The role of electrode-catalyst interactions in enabling efficient CO_2 reduction with Mo(bpy)(CO)$_4$ as revealed by vibrational sum-frequency generation spectroscopy

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EXPERIMENTAL DETAILS:

Materials and methods. 2,2'-bipyridine and Mo(CO)$_6$ were purchased from Sigma and used as received. All electrolyte salts and solvents were purchased from Sigma Aldrich or VWR and used without further purification. Ar, N$_2$ and CO_2 were purchased from BOC at CP grade or higher. [Mo(bpy)(CO)$_4$] was synthesised according to literature procedures[1,2]: Mo(CO)$_6$ (0.7 g) and 2,2'-bypyridine (0.4 g) were refluxed in toluene for 90 minutes under argon and in the dark. Mo(bpy)(CO)$_4$ precipitated as a deep red crystalline solid upon cooling of the reaction mixture. The complex was filtered and washed with cold toluene and diethyl ether, then dried under vacuum. Obtained 0.65 g, yield 72%. **^{1}H NMR** (400 MHz, CD$_3$CN) δ 9.10 – 8.97 (m, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.05 (td, J = 8.0, 1.6 Hz, 1H), 7.49 (ddd, J = 7.5, 5.4, 1.1 Hz, 1H). **Elem. Anal.** Calcd.: C 46.17, H 2.21, N 7.69, found: C 45.68, H 2.16, N 7.55.

Electrochemistry. For the spectroelectrochemical experiments a custom-made cell was used (Scheme S 1 in ESI), containing a CaF$_2$ front window and a pathlength of *ca.* 50 μm. A Pt wire was used as the counter electrode and a Ag wire was used as the *pseudo*-reference electrode, the potential of which was referenced by adding ferrocene as an internal standard. The working electrode was either a gold or platinum polycrystalline disc (Ø = 16 mm). The electrodes were hand polished to mirror finish using decreasing sizes of diamond (15, 6 and 1 μm) and alumina (0.5 μm) slurry before every experiment. A palmsens[3] potentiostat was used to carry out all the electrochemical experiments.

SFG spectroscopy. The SFG experiments were carried out in the Central Laser Facility at the STFC Rutherford Appleton Laboratory using the Ultra B laser system. A single OPA-DFG unit driven with 5W from a 20W, 50 fs, 800 nm Ti:Sapphire amplifer system (Coherent) was used to pump a home-built white light seeded Optical Parametric Amplifier (OPA) based on two BBO stages and AgGaS$_2$ difference frequency generation, producing tuneable IR light across a 500 cm^{-1} useable bandwidth at 10 kHz. 5W of the amplified 800 nm light was passed through two air-spaced etalons (SLS Optics, 21 cm-1 and 9.5 cm-1 transmission) to generate narrowband ps light which was then bandpass filtered to remove weak supercontinuum and

delivered to the sample via a computer controlled delay line. The time-asymmetric intensity profile of the 800 nm light allowed for enhanced discrimination of VSFG signals from NR-SFG[3] by using 0.4-1 ps delays between the IR and visible pulses. The IR and 800 nm beams were focussed at the electrode with spot sizes of ~200 and ~300 um and incident powers of <4 uJ and <5uJ respectively, with the latter typically set at 1-3 uJ to ensure no laser heating or damage. The relatively diffuse SFG signal diverging from the rough electrodes was imaged with a 3 cm PCX lens, filtered (<750 nm shortpass, Semrock) and then focussed onto the entrance slit of an imaging spectrograph (Holospec) and dispersed onto a high sensitivity CCD array (Andor Idus).

