Supporting Information

A Bioinspired Molybdenum-Copper Molecular Catalyst for CO_2 Electroreduction

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Characterization of Complex 1

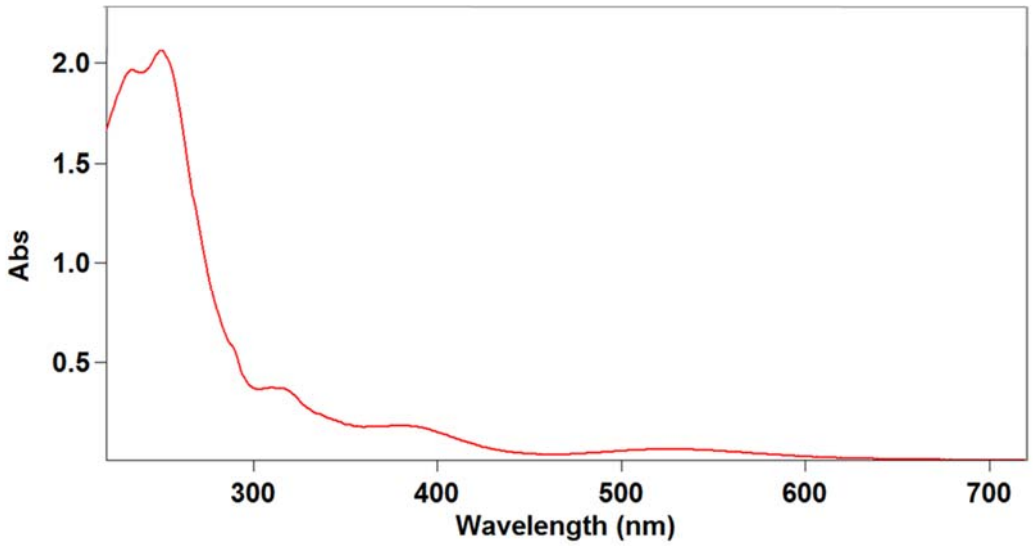


Figure S1. UV-Visible light absorption spectrum of a 10^{-5} M solution of complex **1** in CH_3CN.

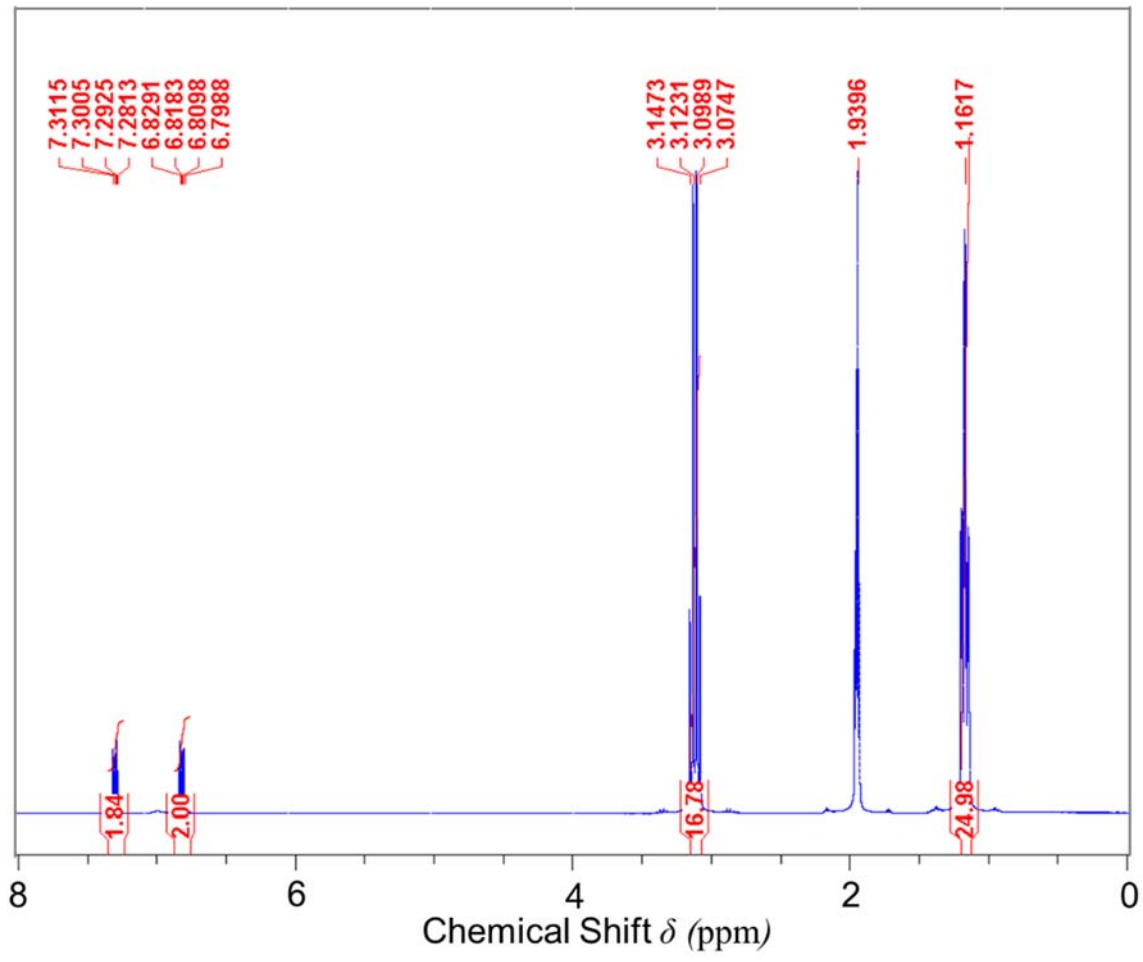


Figure S2. ^1H NMR spectrum of complex **1** in CD_3CN.

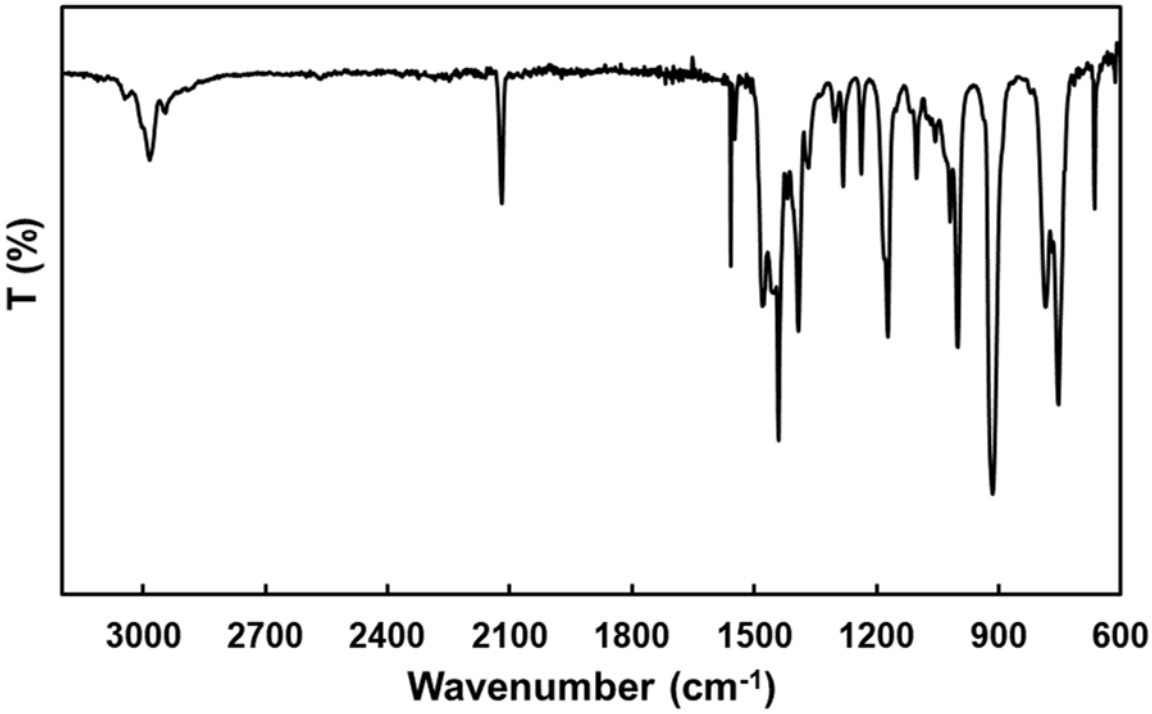


Figure S3. FTIR spectrum of complex **1**.

