer reduction at R(D) to give the 5-coordinate anion [$Mn(CO)_3(bipy)$]$^-$. Conditions: Ar-saturated THF/TBAH, an OTTLE cell (Pt-mesh cathode), $T$ = 298 K.

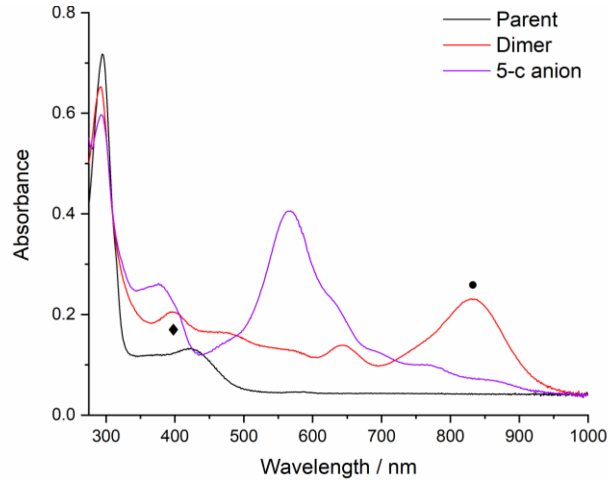

**Figure SI-3.** UV-vis spectra of parent [Mn(CO)$_3$(bipy)Br] (black), the dimer [Mn(CO)$_3$(bipy)]$_2$ (red) and the 5-coordinate anion, [Mn(CO)$_3$(bipy)]$^-$ (purple). The label ♦ denotes the irradiation wavelength used for the dimer to cleave the Mn–Mn bond; the label ● indicates the optical excitation with no photoreaction observed. Conditions: Ar-saturated THF/TBAH, an OTTLE cell (Pt mesh cathode), *T* = 298 K.

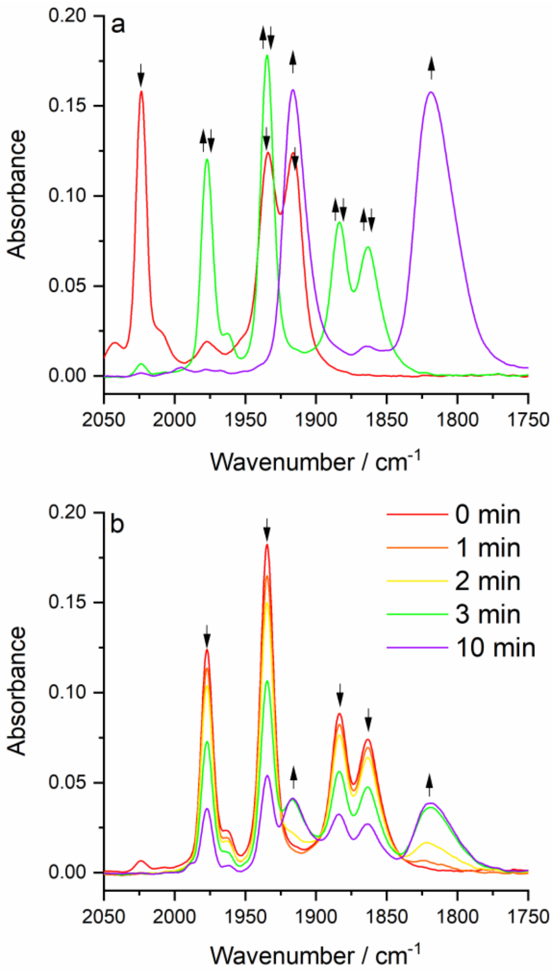

**Figure SI-4.** IR SEC monitoring of (a) the standard electrochemical reduction of [Mn(CO)$_3$(bipy)Br] (**1**) (↓) to [Mn(CO)$_3$(bipy)]$_2$ (↑↓) at R1, and the dimer to [Mn(CO)$_3$(bipy)]$^-$ (↑) at R(D), and (b) the photo-assisted electrochemical reduction of [Mn(CO)$_3$(bipy)]$_2$ ( ↓ ) pre-formed from **1** at R1, to [Mn(CO)$_3$(bipy)]$^-$ ( ↑ ) at the same cathodic potential. Conditions: Ar-saturated THF/TBAH containing 5% TFE, an OTTLE cell (Pt mesh cathode), $\lambda_{exc}$ = 405 nm (irradiation times in minutes), *T* = 298 K.