A typical experiment was carried out by recording one or two CVs to confirm that the electrochemistry was correct. It was then checked that the SFG signal from the electrode showed changes with applied potential, as electrode fouling or incorrect alignment of the SFG signal could lead to spurious signals with no dependence on potential. Having confirmed correct spectroelectrochemistry, the potentiostat could then be scanned whilst SFG spectra were continuously read-out. For CVs recorded at 50 mV s^{-1} the spectra were averaged for one second and read-out every second. For CVs ran at 5 mV s^{-1} the read-out / averaging time was varied between 1-5 seconds.
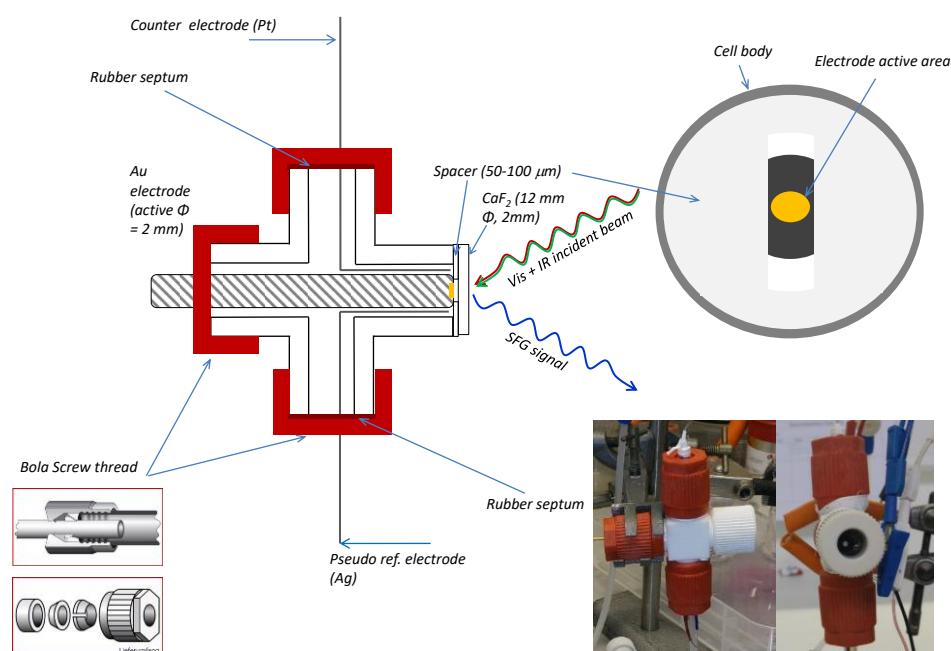
Scheme S1. Side and top view of the spectroelectrochemical cell designed for the SFG experiments. Side and front pictures of the assembled SEC cell are shown in the bottom left corner.
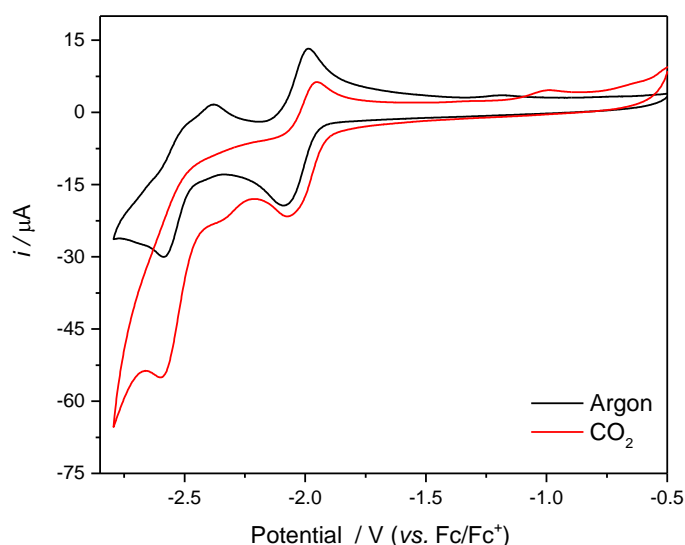
Figure S1. CVs of a 1 mM solution of [Mo(bpy)(CO)$_4$] in acetonitrile with 0.1 M TBAPF$_6$ (Tetrabutylammonium hexafluorophosphate) as the supporting electrolyte on a Glassy Carbon Electrode (GCE), surface area = 0.071 cm^2 under argon (black) and CO$_2$ (red) scan rate = 100 mV s^{-1}; platinum counter electrode, silver wire quasi-reference electrode.

Complex	ν(CO), cm^{-1}	Applied potential	Reference
[Mo(bpy)(CO)$_4$]	2015, 1905, 1875, 1832		this work (FTIR)
	2012, 1900, 1882, 1840		[4]
[Mo(bpy)(CO)$_4$]$^-$	N/O, 1874, 1850, 1808	*ca. -1.9 V*	this work (VSFG)
	1991, 1871, 1843 1805		[4]
[Mo(bpy)(CO)$_3$]$^{2-}$	1835, 1735, N/O	*ca. -2.8 V*	this work (VSFG)
	1846, 1725, 1706		[4]
[Mo(bpy-H)(CO)$_4$]$^-$	N/O, 1870, N/O, 1790	*ca. -2.8 V*	this work (VSFG)
	1994, 1874, 1848, 1807		[4]

Table S1. Assignment of υ(CO) modes measured in this work in CH$_3$CN using Au electrode unless stated otherwise and relevant literature values (THF). The applied potential is given for SFG measurements only as the complexes show vibrational Stark shifting. Spectroelectrochemical experiments in reference [4] utilise a spectroelectrochemical cell where the signal will be dominated by the species in the bulk, away from the electrode surface. N/O indicates not observed in the VSFG experiment.