Electrochemical Experiments

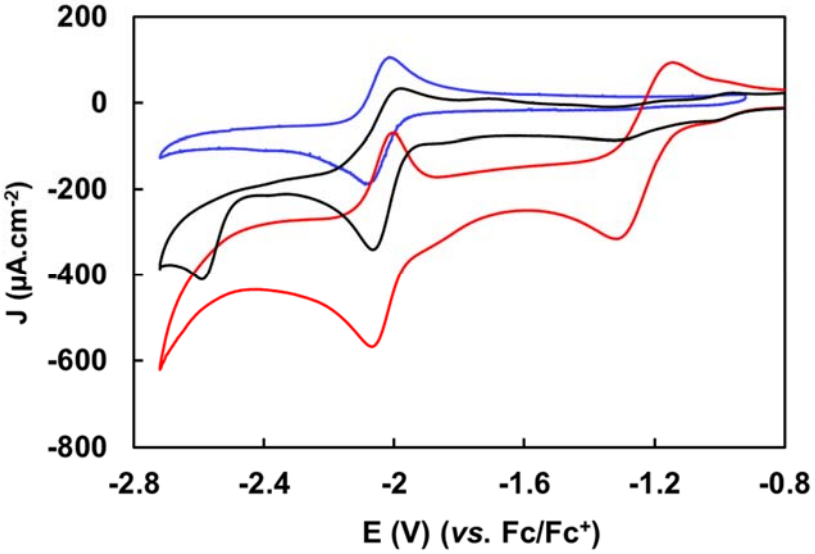


Figure S4. Overlay of the Cyclic Voltammograms of 1mM complex **1** with 0.1 M $TBAPF_6$ in dry CH_3CN under Ar (blue), after 30 min exposure to air (red) and after purging 30 min with Ar to remove air (black). Scan rate = 100 mV s^{-1}.

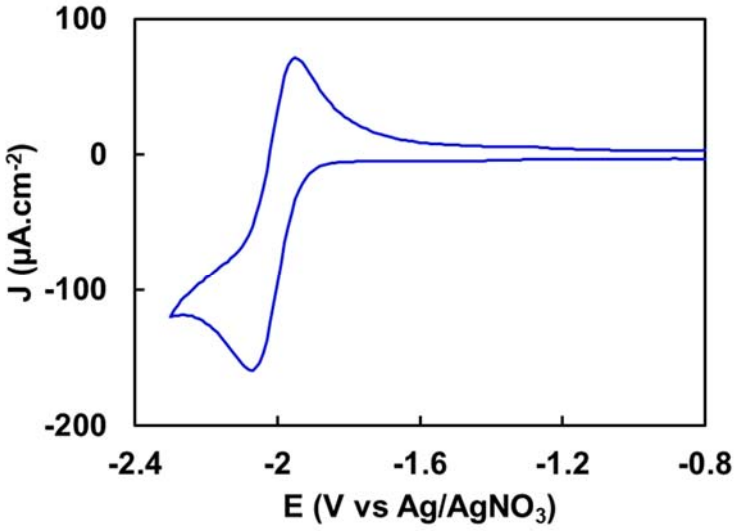


Figure S5. Cyclic Voltammetry of 1 mM solution of complex **1** in dry acetonitrile (0.1 M $TBAPF_6$) under Ar on a 1.6 mm diameter Pt WE and $Ag/AgNO_3$ as RE. The scan rate = 100 $mV.s^{-1}$; (This CV displays the electrochemical behaviour of complex **1** in the same conditions used by Tatsumi et al[1]).

Determination of the number of electrons associated to the redox events[2]

The number of electrons exchanged during the reduction of complex **1** at $E_{1/2}$ = -2.07 V vs Fc/Fc^+ was determined by the combination of a chronoamperometry experiment and a study of the stationary regime obtained at a carbon microelectrode. Solutions of complex **1** and ferrocene (20 mM in complex with 0.1 M $TBAPF_6$ in CH_3CN) were prepared. A chronoamperometry study was carried out on both solutions using exactly the same experimental conditions (Glassy carbon foam as working electrode, platinum wire counter electrode and Ag/AgCl reference electrode). The plot of the current i versus $t^{-1/2}$ (**Figure S6**) obey the Cottrell equation {A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley, New York, 2001}:

$$i = kt^{-1/2} \text{ with } k = nFACD^{1/2}(\pi)^{-1/2}$$

where i is the current, n the number of electrons, F the Farraday constant, A the electroactive area of the electrode, D the diffusion coefficient of the species and t the time. As the concentration of the ferrocene solution is equal to the one of the complex **1** solution, and as the number of electrons involved in the oxidation of ferrocene is 1, the ratio of the director coefficient k of the plot measured for the ferrocene and the complex **1** solutions is:

$$k_{Cpx}/k_{Fc} = n(D/D')^{1/2}$$

where D' is the diffusion coefficient for ferrocene, D is the diffusion coefficient for complex **1** and n is the number of electrons involved in its reduction.

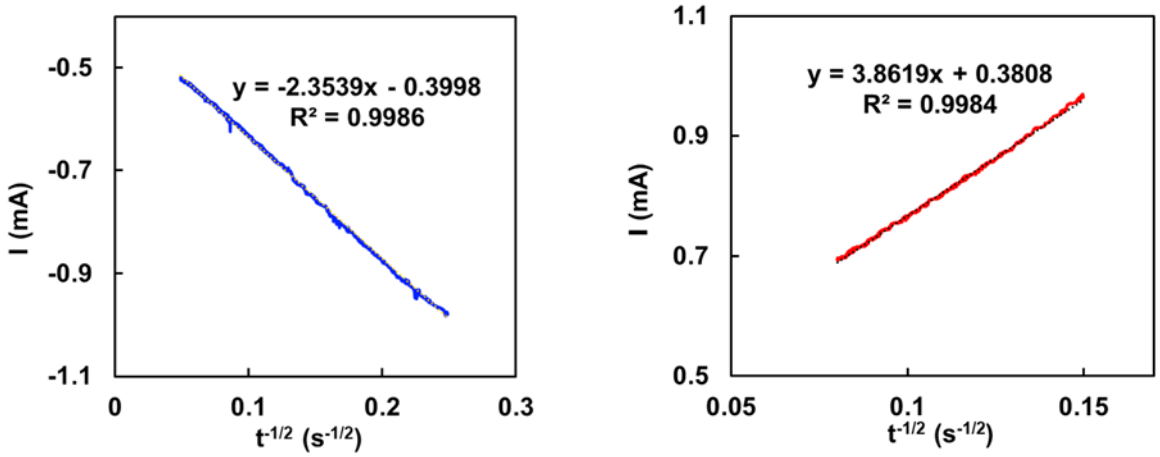


Figure S6. I vs $t^{-1/2}$ plot of the chronoamperometry data obtained from a 20 mM complex **1** (in blue, left) solution and a 20 mM ferrocene solution (in red, right) in 0.1 M $TBAPF_6$ in CH_3CN.

In parallel, the intensity of the current at a microelectrode in stationary regime was measured for both solutions (Figure S7). The following relation gives the value of the limiting current:

$$i^{lim} = 4nFrCD$$

Where i is the current, n the number of electrons, F the Farraday constant, D the diffusion coefficient of the species, r the radius of the carbon microelectrode and C the concentration of the complex in the bulk solution.

Similarly, the ratio of the limit intensities measured for the ferrocene and complex **1** solutions is:

$$i^{lim}_{Cpx}/i^{lim}_{Fc} = nD/D'$$

where D' is the diffusion coefficient for ferrocene, D is the diffusion coefficient for complex **1** and n is the number of electrons involved in its reduction at $E_{1/2}$ = -2.07 V vs Fc/Fc^+.