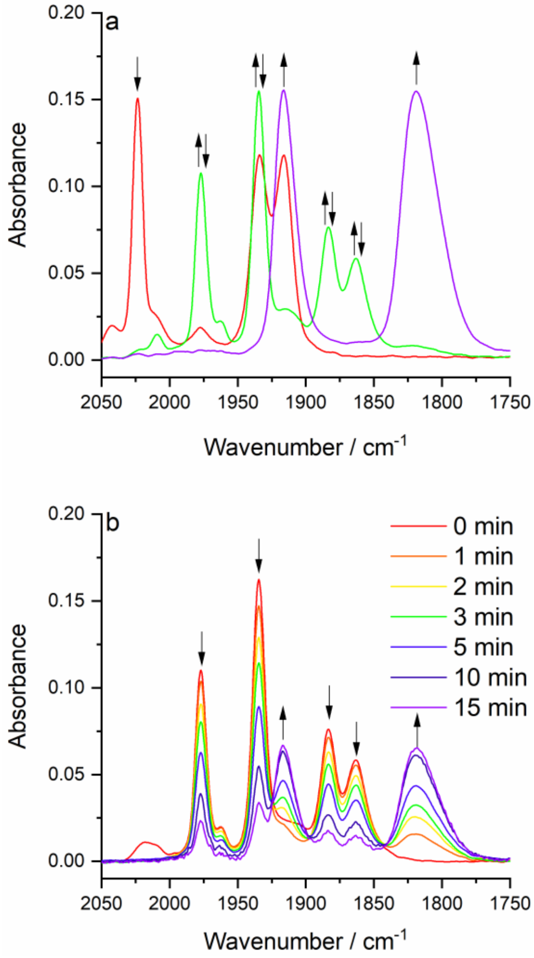

**Figure SI-5.** IR SEC monitoring of (a) the standard electrochemical reduction of [Mn(CO)$_3$(bipy)Br] (**1**) (↓) to [Mn(CO)$_3$(bipy)]$_2$ (↑↓) at R1, and the dimer to [Mn(CO)$_3$(bipy)]$^-$ (↑) at R(D), and (b) the photo-assisted electrochemical reduction of [Mn(CO)$_3$(bipy)]$_2$ (↓) pre-formed from **1** at R1, to [Mn(CO)$_3$(bipy)]$^-$ (↑) at the same cathodic potential. Conditions: Ar-saturated THF/TBAH containing 5% MeOH, an OTTLE cell (Pt mesh cathode), $\lambda_{exc}$ = 405 nm (irradiation times in minutes), *T* = 298 K.

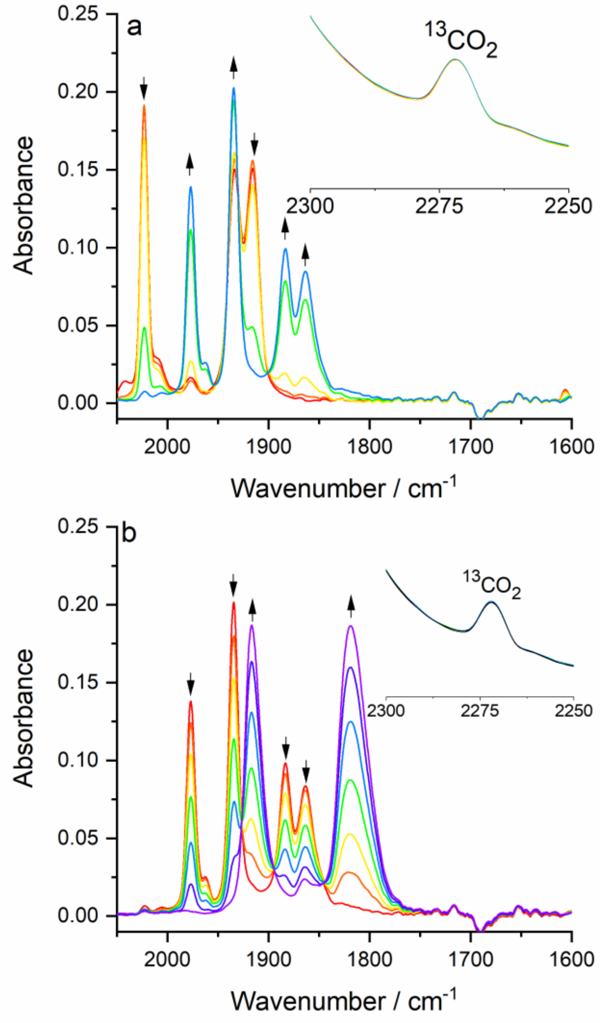

**Figure SI-6**. IR SEC monitoring of the electrochemical reduction of (a) 1 (↓) at the cathodic wave R1 to $[Mn(CO)_3(bipy)]_2$ (↑), and (b) the dimer (↓) to $[Mn(CO)_3(bipy)]^-$ (↑) at the cathodic wave R(D). Insets: the $^{13}CO_2$ satellite peak used as a reference. Conditions: $CO_2$-saturated dry THF/TBAH, an OTTLE cell (Pt mesh cathode), $T$ = 298 K. No catalytic activation of $CO_2$ was observed under these conditions.