Phantom transitions: It has been recently highlighted that potential dependent phantom transitions can arise in electrochemical VSFG studies which are not solely due to interfacial species.[7,8] It is therefore important to identify if such features are contributing to the spectral

data reported here. We believe that the probability of the spectral features being due to phantom transitions is minimised as:

(i) The transmission FTIR spectrum of $[Mo(bpy)(CO)_4]$ (1 mM, pathlength ~50 µm, as used in the VSFG study, Figure 2a) shows that the strongest $\nu(CO)$ mode is A ~ 0.04. As these samples are optically thin in the IR region of interest it is unlikely that significant spectral distortion of the IR beam is occurring as it passes through the electrolyte, a requirement for the formation of phantom peaks.[7,8]

(ii) We observe $\nu(CO)$ modes that are Stark shifted, including for $[Mo(bpy)(CO)_4]$ (see Figure 2, 5) which would be the most likely species to give rise to phantom peaks. The significant Stark shifts indicate that that the VSFG response is due to species experiencing a large electric field at or very close to the electrode surface.

(iii) Figure S2 shows how VSFG responses can be nearly completely supressed by applied potentials. At -2.9 V the electrode appears sufficiently negative to prevent the sustained build-up of Mo complexes and the VSFG signal is greatly reduced (only a small quantity of $[Mo(bpy-H)(CO)_4]^-$ remains). If phantom transitions were dominating the SFG response then (assuming that the cell pathlength exceeded the diffusion layer thickness) the peak positions would appear constant and the intensity of the peak would be proportional to the NR intensity which is not observed to be the case here (figure S13).
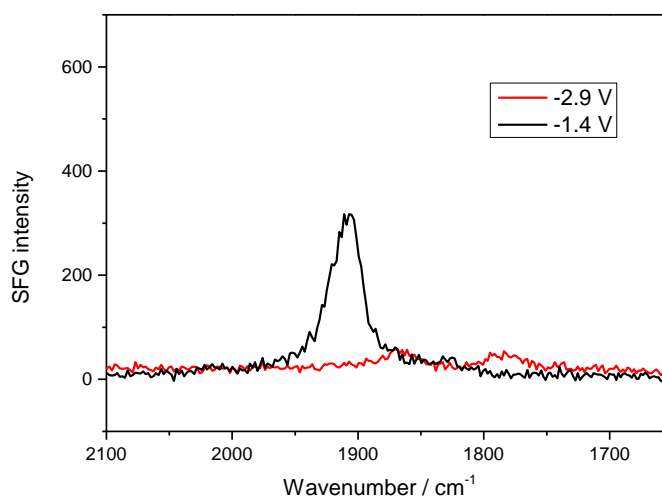

Figure S2: VSFG spectra of [Mo(bpy)(CO)₄] (1 mM) in CH₃CN and 0.1 M TBAPF₆ under Ar on a gold working electrode at the applied potentials indicated. At -2.9 V minimal VSFG response is recorded during a fast (50 mV s⁻¹) CV scan.