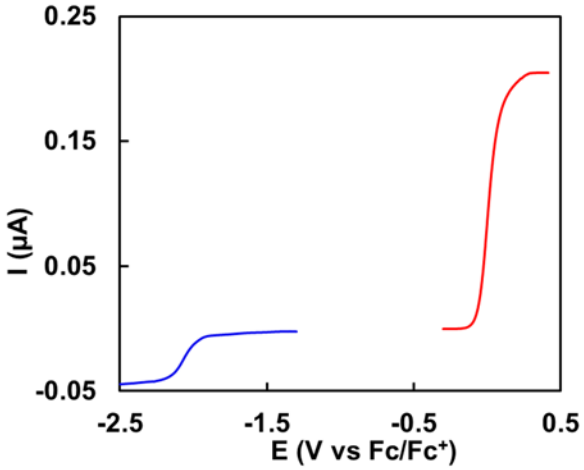


Figure S7. Overlay of linear sweep voltammograms of a 20 mM complex **1** solution (blue) and a 20 mM ferrocene (red) in a 0.1 M $TBAPF_6$ solution in CH_3CN obtained in stationary regime at a carbon microelectrode (5 $mV.s^{-1}$ scan rate).

The number of electrons exchanged during the reduction of complex **1** is then given by:

$$n = (k_{Cpx}/k_{Fc})^2/(i^{lim}_{Cpx}/i^{lim}_{Fc}).$$

Table S1. Key parameters for the determination of the number of electrons

k_{cpx} ($mA.s^{1/2}$)	k_{Fc} ($mA.s^{1/2}$)	I^{lim}_{Cpx} (µA)	I^{lim}_{Fc} (µA)	n
2.3539	3.8619	0.042	0.204	**1.805**

From our electrochemical data (Table S1), we find **n = 1.805**. Accordingly, the process observed by electrochemistry for the reduction of complex **1** at $E_{1/2}$ = -2.07 V vs Fc/Fc^+ involves a transfer of **2 electrons**.

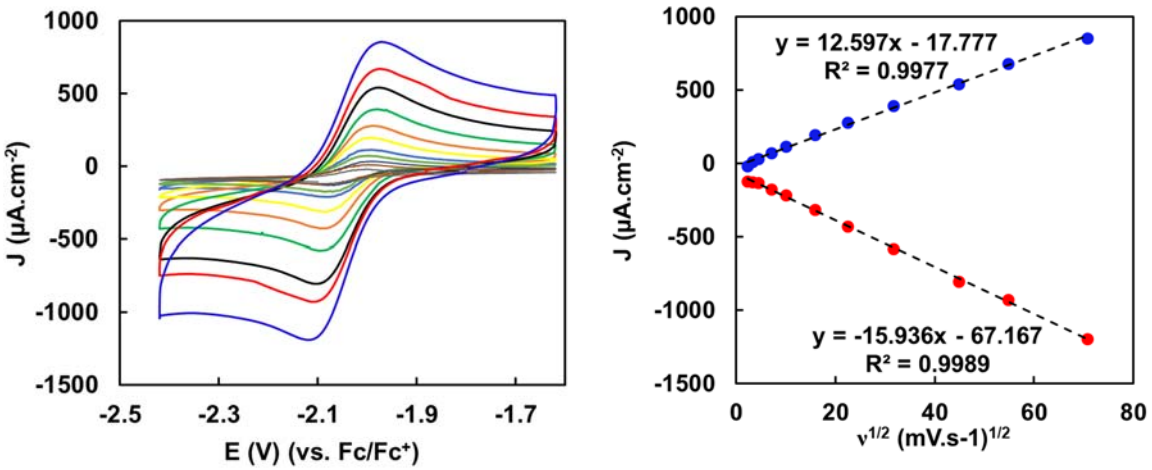


Figure S8. Cyclic Voltammetry data of complex **1** at different scan rates in CH_3CN (0.1 M $TBAPF_6$) under Ar (left); scan rates was varied from 5 to 5000 $mV.s^{-1}$. Plot of the anodic current peak (blue dots) and the cathodic current peak (red dots) as a function of the square root of scan rate (right).

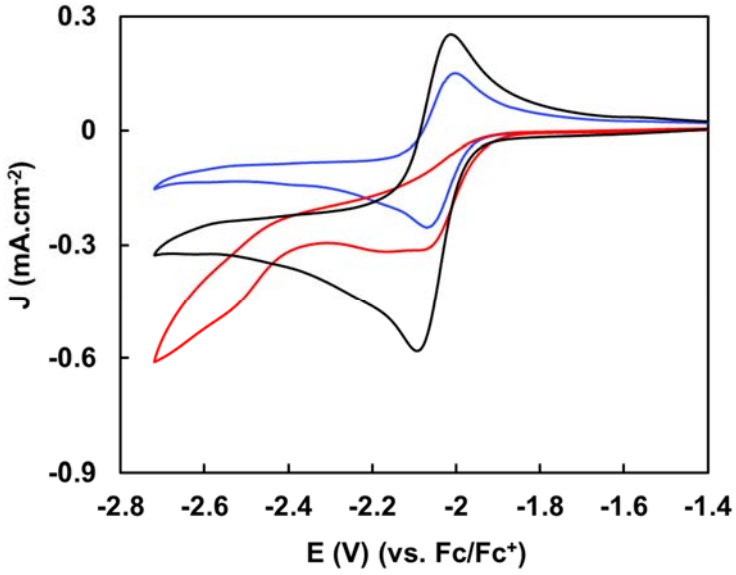


Figure S9. Cyclic voltammograms of complex **1** in dry CH_3CN (0.1 M $TBAPF_6$) under Ar (blue), after 30 min purging with CO_2 (red) and after purging 30 min with Ar to remove CO_2 (black). Scan rate = 50 mVs^{-1} (The increase of current density of the voltammogram before and after purging (blue vs. black) is due to the increase of concentration of the complex occurring in the long and vigorous purging process causing partial evaporation of the solvent)

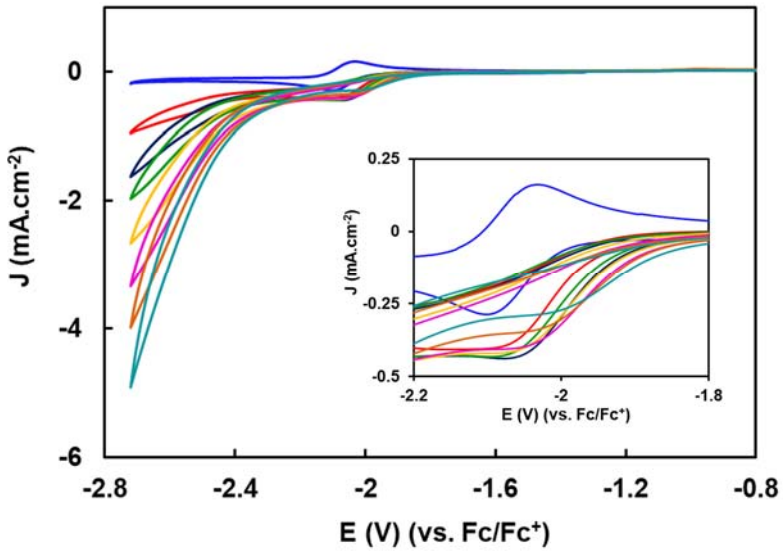


Figure S10. Cyclic voltammograms of 1mM complex **1** with 0.1 M $TBAPF_6$ in dry CH_3CN under Ar (blue), under CO_2 (red) and under CO_2 with different TFE concentrations (0.01 M (black), 0.02 M (green), 0.05 M (yellow), 0.1 M (pink), 0.2 M (orange) and 0.6 M (turquoise)). The scan rate was 50 mV s^{-1}. Inset: zoom on the potential window between -2.2 V and -1.8 V vs Fc/Fc^+.

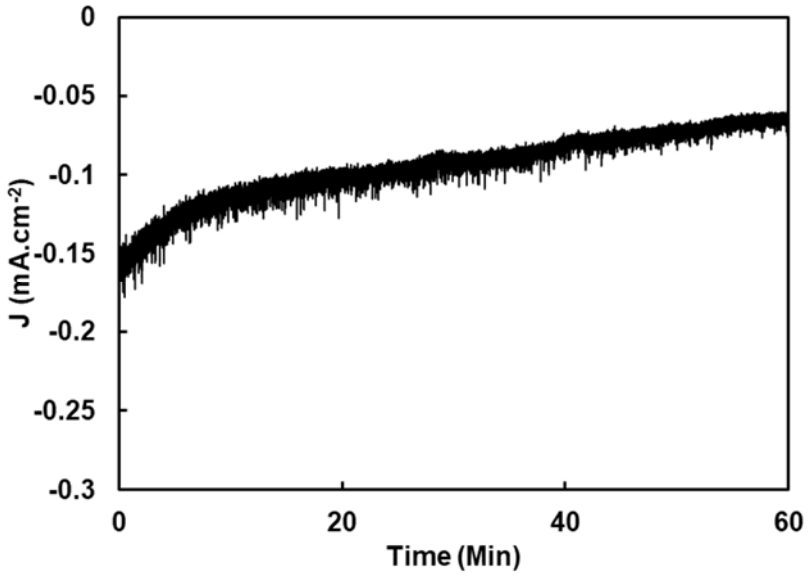


Figure S11. Current density plot with respect to time for CPE at -2.17 V.