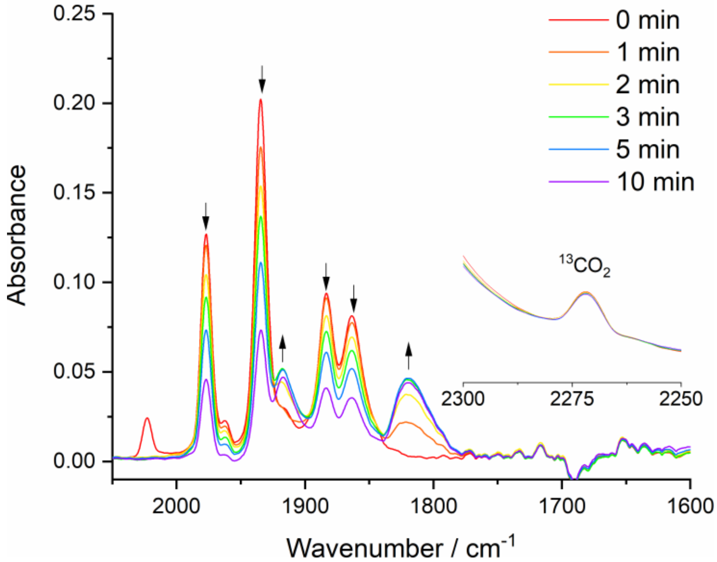

**Figure SI-7.** IR SEC monitoring of the photo-assisted electrochemical reduction of $[Mn(CO)_3(bipy)]_2$ ( ↓ ) pre-formed from **1** at R1, to $[Mn(CO)_3(bipy)]^-$ ( ↑ ) at the same cathodic potential. Inset: the $^{13}CO_2$ satellite peak used as a reference. Conditions: $CO_2$-saturated dry THF/TBAH, an OTTLE cell (Pt mesh cathode), $\lambda_{exc}$ = 405 nm (irradiation times in minutes), $T$ = 298 K. No catalytic activation of $CO_2$ was observed under these conditions.

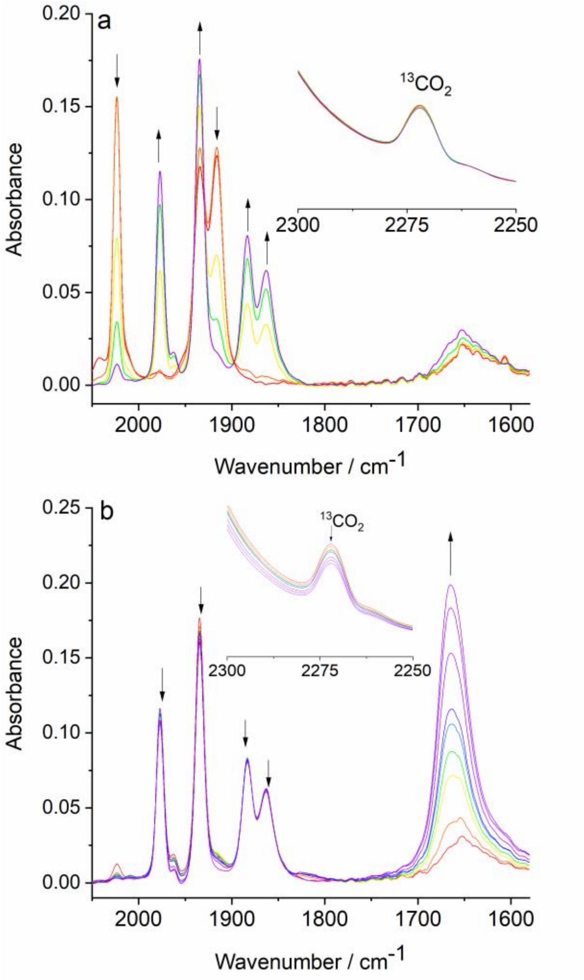

**Figure SI-8.** IR SEC monitoring of (a) the standard electrochemical reduction of $[Mn(CO)_3(bipy)Br]$ (**1**) ( ↓ ) to $[Mn(CO)_3(bipy)]_2$ ( ↑ ) at R1, and (b) the dimer (↓) to $[Mn(CO)_3(bipy)]^-$ ( ↑ ) at R(D) (cf. Figure SI-5a), triggering electrocatalytic reduction of $CO_2$. Inset: the $^{13}CO_2$ satellite peak used as a reference. Conditions: $CO_2$-saturated THF/TBAH containing 5% MeOH, an OTTLE cell (Pt mesh cathode), *T* = 298 K.