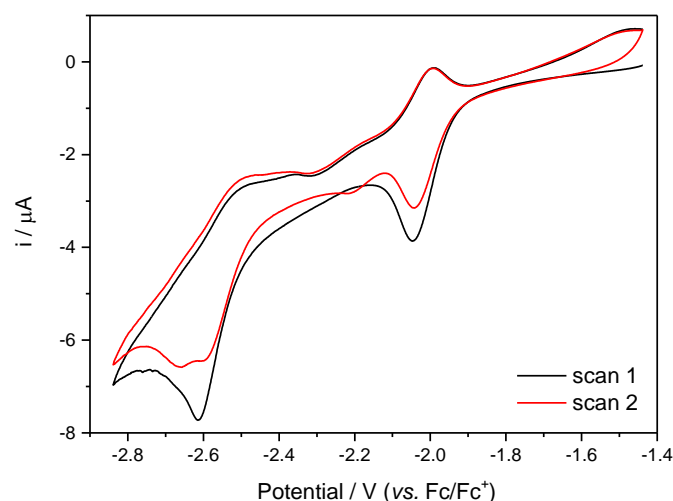*Figure S3. CVs recorded during the SEC-SFG experiment shown in Figure 2 of the main paper. 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆, Gold working electrode (surface area = 0.02 cm²,), scan rate = 5 mV s⁻¹; platinum counter electrode, silver wire quasi-reference electrode.*
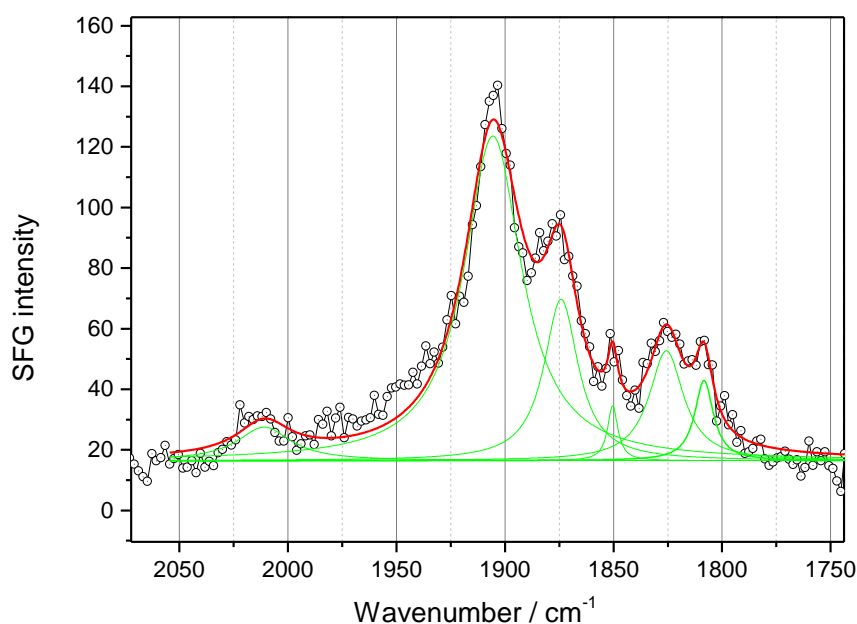

Figure S4. Multi-Lorentzian fitting for the VSFG spectrum of a 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆, at a potential of -1.9 V. Peaks assignable to both [Mo(bpy)(CO)₄] (1826, 1904, 2010 cm⁻¹) and [Mo(bpy)(CO)₄]⁻ (1808, 1850 cm⁻¹) are identifiable. Both [Mo(bpy)(CO)₄] and [Mo(bpy)(CO)₄]⁻ are anticipated to have a υ(CO) mode at 1875 to 1870 cm⁻¹ and a minimum of 1 lorentzian peak at 1874 cm⁻¹ is required within this fitting. It is feasible that this single fitted peak comprises of the υ(CO) modes of both species but identification of this is beyond the spectral resolution of the experiment.
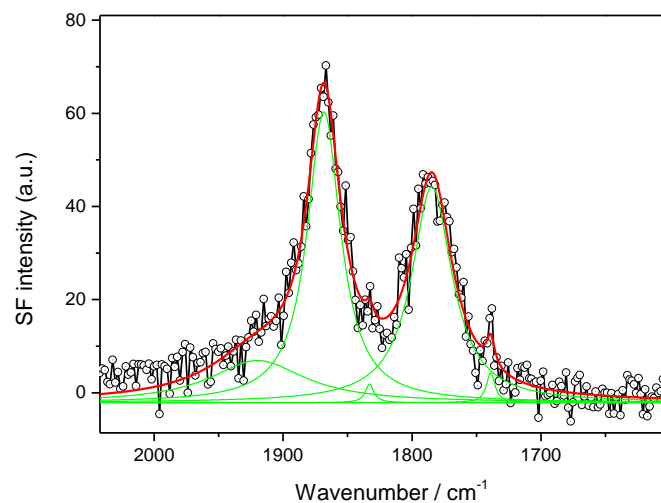
Figure S5. Multi-Lorentzian fitting for the SFG spectrum of a 1 mM solution of [Mo(bpy)(CO)$_4$] in acetonitrile with 0.1 M TBAPF$_6$, recorded at a potential of -2.7 V. Peaks were set to a have a minimum width threshold (8 cm^{-1}) to help discriminate from noise. The broad feature at 1914 cm^{-1} is due to residual NR signal. The feature at 1736 cm^{-1} is assigned to one of the modes of [Mo(bpy)(CO)$_3$]$^{2-}$.
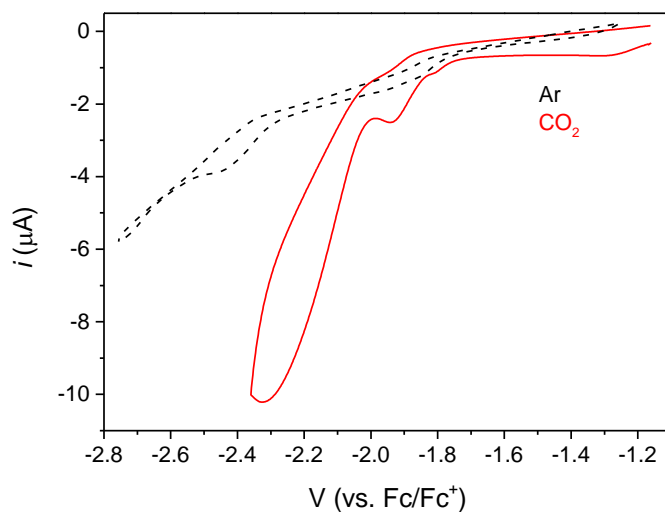

