Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Operando Systems Chemistry Reaction Catalysis (OSCR-Cat) for Visible Light Driven CO_2 Conversion

Kousik Das,[a] Ratnadip De,[a] Francis Verpoort*[b,c,d] and Soumyajit Roy*[a]

* Correspondence: s.roy@iiserkol.ac.in (SR), francis.verpoort@ghent.ac.kr (FV)

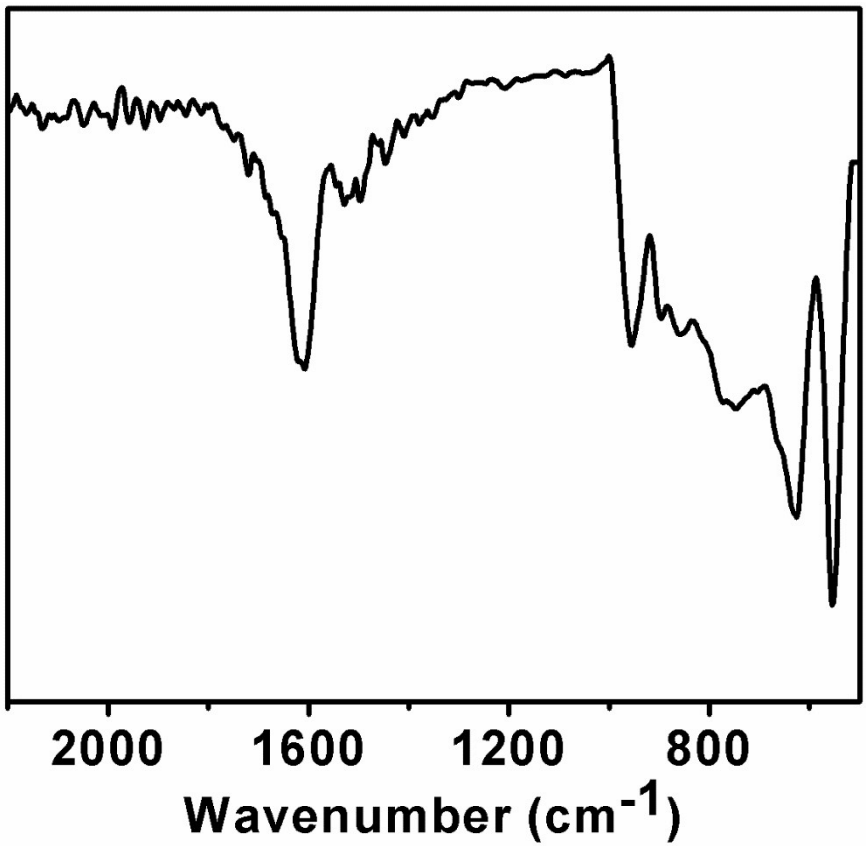

Figure S1. IR spectrum of $\{Mo_{154}\}$ taken from the aqueous solution of the same deposited over the diamond censor of the Bruker IR instrument.