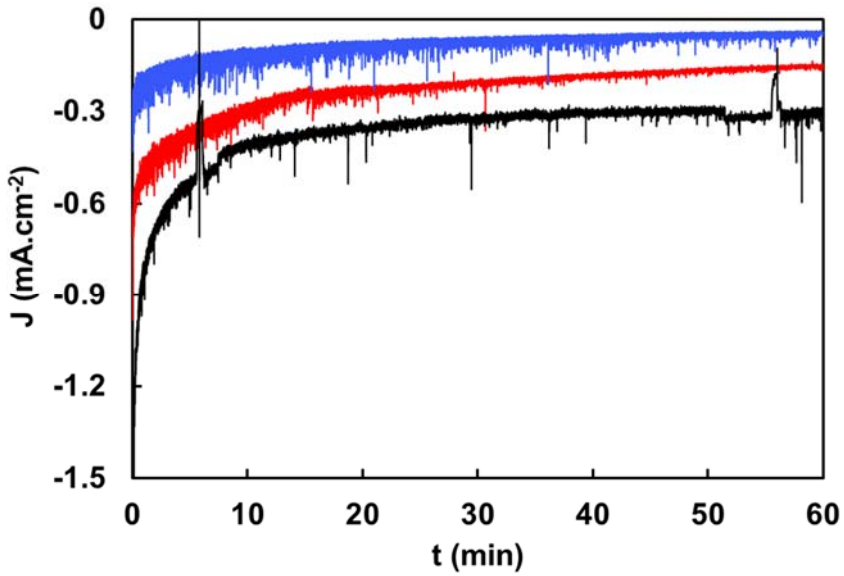


Figure S12. Current density as a function of time during 1 h controlled potential electrolysis on a glassy carbon plate electrode at -2.62 V (black line), at -2.37 V (red line) of a 1 mM solution of complex **1** and at -2.62 V vs Fc/Fc^+ without complex **1** (background, blue) in a CO_2 saturated CH_3CN solution containing 0.1 M $TBAPF_6$ and 0.1 M TFE.

Rinse test

A 1 h constant potential electrolysis at -2.62 V vs Fc/Fc^+ of a 1 mM solution of complex **1** with 0.1 M $TBAPF_6$ and 0.1 M TFE in 7 mL CH_3CN was carried out using a glassy carbon plate electrode, in the exact conditions reported for catalytic activity studies. Without exposure to air the solution was syringed out before being replaced by the same volume of a fresh solution without complex **1** in the same electrolyte. After bubbling CO_2 in that solution for 30 min a second 1h constant potential electrolysis at -2.62 V vs Fc/Fc^+ was carried out. Current density vs. time is presented in Fig. S13 below.

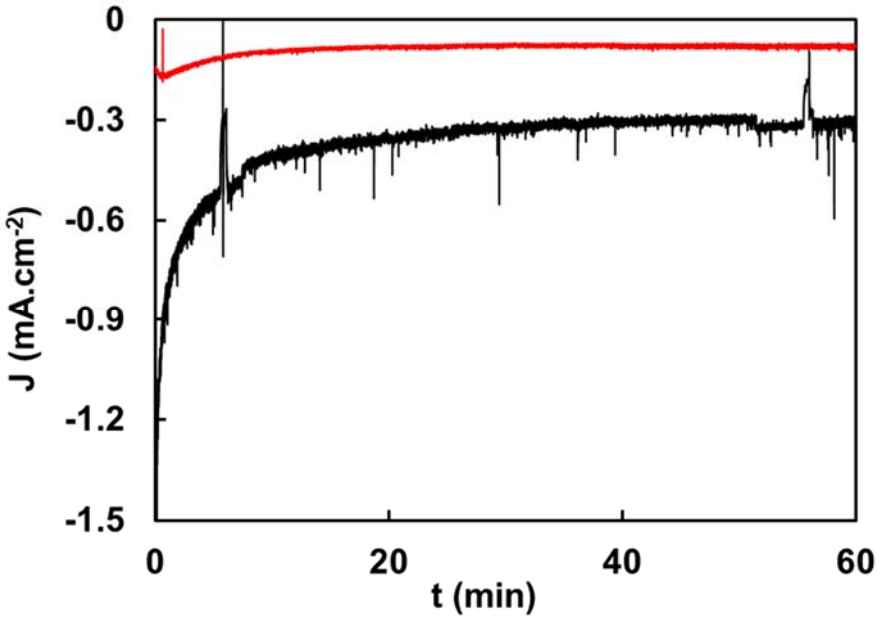


Figure S13. Current density as a function of time during 1 h electrolysis on glassy carbon plate electrode at −2.62 V vs Fc/Fc^+ of 1 mM of complex **1** before rinse test (black) and after (red), in a CO_2 saturated atmosphere, in CH_3CN with 0.1 M $TBAPF_6$ and 0.1 M TFE.

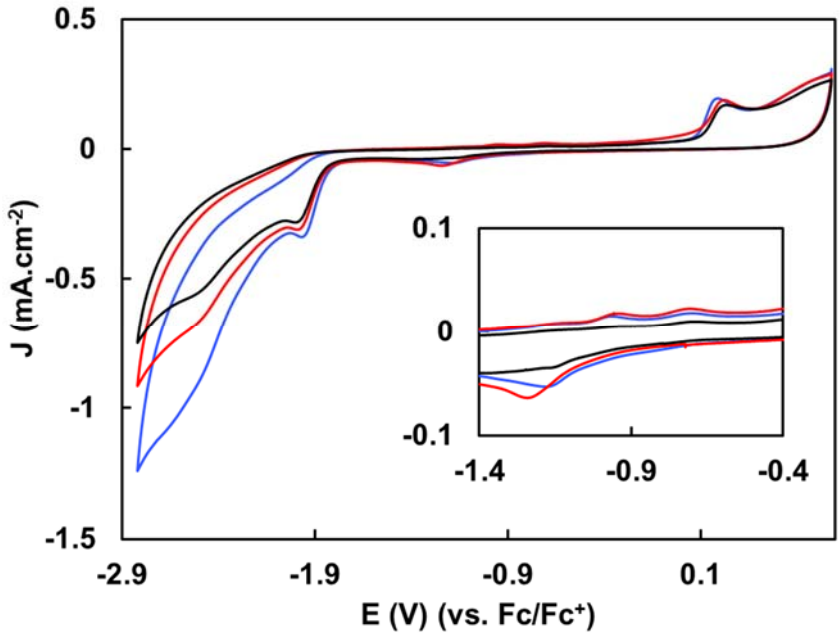


Figure S14. Cyclic voltammograms of 1 mM complex **1** with 0.1 M $TBAPF_6$ and 0.1 M TFE in dry CH_3CN on glassy carbon plate electrode under CO_2 (blue), after 30 min controlled potential electrolysis at -2.62 V vs Fc/Fc^+ under CO_2 (red) and after 60 min controlled potential electrolysis at -2.62 V vs Fc/Fc^+ under CO_2 (black). The scan rate was 50 mV s^{-1}. Inset: zoom on the potential window between -1.4 V and -0.4 V vs Fc/Fc^+.