Figure S6. CVs of a 1 mM solution of [Mo(bpy)(CO)$_4$] in acetonitrile with 0.1 M TBAPF$_6$ on a gold working electrode (surface area = 0.02 cm^2) under argon (black) and CO$_2$ (red), scan rate = 5 mV s^{-1}; platinum counter electrode, silver wire quasi-reference electrode.
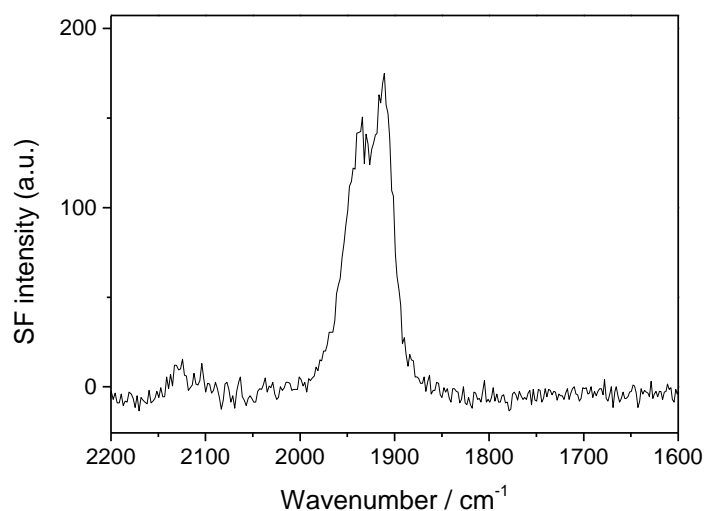
Figure S7. VSFG spectrum at open circuit potential of a 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆ on a gold working electrode (surface area = 0.02 cm²) under CO₂; platinum counter electrode, silver wire quasi-reference electrode, recorded prior to the SEC-SFG in figure 5 of the main paper. The presence of modes attributed to CO on Gold (2115, 1932 cm⁻¹) is due to some CO₂ reduction occurred during a CV recorded to verify the successful construction of the SEC cell.[5,6]
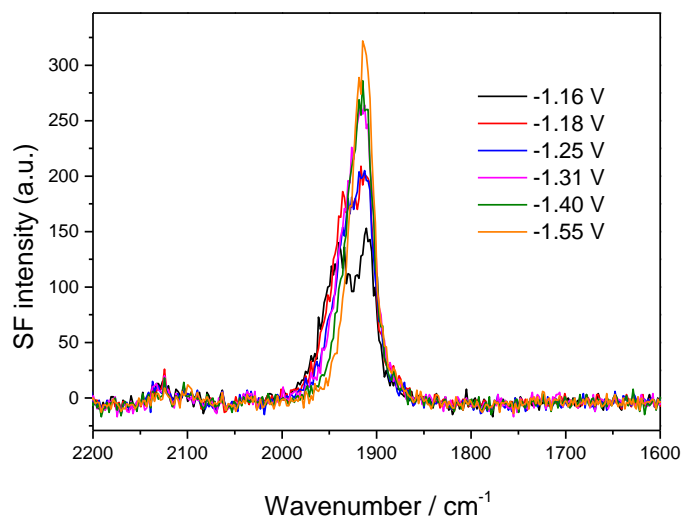