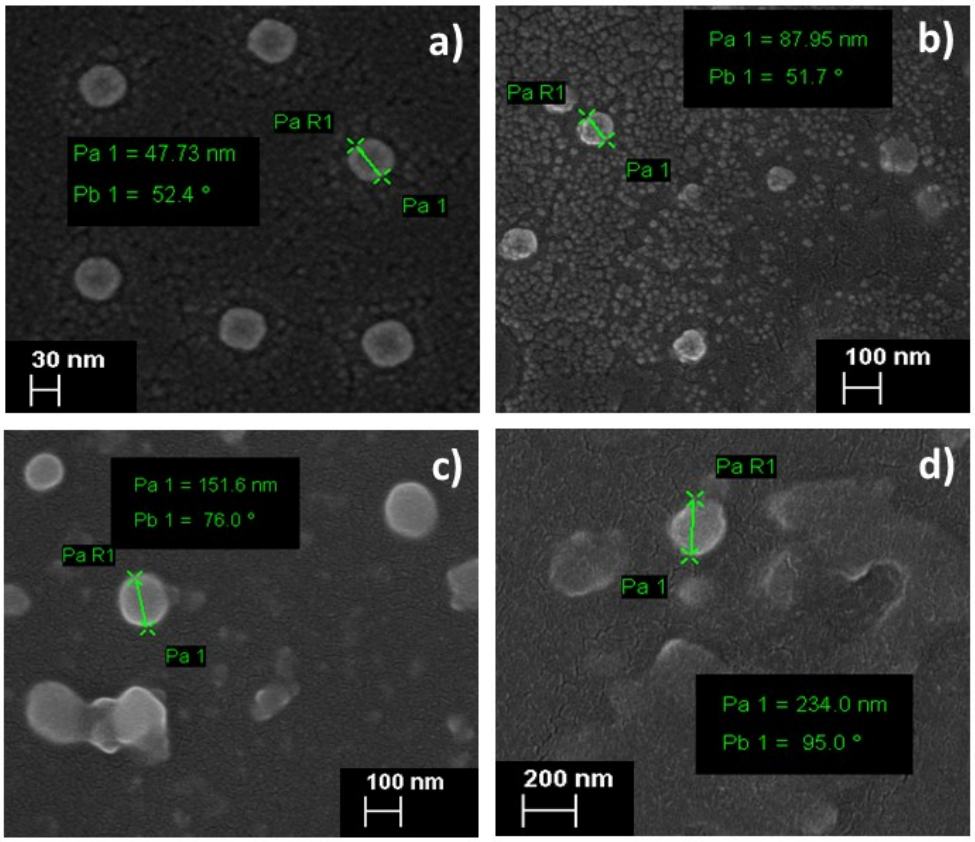

Figure S2. SEM images of Mo_{154} sphere prepared in a) water, b) 8:2 water: acetone, c) 5.5:4.5 water: acetone and d) 2.5:7.5 water: acetone solvent mixture.

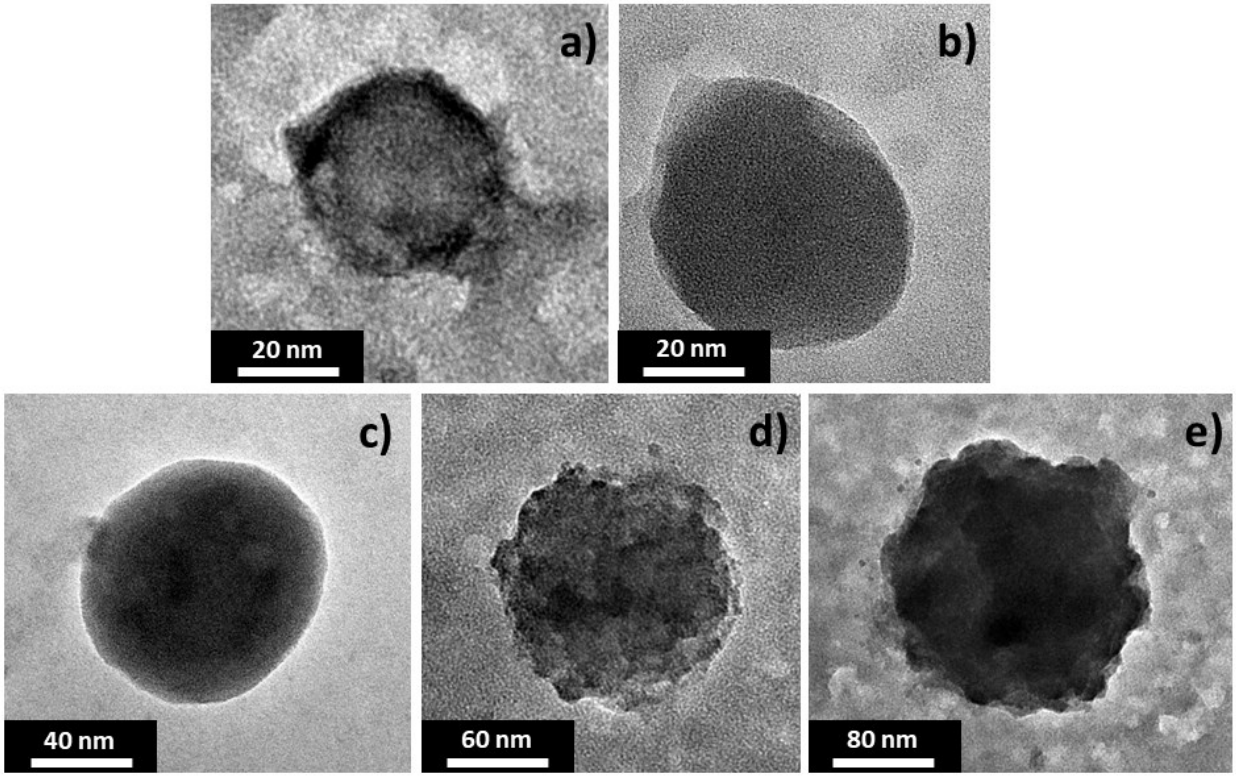

Figure S3. TEM images of Mo_{154} sphere prepared in a) water, b) 8:2 water: acetone, c) 5.5:4.5 water: acetone, d) 4:6 water: acetone and e) 2.5:7.5 water: acetone solvent mixture.