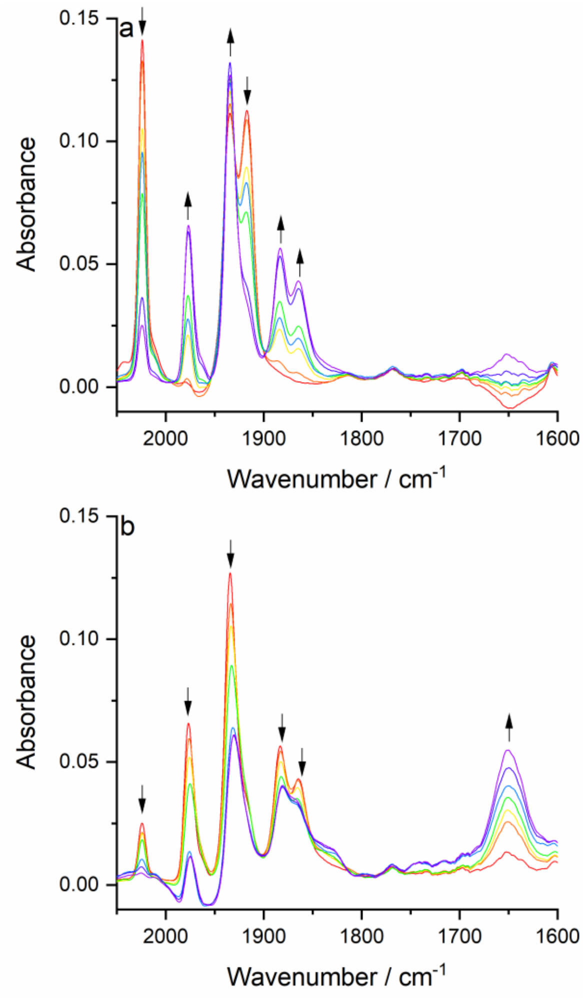

**Figure SI-9.** IR SEC monitoring of (a) the standard electrochemical reduction of $[Mn(CO)_3(bipy)Br]$ (1) ( ↓ ) to $[Mn(CO)_3(bipy)]_2$ ( ↑ ) at R1, and (b) the dimer ( ↓ ) to $[Mn(CO)_3(bipy)]^-$ ( ↑ ) at R(D), triggering electrocatalytic reduction of $^{13}CO_2$. Conditions: $^{13}CO_2$-saturated THF/TBAH containing 5% TFE, an OTTLE cell (Pt mesh cathode), *T* = 298 K.

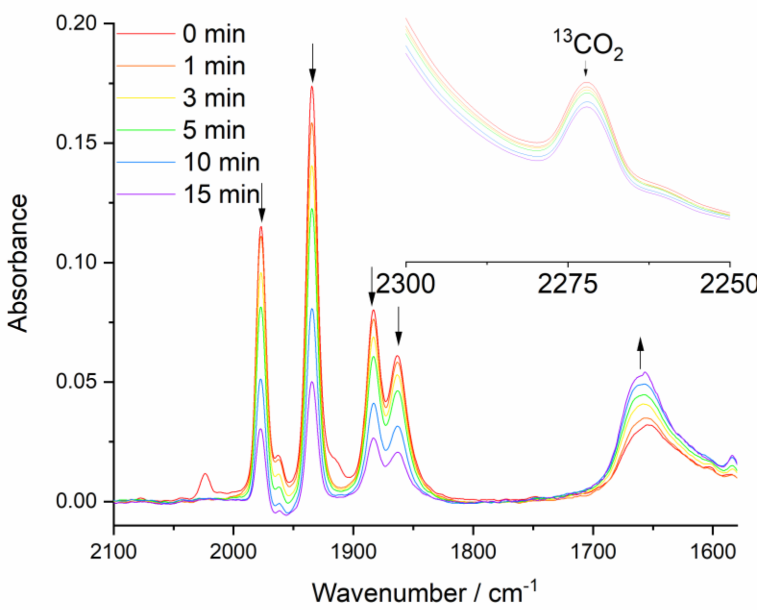

**Figure SI-10**. IR SEC monitoring of the photo-assisted electrochemical reduction of $[Mn(CO)_3(bipy)]_2$ ( ↓ ) pre-formed from **1** at R1, to $[Mn(CO)_3(bipy)]^-$ ( ↑ ) at the same cathodic potential (cf. Figure SI-5b), triggering electrocatalytic reduction of $CO_2$. Inset: the $^{13}CO_2$ satellite peak used as a reference. Conditions: $CO_2$-saturated THF/TBAH containing 5% MeOH, an OTTLE cell (Pt mesh cathode), $\lambda_{exc}$ = 405 nm (irradiation times in minutes), *T* = 298 K.

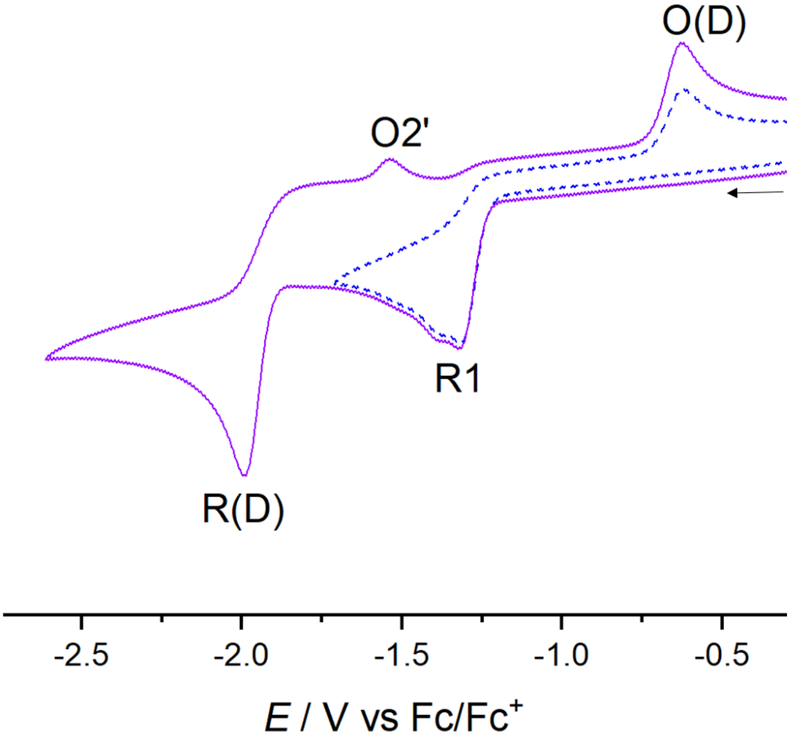

**Figure SI-11.** Cyclic voltammogram of [Mn(CO)$_3$(bipy)OTf)]. Conditions: Ar-saturated THF/TBAH, Pt microdisc, *v* = 100 mV s$^{-1}$ , *T* = 298 K. Legend: R1 – reduction of the parent complex; R(D) and O(D) – reduction and oxidation of [Mn(CO)$_3$(bipy)]$_2$; O2' – oxidation of [Mn(CO)$_3$(bipy)]$^-$.