Figure S8. VSFG spectra at the potentials indicated of a 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆ on a gold working electrode (surface area = 0.02 cm²) under CO₂; platinum counter electrode, silver wire quasi-reference electrode, recorded during the SEC-SFG in figure 5 of the main paper. Prior to the first reduction the CO mode at 1932 cm⁻¹ appears to disappear, leaving a single resonant mode of [Mo(bpy)(CO)₄], however it is also feasible that the CO mode is stark shifting at different rate to the band of [Mo(bpy)(CO)₄] leading to overlap of the spectral features.
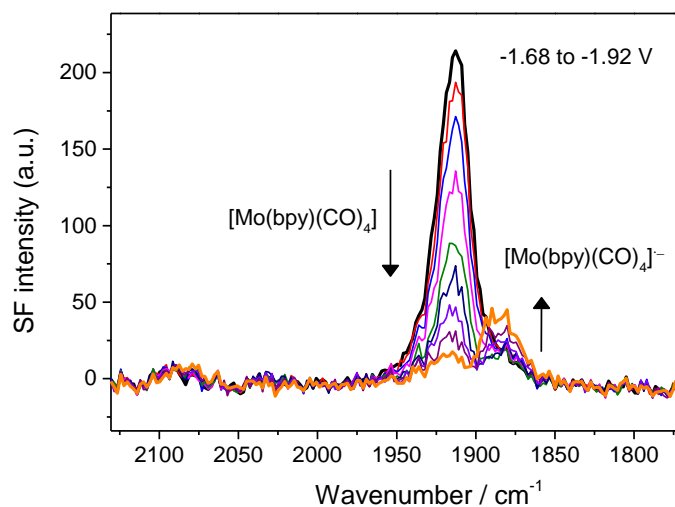
Figure S9. SFG spectra of a 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆ on a gold working electrode (surface area = 0.02 cm²) under CO₂ recorded between -1.68 and -1.92 V (scan rate = 5 mV s⁻¹); platinum counter electrode, silver wire quasi-reference electrode, recorded during the SEC-SFG in figure 5 of the main paper. The spectra show a new resonant feature growing as the main resonant mode of [Mo(bpy)(CO)₄] decreases, assigned to [Mo(bpy)(CO)₄]⁻ .