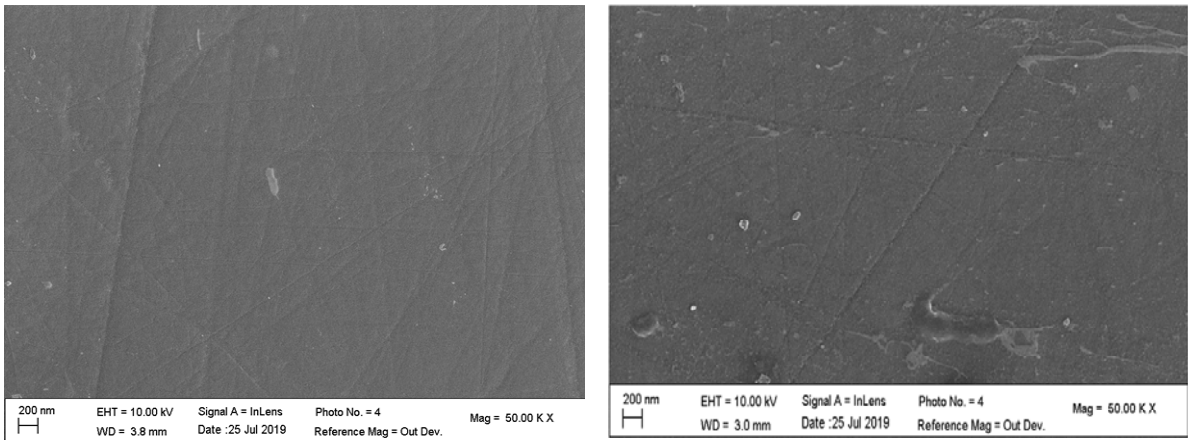


Figure S15. SEM images of glassy carbon plate electrode surface before controlled potential electrolysis (left) and after a 1-hour controlled potential electrolysis at -2.62 V vs Fc/Fc^+ in presence of 1 mM complex **1** with 0.1 M $TBAPF_6$ and 0.1 M TFE in dry CH_3CN (right). Corresponding energy dispersive x-ray spectra are displayed in Figure S15 and Figure S16.

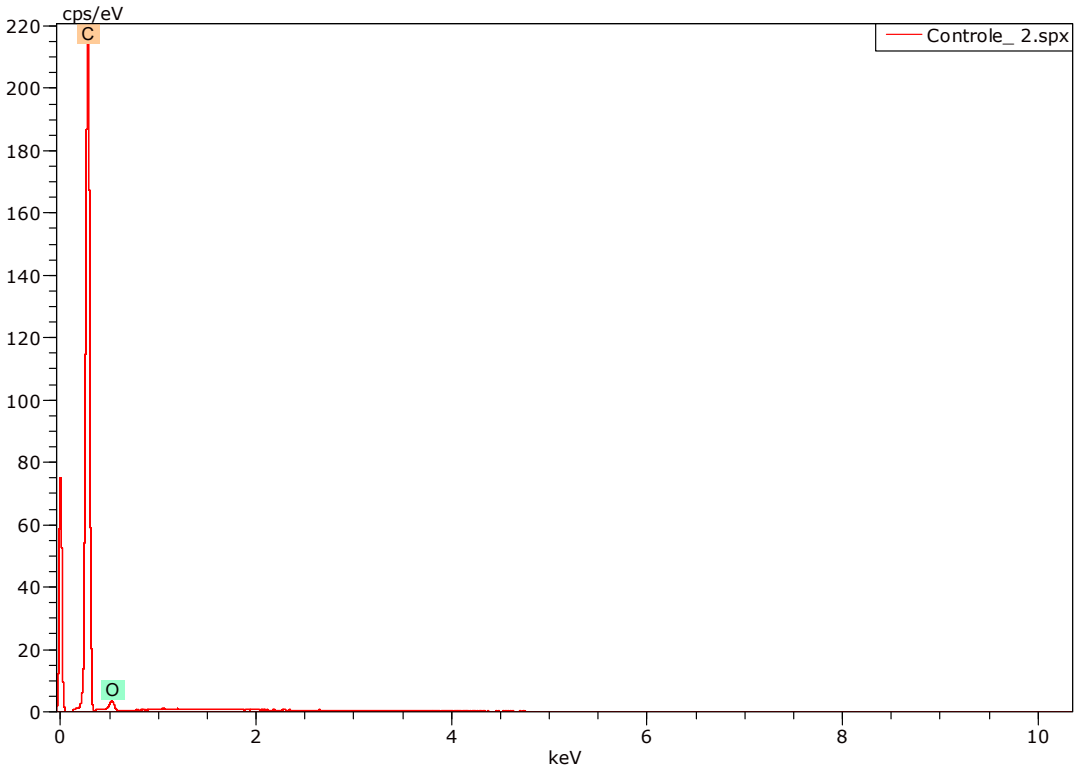


Figure S16. Energy dispersive x-ray spectrum of a 1 cm square glassy carbon plate electrode before controlled potential electrolysis (shown in Figure S14-left).

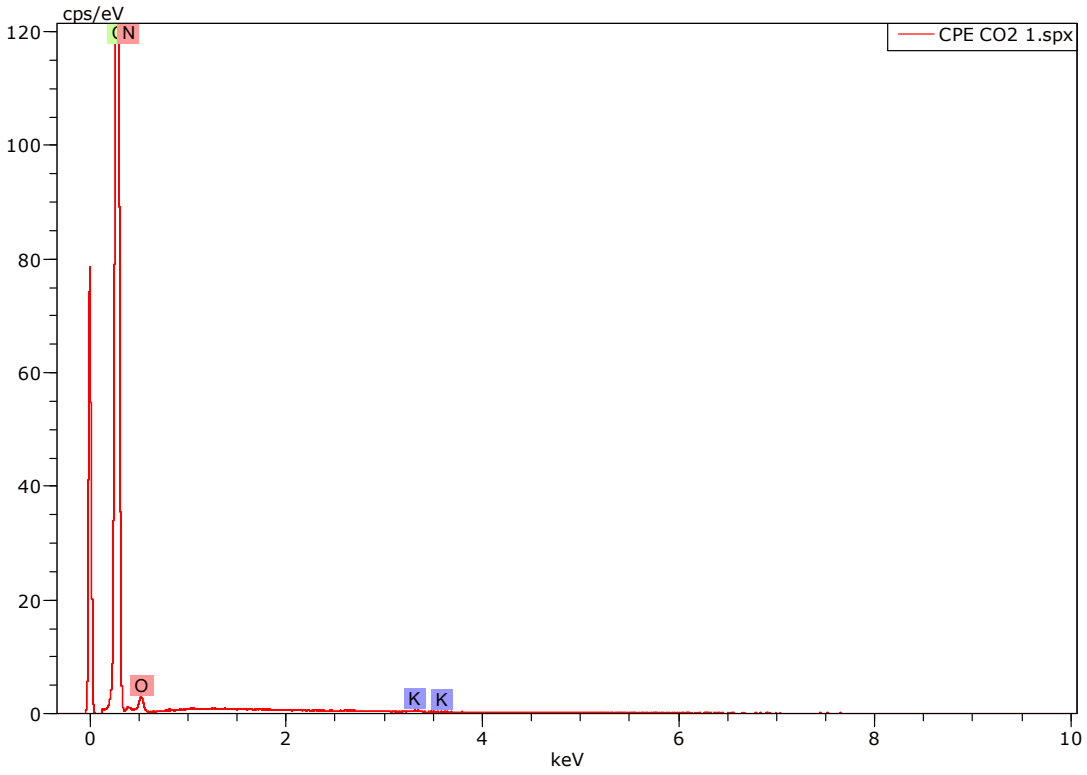


Figure S17. Energy dispersive x-ray spectrum of a 1 cm square glassy carbon plate electrode after 1-hour controlled potential electrolysis of complex **1** at -2.62 V vs Fc/Fc^{+} under CO_2 in presence of 1 mM complex **1** with 0.1 M $TBAPF_6$ and 0.1 M TFE in dry CH_3CN (shown in Figure S 14-right).

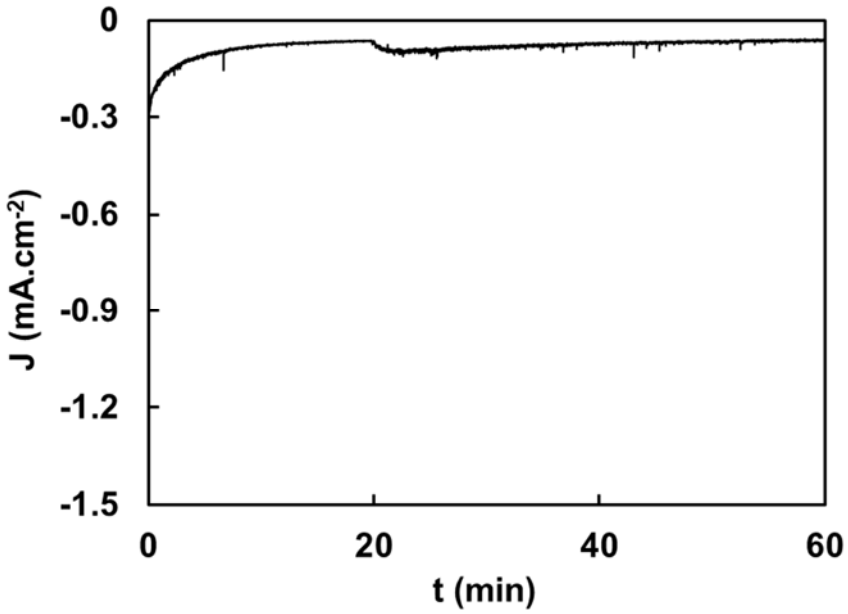


Figure S18. Current density as a function of time over 1 h electrolysis on a glassy carbon plate electrode at -2.62 V vs Fc/Fc^+ of 1 mM of **$[Mo(O)(bdt)_2][Et_4N]_2$** in a CO_2 saturated atmosphere, in CH_3CN with 0.1 M $TBAPF_6$ and 0.1 M TFE. Only detected product was H_2.