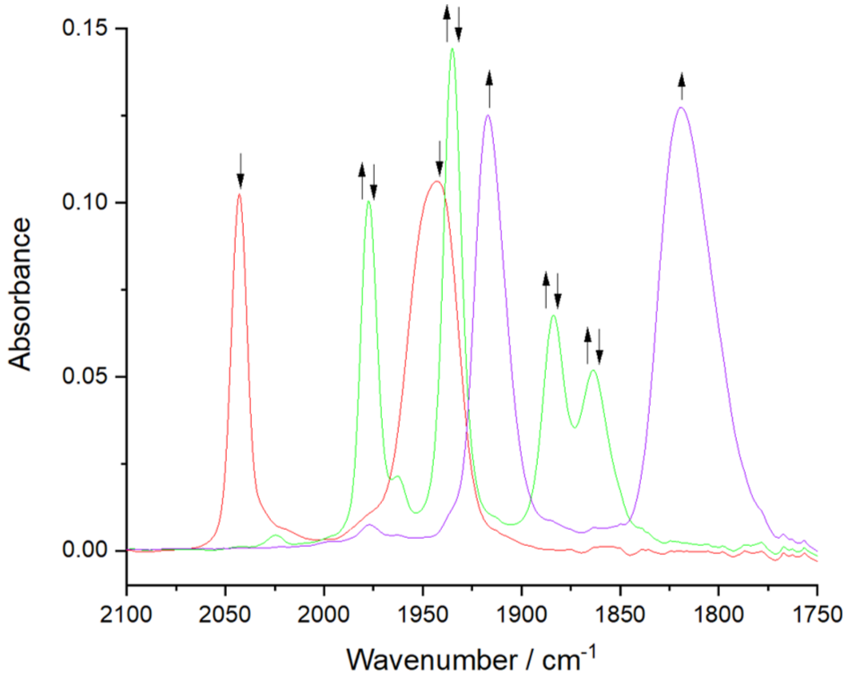

**Figure SI-12.** IR SEC monitoring of (a) the standard electrochemical reduction of [Mn(CO)$_3$(bipy)(OTf)] (1) (↓) to [Mn(CO)$_3$(bipy)]$_2$ (↑↓) at R1, and the dimer to [Mn(CO)$_3$(bipy)]$^-$ (↑) at R(D).

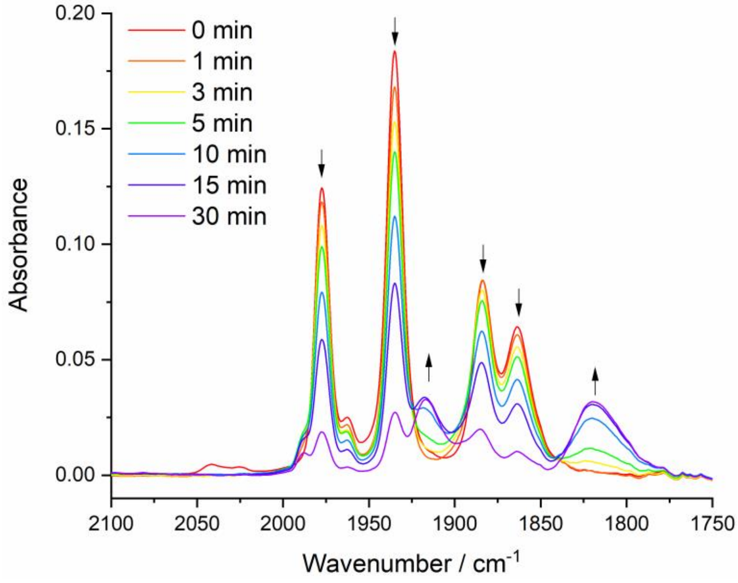

**Figure SI-13.** IR SEC monitoring of the photo-assisted electrochemical reduction of [Mn(CO)$_3$(bipy)(OTf)] (↓) at R2' which ultimately yields the 5-coordinate anion [Mn(CO)$_3$(bipy)]$^-$ (↑), following 405-nm irradiation of electrogenerated [Mn(CO)$_3$(bipy)]$_2$ (↓) over the course of several minutes. Some photodecarbonylation of the dimer has also taken place. Conditions: Ar-saturated THF/TBAH, an OTTLE cell (Pt mesh cathode), $T$ = 298 K.