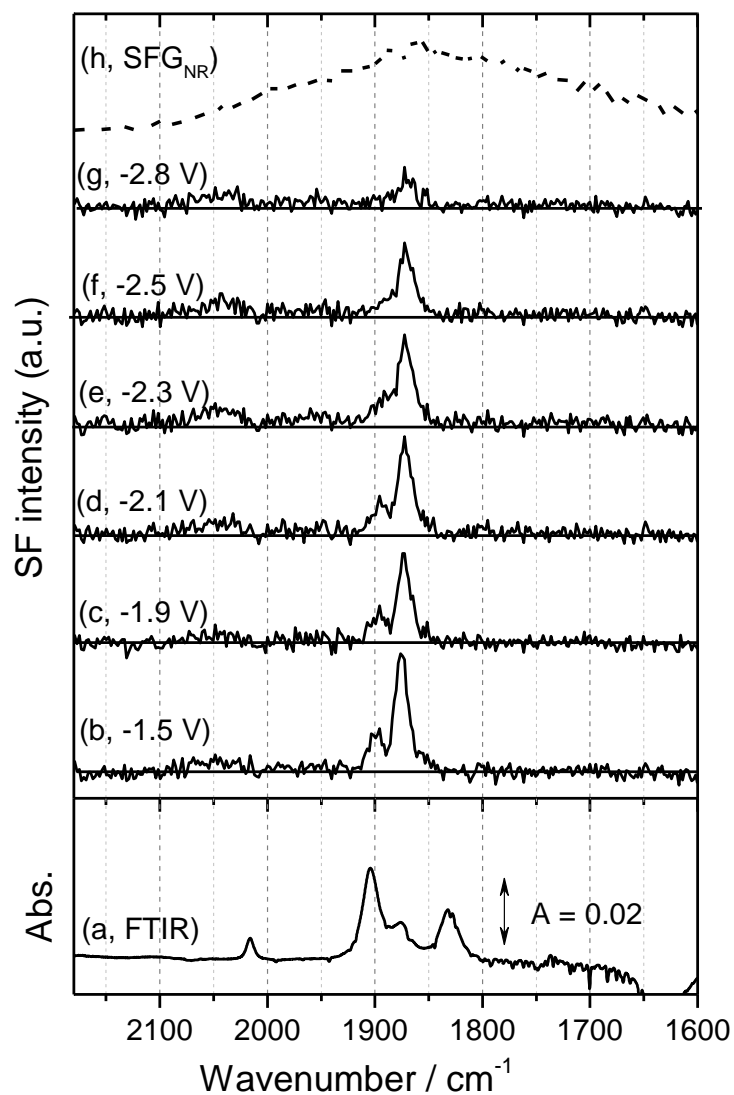
Figure S10. FTIR (a) and In-situ VSFG spectra (b-g) of [Mo(bpy)(CO)₄] (1 mM) in CH₃CN and 0.1 M TBAPF₆ under Ar on a platinum working electrode. The FTIR is recorded at open circuit and the SF spectra at the potentials indicated. The intensity of the NR background (dashed line, h) of the cell recorded with 0 ps time-delay between the IR and 800 nm laser pulses provides an approximation of the spectrum of the broadband IR pulse. Spectra (b-g) are recorded with a 0.45 ps delay between the IR and 800 nm laser pulses.
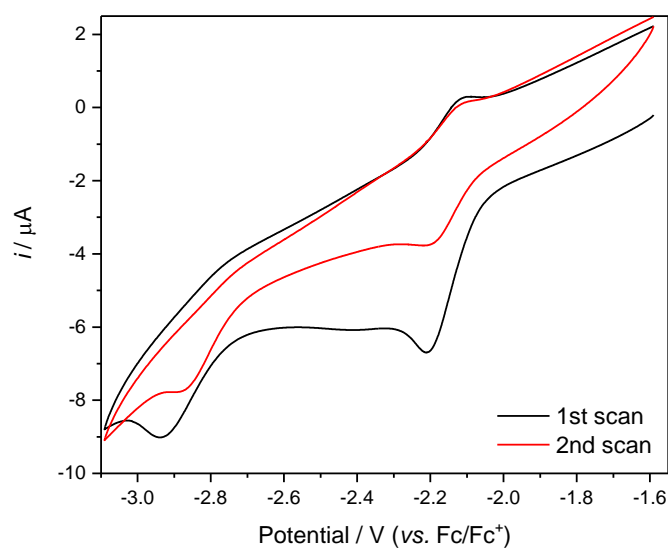
Figure S11. CVs recorded during the SEC-SFG experiment shown in Figure 6 of the main paper. 1 mM solution of [Mo(bpy)(CO)$_4$] in acetonitrile with 0.1 M TBAPF$_6$, platinum working electrode (surface area = 0.02 cm^2), scan rate = 50 mV s^{-1}; platinum counter electrode, silver wire quasi-reference electrode.
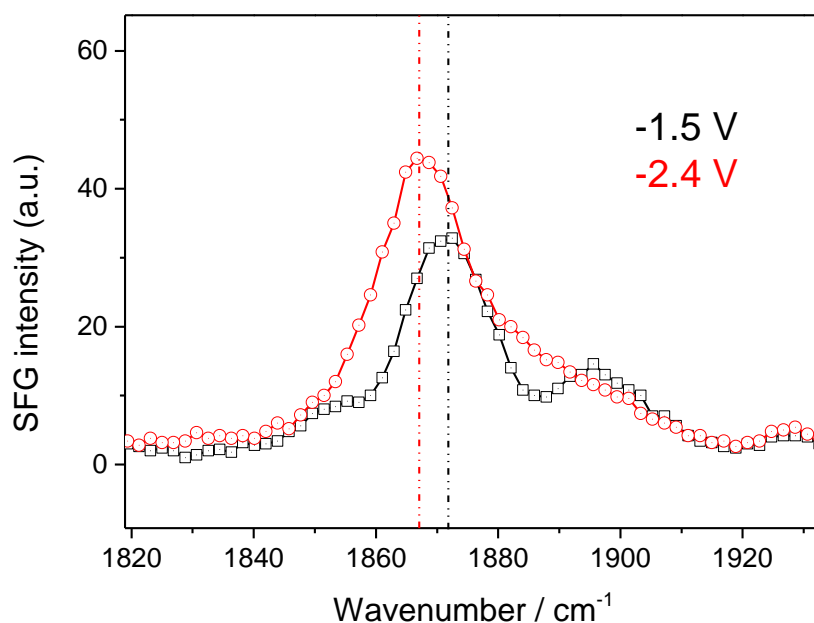