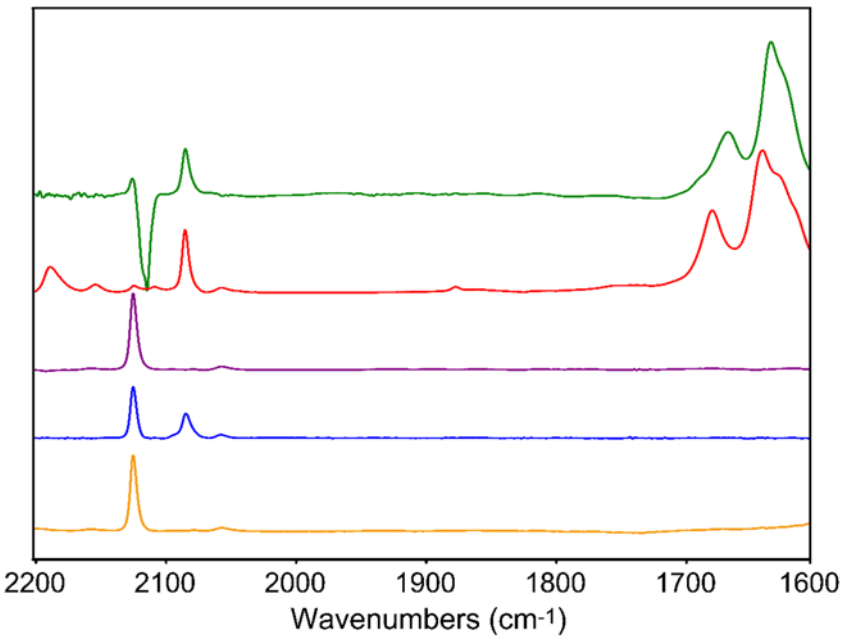
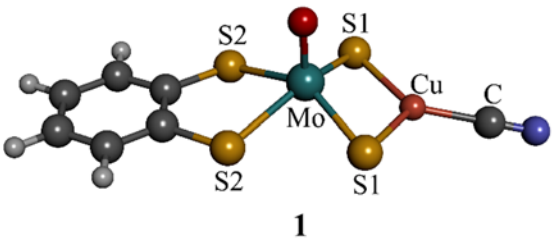
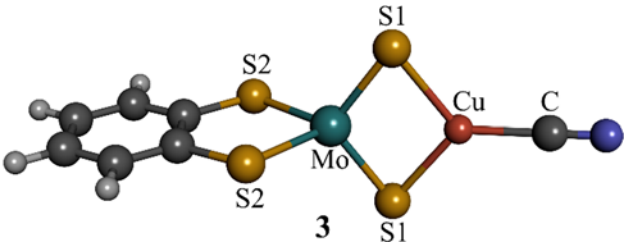


Figure S19. IR-SEC spectrum of complex **1** in dry CH_3CN with 0.1 M $TBAPF_6$ at resting potential under Ar (yellow), at -2.24 V vs Fc/Fc^+ under Ar (blue), at resting potential under CO_2 (purple), at -2.24 V vs Fc/Fc^+ under CO_2 (red), and in dry CD_3CN at -2.24 V vs Fc/Fc^+ under CO_2 (green). Lab-O-Mak IR-SEC cell equipped with Pt grid for working and counter electrodes and an Ag pseudo-reference electrode.

Computational Details



1



3

Table S2. Selected bond distances (in Å) and angles (in deg). Experimental values are given in italic.

Structure	Mo–O [Å]	Mo–S1 [Å]	Mo–S2 [Å]	Cu–S1 [Å]	Cu–C [Å]	Mo–Cu [Å]	S1–Mo–S2 (deg)	Mo–Cu–C (deg)
1	1.694 *1.694(4)*	2.311 *2.306(2)* *2.307(2)*	2.474 *2.434(2)* *2.448(2)*	2.242 *2.181(2)* *2.180(2)*	1.914	2.665 *2.599(1)*	79.5/79.8	178.7
1$_{red}$	1.714	2.511/2.500	2.418/2.412	2.332/2.329	1.918	3.057	84.6/84.4	142.8
2a	1.930	2.445/2.312	2.562/2.389	2.337/2.298	1.927	3.011	85.9/89.7	174.5
2b	1.707	2.520/2.487	2.404/2.402	2.395/2.274	1.908	3.198	85.1/89.7	145.5
3	N.A.	2.264	2.383/2.375	2.320/2.314	1.918	2.755	112.9/117.9	177.4
3$_{red}$	N.A.	2.300	2.352/2.344	2.326/2.322	1.922	2.805	115.5/117.5	177.1

Table S3. Calculated scaled (scaling factor 0.9674[3]) and experimental ν_{CN} stretching frequencies (cm^{-1}).

Structure	Calculated CN stretch (cm^{-1})	Experimental CN stretch (cm^{-1})
1	2141	2124
1$_{red}$	2059	2081
2a	2091	
2b	2086	
3	2128	2150
3$_{red}$	2109	

Table S4. Calculated scale (scaling factor 0.9674[3]) vibrational frequencies (in cm^{-1}) of some key intermediates formed during the CO_2 reduction reaction. The experimental values are given in parentheses.

Structure	CN stretch (cm^{-1})	Mo–H stretch (cm^{-1})
4-Mo^{V}H	2135 (2187)	1858 (1874)
5-Mo^{V}H-SH	2147	1807

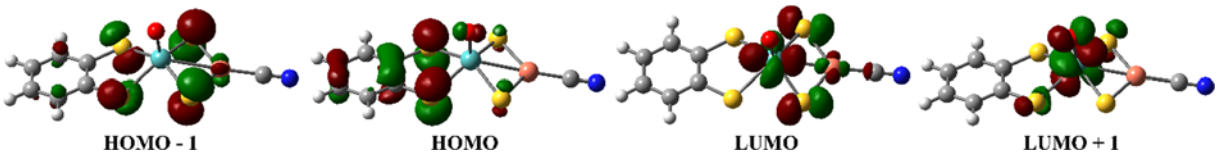


Figure S20. Kohn-Sham frontier molecular orbitals (isovalue 0.5) for complex **1**.

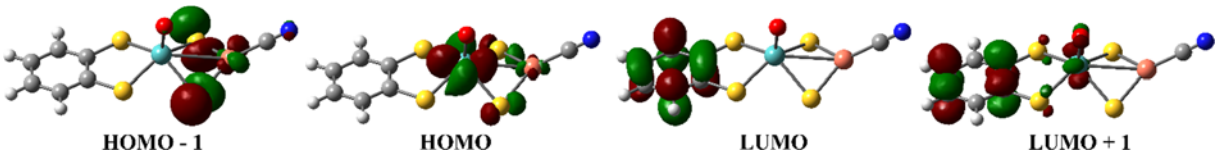


Figure S21. Kohn-Sham frontier molecular orbitals (isovalue 0.5) for two-electron reduced complex $\mathbf{1}_{red}$.