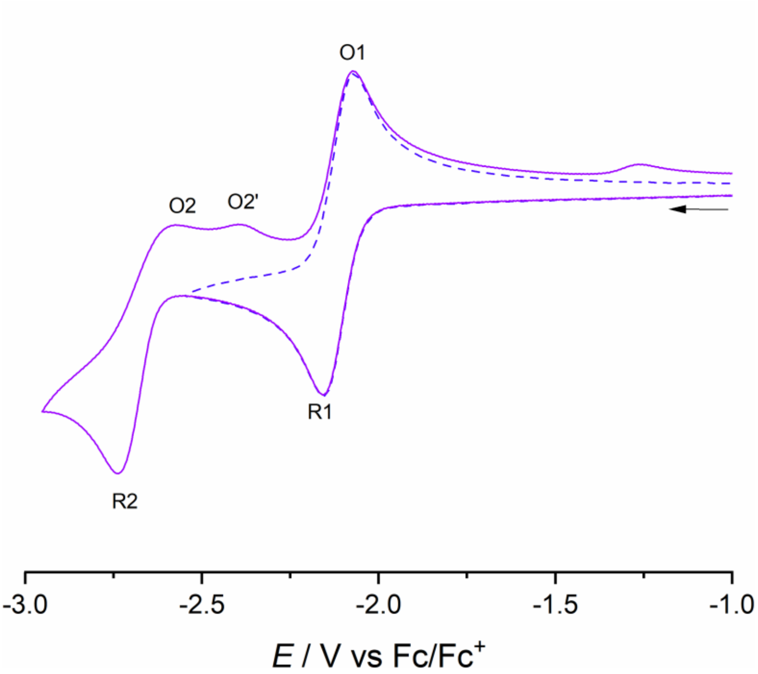

**Figure SI-14.** Cyclic voltammogram of [Mo(CO)$_4$(6,6'-dmbipy)]. Conditions: Ar-saturated THF/TBAH, Pt microdisc, $v$ = 100 mV s$^{-1}$, $T$ = 298 K.

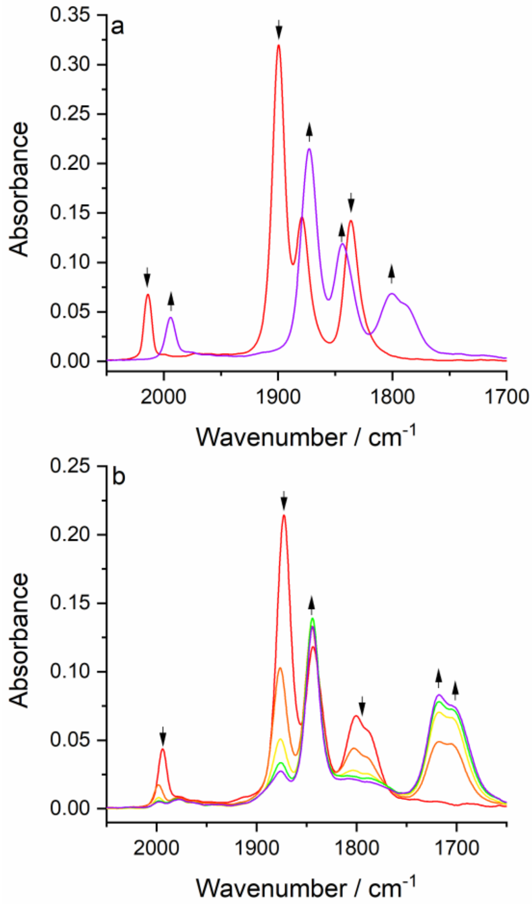

**Figure SI-15** IR SEC monitoring of (a) reduction of [Mo(CO)$_4$(6,6'-dmbipy)] at R1 (see Figure SI-14) to [Mo(CO)$_4$(6,6'-dmbipy)]$^{\bullet-}$, and (b) reduction of the radical anion at R2 to 5-coordinate dianion, [Mo(CO)$_3$(6,6'-dmbipy)]$^{2-}$. Conditions: Ar-saturated THF/TBAH, OTTLE cell (Pt mesh cathode), *T* = 298 K.

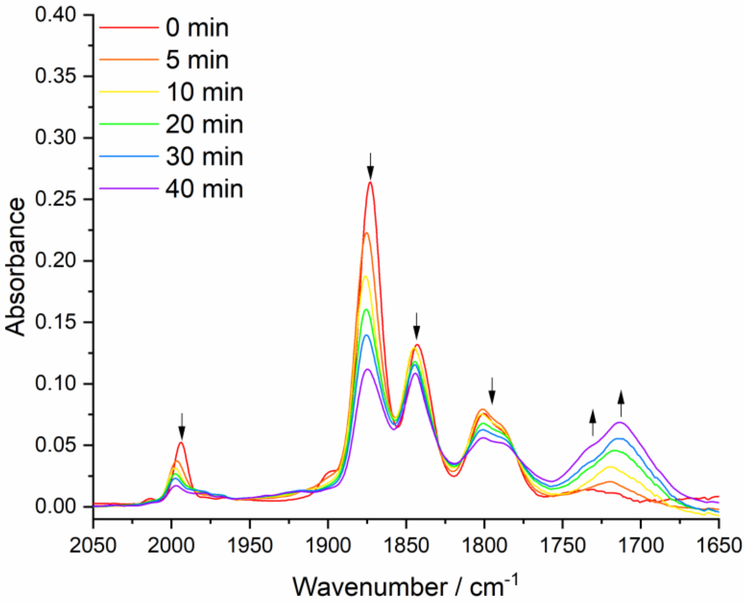

**Figure SI-16** IR SEC monitoring of the photo-assisted electrochemical reduction of [Mo(CO)$_4$(6,6'-dmbipy)]$^{\bullet-}$ ( ↓ ) at R2' to the 5-coordinate dianion [Mo(CO)$_3$(6,6'-dmbipy)]$^{2-}$ ( ↑ ). Conditions: Ar-saturated THF/TBAH, OTTLE cell (Au mesh cathode), $\lambda_{exc}$ = 365 nm (irradiation times in minutes), *T* = 298 K.