Figure S12. VSFG spectra of [Mo(bpy)(CO)$_4$] (1 mM) in CH$_3$CN and 0.1 M TBAPF$_6$ under Ar on a platinum working electrode at the applied potentials indicated. [Mo(bpy)(CO)$_4$] (stable at -1.5 V) is fully reduced to [Mo(bpy)(CO)$_4$]$^{\cdot-}$ by -2.4 V.
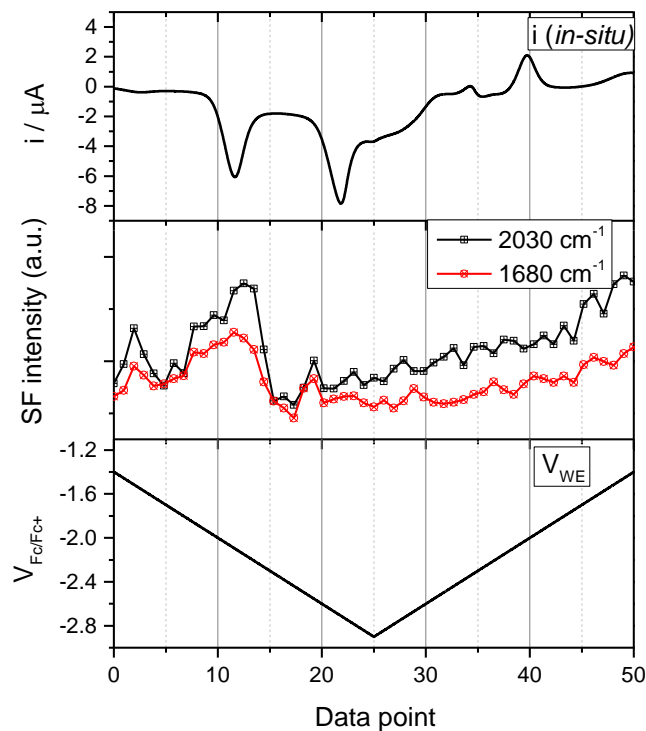
Figure S13. (top) CV recorded during a VSFG experiment of 1 mM solution of [Mo(bpy)(CO)₄] in acetonitrile with 0.1 M TBAPF₆, Gold working electrode (surface area = 0.02 cm², scan rate = 5 mV s⁻¹; platinum counter electrode, silver wire quasi-reference electrode; (middle) peak intensity of the non-resonant background with the potential scanning and (bottom) Potential waveform of the CV in (top). 2030 and 1680 cm⁻¹ are chosen as frequencies where resonant SFG responses are not anticipated and the IR and Vis pulses are temporally overlapped to maximise the NR signal. The NR response shows a large change from anticipated step change when [Mo(bpy)(CO)₄] is reduced.
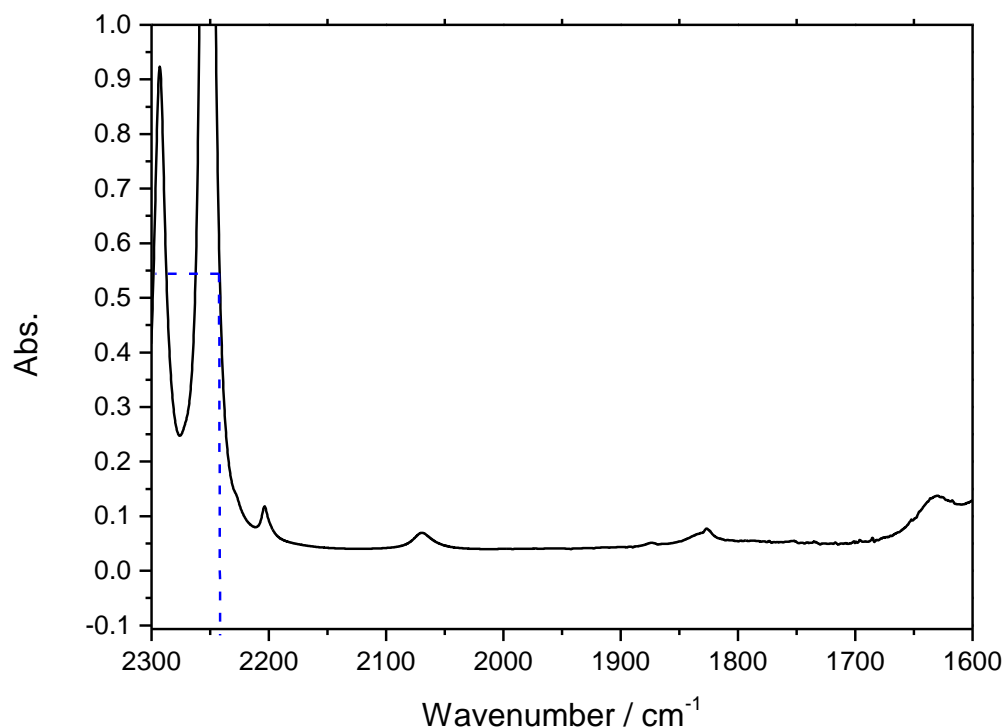
Figure S14. Transmission FTIR spectrum of CH₃CN, 50 μm pathlength

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