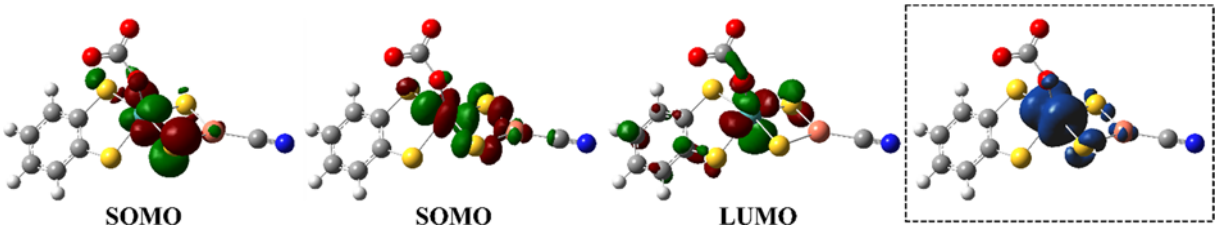


Figure S22. Kohn-Sham frontier molecular orbitals (isovalue 0.5) along with the total spin density for complex **2a**.

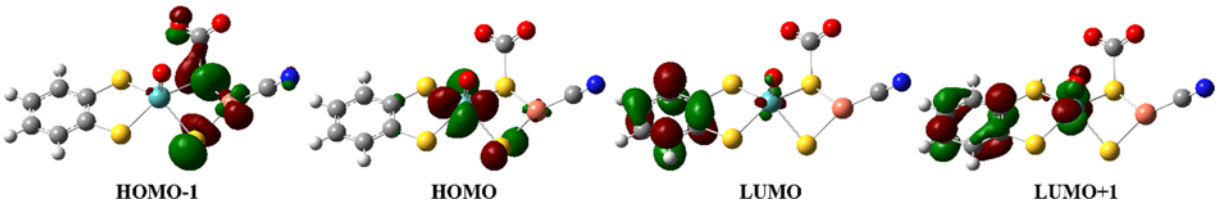


Figure S23. Kohn-Sham frontier molecular orbitals (isovalue 0.5) for complex **2b**.

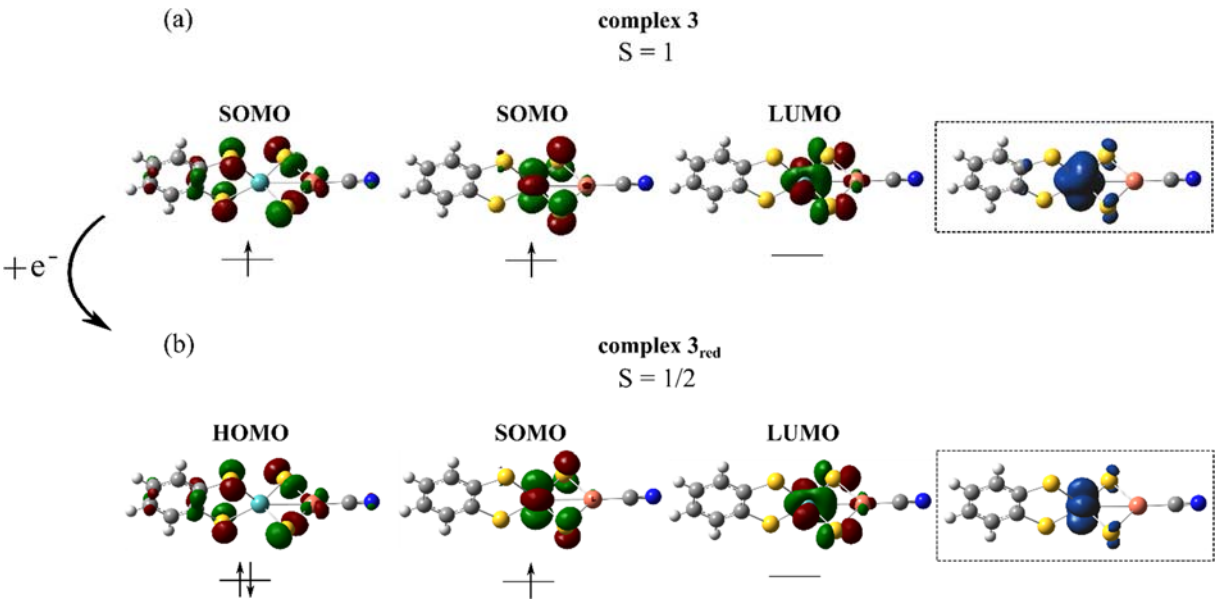


Figure S24. Frontier MO (isovalue 0.05) along with the total spin density for complex **3** (a) and its singly-reduced complex $\mathbf{3}_{red}$ (b).

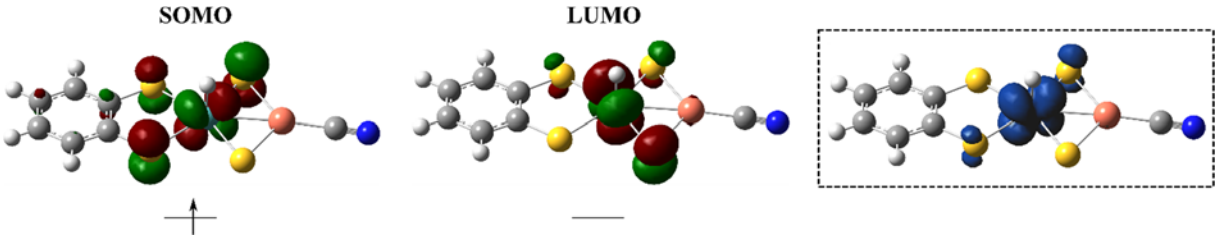


Figure S25. Frontier MO (isovalue 0.05) along with the total spin density for complex 4-$Mo^{V}H$.

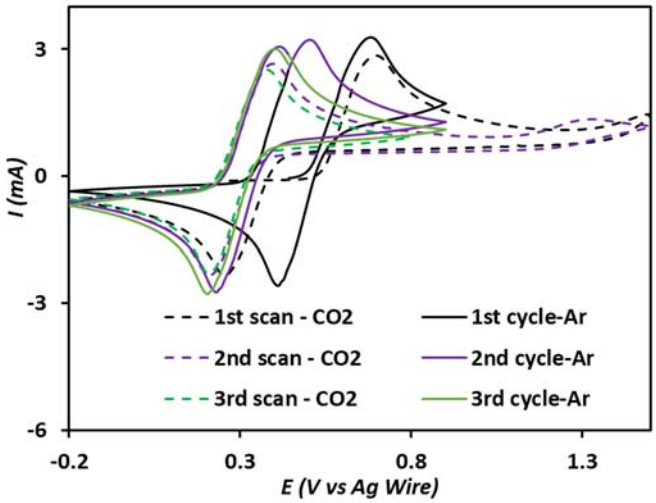


Figure S26. Potential shift observed for the Fc/Fc^{+} couple in the IR-SEC cell after the FTIR measurements shown in Figure 4 (20 s controlled potential electrolysis at -1.9V *vs*. the Ag pseudo-reference electrode): under Ar (black FTIR spectra in Figure 4, full line) and under CO_2 (red FTIR spectra in Figure 4, dashed line).

The coordinates of all intermediates (in xyz format)

1

Mo	-4.248930	-0.786359	-4.878644
Cu	-4.075067	1.405573	-6.384691
H	-5.128235	-2.010660	0.127998
H	-1.115696	-3.890592	-2.068807
S	-2.350242	-2.030864	-3.894658
S	-4.911360	-0.838452	-2.496449
S	-5.600278	1.085143	-4.774798
S	-2.590287	-0.274375	-6.402840
C	-3.915946	2.993850	-7.441606
O	-5.191648	-1.991901	-5.604413
C	-2.796756	-2.568681	-2.280874
C	-3.934280	-2.036850	-1.658560
C	-4.250727	-2.426811	-0.352612
C	-3.453298	-3.338415	0.326391
C	-2.322051	-3.868936	-0.293449
C	-1.996446	-3.482891	-1.586913
N	-3.816324	3.957002	-8.082948
H	-3.713549	-3.635032	1.334923
H	-1.696249	-4.581587	0.229377

1_{red}

Mo	-3.904544	-0.410922	-4.509391
Cu	-3.879860	1.956950	-6.442153
H	-5.138416	-2.142410	0.200382
H	-1.204773	-4.079463	-2.069211
S	-2.168823	-1.885435	-3.698185
S	-4.744485	-0.681893	-2.264728
S	-4.882333	1.896093	-4.340945
S	-2.042079	0.697159	-5.754956
C	-4.476391	2.518672	-8.176273
O	-4.879015	-1.327173	-5.581574
C	-2.744386	-2.588886	-2.173708
C	-3.874647	-2.043890	-1.530057
C	-4.277879	-2.574774	-0.299455
C	-3.601359	-3.639095	0.288342
C	-2.493610	-4.189179	-0.355563
C	-2.072130	-3.658955	-1.571091
N	-4.822853	2.893806	-9.228602
H	-3.938377	-4.037418	1.238255
H	-1.961409	-5.024026	0.085339