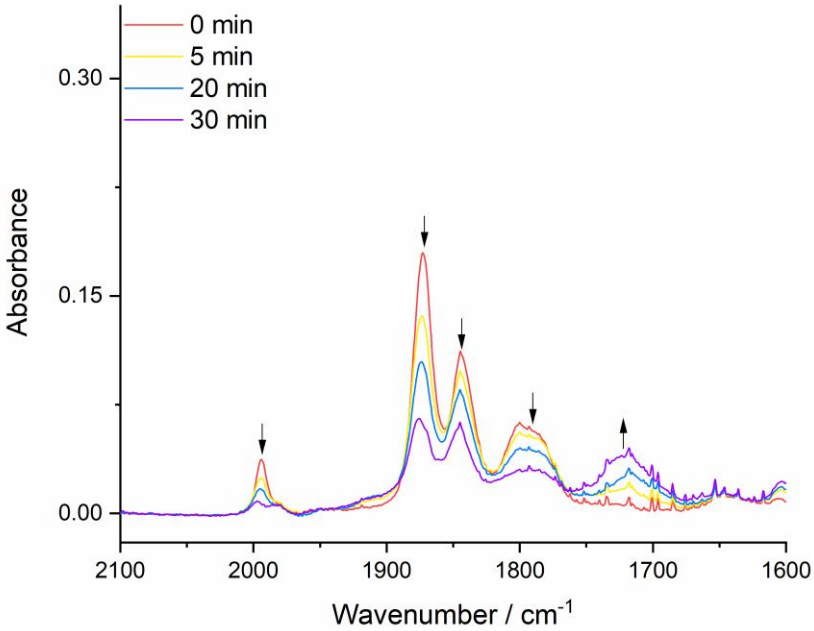

**Figure SI-17** IR SEC monitoring of the photo-assisted electrochemical reduction of [Mo(CO)$_4$(6,6'-dmbipy)]$^{•–}$ ( ↓ ) at R2' to the 5-coordinate dianion [Mo(CO)$_3$(6,6'-dmbipy)]$^{2–}$ ( ↑ ). Conditions: Ar-saturated THF/TBAH, OTTLE cell (Cu mesh cathode), $\lambda_{exc}$ = 365 nm (irradiation times in minutes), *T* = 298 K.

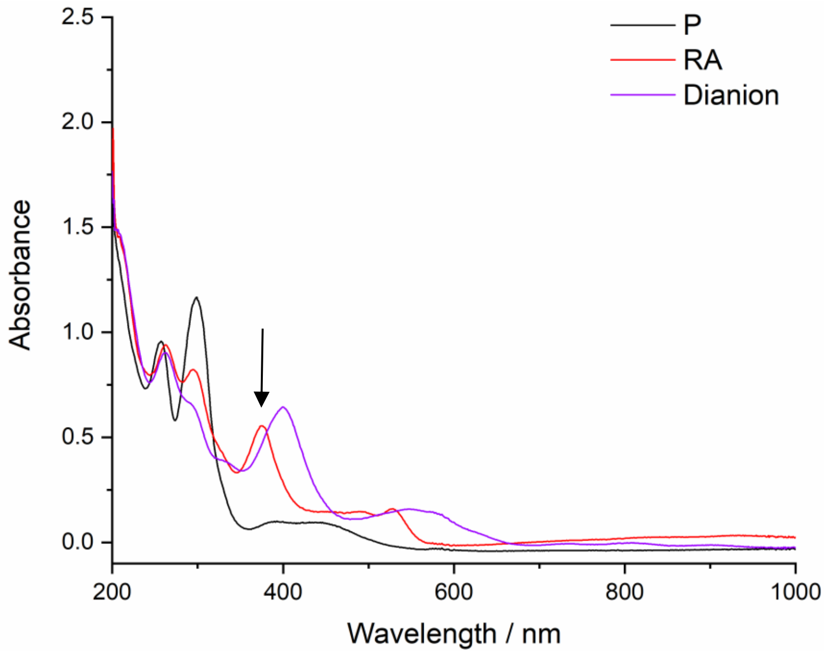

**Figure SI-18.** UV-vis absorption spectra of parent [Mo(CO)$_4$(6,6'-dmbipy)] (**2**, black), the radical anion [Mo(CO)$_4$(6,6'-dmbipy)]$^{•–}$ (red) and the 5-coordinate dianion [Mo(CO)$_3$(6,6'-dmbipy)]$^{2–}$ (purple). The arrow indicates the LED irradiation wavelength (365 nm) used to optically populate the MLCT excited state of the 1e$^–$ reduced radical anion. Conditions: Ar-saturated THF/TBAH, an OTTLE cell (Pt mesh cathode), *T* = 298 K.