2a

C	-2.387946	-3.860231	-1.681832
C	-3.069134	-2.866934	-2.408963
C	-3.859552	-1.944782	-1.686172
C	-3.945946	-2.047668	-0.294030
C	-3.267470	-3.039632	0.405221

C	-2.481785	-3.951046	-0.299943
S	-2.928357	-2.778356	-4.149539
Mo	-4.433485	-0.826631	-4.874181
O	-5.494466	-2.009526	-5.964298
S	-4.758659	-0.656865	-2.509565
Cu	-4.211244	1.834060	-6.260638
C	-3.999344	3.446096	-7.293267
N	-3.869737	4.425298	-7.913918
S	-5.994615	1.038101	-5.051507
S	-2.622721	0.149914	-5.933548
C	-5.494259	-3.370947	-6.254456
O	-6.257992	-4.071146	-5.552756
O	-4.795163	-3.726819	-7.227805
H	-4.560595	-1.334595	0.244194
H	-1.777780	-4.572556	-2.225328
H	-3.352230	-3.100710	1.483321
H	-1.944910	-4.732624	0.224975

2b

Mo	-3.993977	-0.605210	-4.514534
Cu	-4.083446	1.787760	-6.634671
H	-4.950343	-1.880281	0.391076
H	-1.539793	-4.438255	-2.100873
S	-2.419873	-2.274472	-3.803825
S	-4.580878	-0.596803	-2.183232
S	-4.250474	1.863973	-4.367757
S	-2.386464	0.129711	-6.310449
C	-4.804234	2.390914	-8.294614
O	-5.295831	-1.322490	-5.353357
C	-2.886718	-2.769444	-2.159870
C	-3.856171	-2.038725	-1.448470
C	-4.203922	-2.446467	-0.155675
C	-3.614008	-3.560079	0.433083
C	-2.649437	-4.281389	-0.269511
C	-2.291686	-3.880543	-1.552851
N	-5.217150	2.775587	-9.316388
H	-3.905941	-3.862232	1.432028
H	-2.180688	-5.150169	0.177311
C	-2.086282	-1.253288	-7.590773
O	-2.623686	-1.047049	-8.695238
O	-1.366896	-2.198850	-7.230005

3

Mo	-3.897079	-0.172294	-4.337616
Cu	-4.044659	1.539543	-6.491657
H	-5.559108	-2.886078	-0.311363
H	-0.790098	-3.172688	-1.583348
S	-2.070753	-1.383469	-3.422501
S	-5.167047	-1.193187	-2.598238
S	-3.624647	2.074450	-4.273573
S	-4.356325	-0.753636	-6.477011
C	-4.061508	2.725651	-7.999406
C	-2.695273	-2.296026	-2.044821

C	-4.050278	-2.214500	-1.683858
C	-4.513516	-2.951140	-0.587661
C	-3.651504	-3.756944	0.141429
C	-2.304800	-3.837416	-0.217186
C	-1.834543	-3.112183	-1.301581
N	-4.062162	3.443332	-8.914531
H	-4.026755	-4.320353	0.986594
H	-1.625144	-4.463862	0.346926

3_{red}

Mo	-3.835309	-0.173673	-4.358506
Cu	-4.058093	1.580604	-6.536212
H	-5.559534	-2.884119	-0.313793
H	-0.777392	-3.215902	-1.531753
S	-2.067383	-1.388139	-3.412341
S	-5.095680	-1.178786	-2.646383
S	-3.621336	2.116068	-4.315272
S	-4.363262	-0.721353	-6.528614
C	-4.114178	2.773037	-8.042373
C	-2.671766	-2.324872	-2.014339
C	-4.026718	-2.231103	-1.670522
C	-4.509378	-2.959371	-0.578229
C	-3.664036	-3.773444	0.166726
C	-2.312016	-3.867064	-0.177047
C	-1.826225	-3.145647	-1.260934
N	-4.135173	3.494023	-8.956948
H	-4.053133	-4.331976	1.010055
H	-1.644586	-4.499081	0.397086

4-$Mo^{V}H$

Mo	-3.891056	-0.278245	-4.582726
Cu	-3.984005	1.523941	-6.555411
H	-5.269461	-2.282676	0.109724
H	-1.048047	-3.796030	-1.965698
S	-2.237798	-1.879107	-3.722105
S	-4.921007	-0.825982	-2.348626
S	-5.311281	1.444900	-4.667370
S	-2.502160	-0.203151	-6.418945
C	-4.106044	2.908006	-7.875818
C	-2.751001	-2.503331	-2.160146
C	-3.948911	-2.058448	-1.570746
C	-4.343077	-2.613523	-0.344042
C	-3.569286	-3.575958	0.287960
C	-2.374235	-4.003338	-0.292170
C	-1.972795	-3.466793	-1.507051
N	-4.178635	3.759471	-8.663516
H	-3.896942	-3.993925	1.232009
H	-1.762945	-4.750956	0.197736
H	-4.938010	-1.368458	-5.319261

$TS_{4\text{-}3red}$

Mo	-4.351237	-0.620679	-4.848037
Cu	-4.511112	1.862733	-5.992995
H	-3.782230	-1.121733	0.185536
H	-2.668744	-4.974248	-2.713901
S	-3.815667	-2.902414	-4.374228
S	-4.601827	-0.483590	-2.506131
S	-6.241983	0.614355	-5.198685
S	-2.625972	0.549558	-5.504351
C	-4.381224	3.583698	-6.827471
C	-3.480546	-2.986107	-2.642043
C	-3.800575	-1.897902	-1.818271
C	-3.532640	-1.964557	-0.447648
C	-2.954066	-3.100704	0.100543
C	-2.643706	-4.187628	-0.716832
C	-2.909666	-4.131091	-2.077946
N	-4.293055	4.623587	-7.338670
H	-2.745816	-3.139449	1.162375
H	-2.194087	-5.077123	-0.293614
H	-4.902689	-1.615389	-6.260161
C	-5.525700	-1.974458	-7.508112
O	-4.959187	-1.376978	-8.376566
O	-6.378168	-2.765281	-7.225186

5-Mo^{V}H-SH

C	-1.749131	-2.774505	-1.221381
C	-2.699129	-2.349674	-2.155091
C	-4.063976	-2.515731	-1.883552
C	-4.461189	-3.119202	-0.685996
C	-3.512853	-3.537271	0.234684
C	-2.154267	-3.362946	-0.033323
S	-2.187727	-1.640348	-3.684828
Mo	-4.126747	-0.669398	-4.646988
S	-3.159396	-0.845910	-6.856556
Cu	-3.468784	1.428286	-6.358181
C	-3.114096	3.002900	-7.402639
N	-2.893299	3.953564	-8.031150
S	-5.265547	-2.017784	-3.075028
S	-4.384020	1.445091	-4.212042
H	-5.516258	-3.252163	-0.481155
H	-0.695454	-2.644218	-1.433909
H	-3.830196	-3.996368	1.162245
H	-1.411868	-3.687951	0.684360
H	-5.510312	-1.278820	-5.427002
H	-4.265710	-0.956299	-7.618873

TS$_{5\text{-}3red}$

C	-5.399743	-0.065794	-0.531947
C	-5.118052	1.298911	-0.608135
C	-3.829016	1.756570	-0.381582
C	-2.807061	0.852119	-0.079343
C	-3.086847	-0.517649	-0.008332
C	-4.391183	-0.968901	-0.231890
S	-1.175662	1.429516	0.254384

Mo	0.240763	-0.446420	0.281988
S	1.781861	0.460415	1.837913
Cu	2.942391	0.164061	-0.173808
C	4.771160	0.466353	-0.665290
N	5.878898	0.644998	-0.962461
S	-1.800021	-1.654564	0.396574
S	1.270954	-0.675946	-1.618081
H	-4.607118	-2.028415	-0.172421
H	-3.607845	2.815180	-0.435470
H	-6.405810	-0.423769	-0.709170
H	-5.904540	2.005130	-0.841378
H	0.540697	-1.825913	1.325487
H	1.321304	-0.945706	1.873567

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