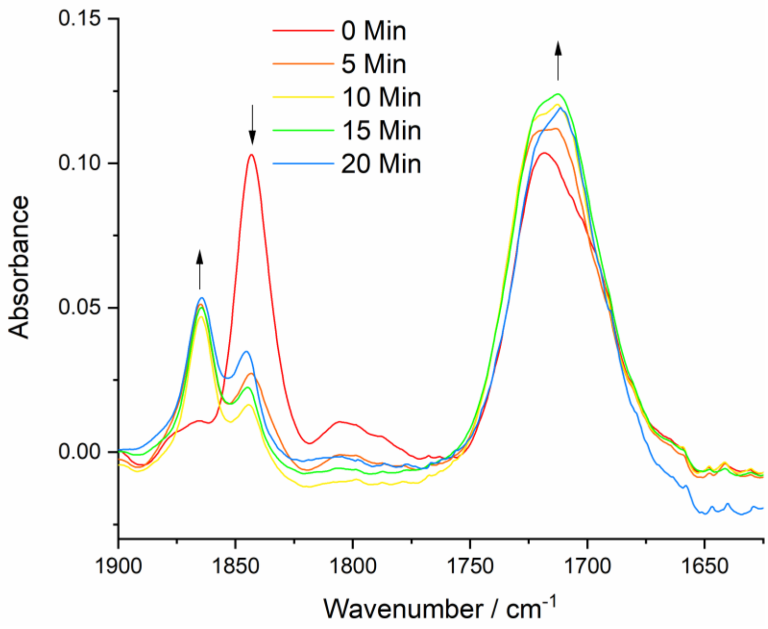

**Figure SI-19** IR SEC monitoring of the photochemical ($\lambda_{exc}$ = 365 nm) transformation of the 5-coordinate dianion, [Mo(CO)$_3$(6,6'-dmbipy)]$^{2-}$ ( ↓ ), at R2 to an unknown tricarbonyl photoproduct ( ↑ ). Conditions: THF/TBAH, OTTLE cell (Pt mesh cathode), *T* = 298 K.

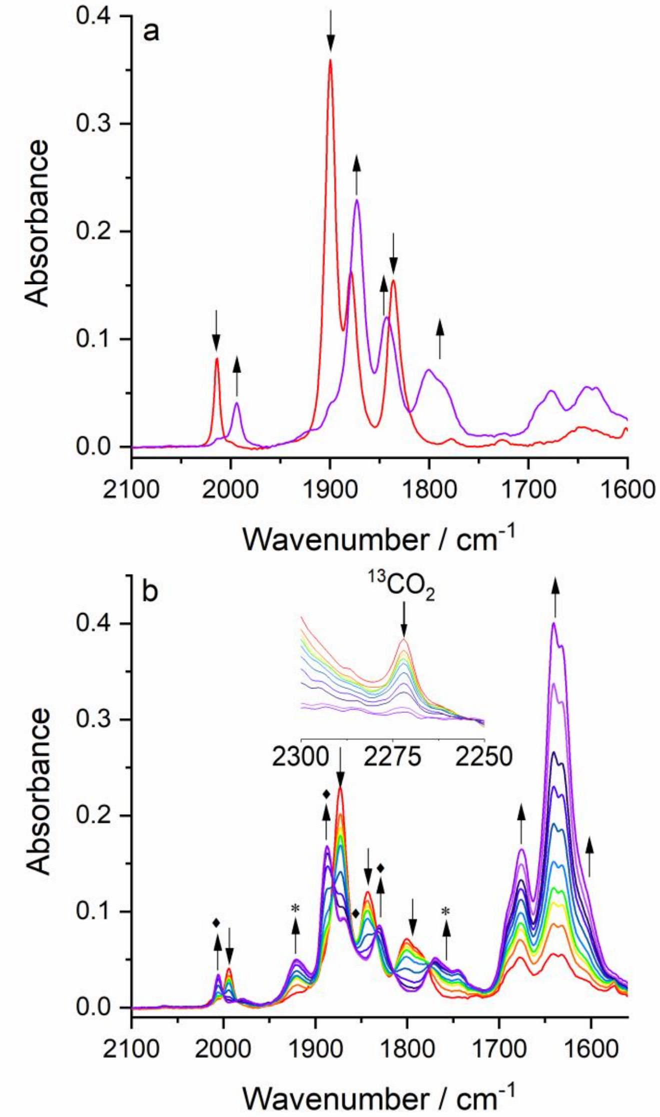

**Figure SI-20** IR spectral monitoring of (a) the initial reduction of **2** at R1 producing the radical anion [Mo(CO)$_4$(6,6'-dmbipy)] ]$^{•-}$, and (b) the subsequent cathodic step at R2 triggering the catalytic conversion of $CO_2$ to CO and formate, with some amount of accompanying bicarbonate also formed. The labels ♦ denote an inactive tetracarbonyl complex, most likely an adduct of protonated anion [Mo(CO)$_4$(6,6'-dmbipy-H)]$^-$ with $CO_2$, replacing [Mo(CO)$_3$(6,6'-dmbipy)]$^{2-}$ (see Figure SI-15). Unassigned carbonyl side products are labelled with asterisk. Conditions: $CO_2$-saturated THF/TBAH, an OTTLE cell (Pt mesh cathode), *T* = 298 K.

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