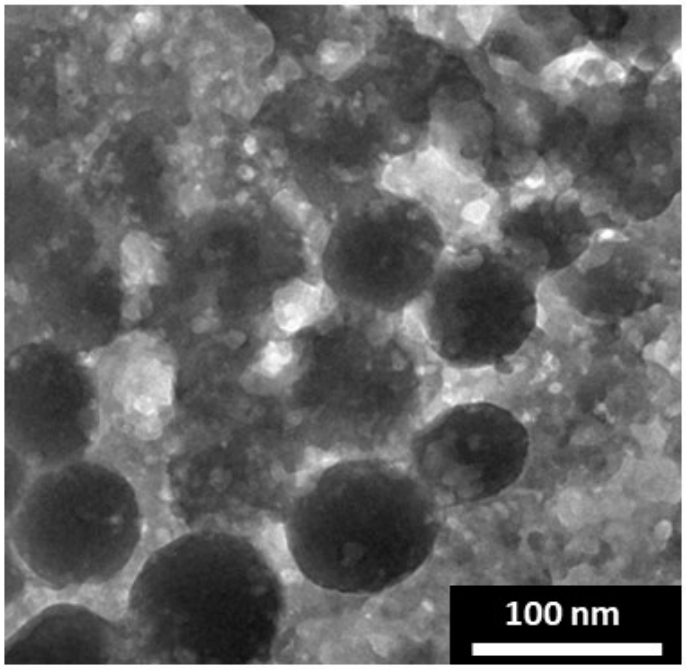

Figure S4. TEM image of {Mo_{154}} nanospheres after addition of Rubpy.

Isotope labelling study:

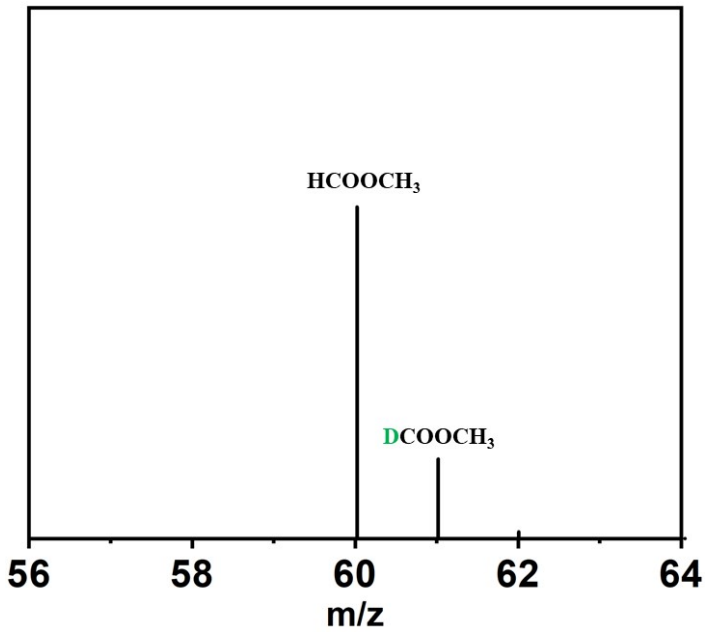

Figure S5. Mass spectrum of methyl ester of deuteriated formic acid showing the molecular ion peak at 61 beside the previous peak at 60.

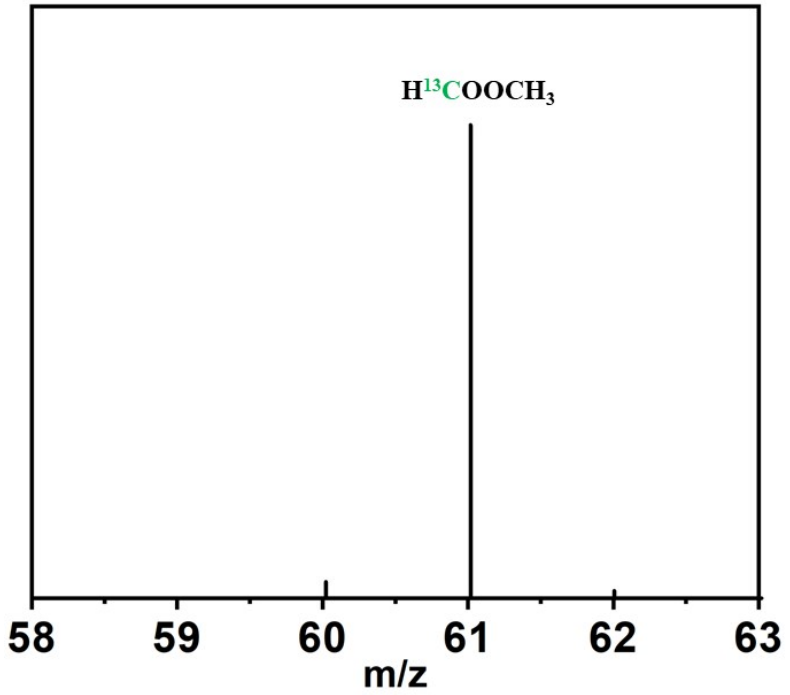

Figure S6. Mass spectrum of methyl ester of formic acid obtained from $^{13}CO_2$ reduction. Molecular ion peak shifts from 60 to 61 indicating the incorporation of ^{13}C.

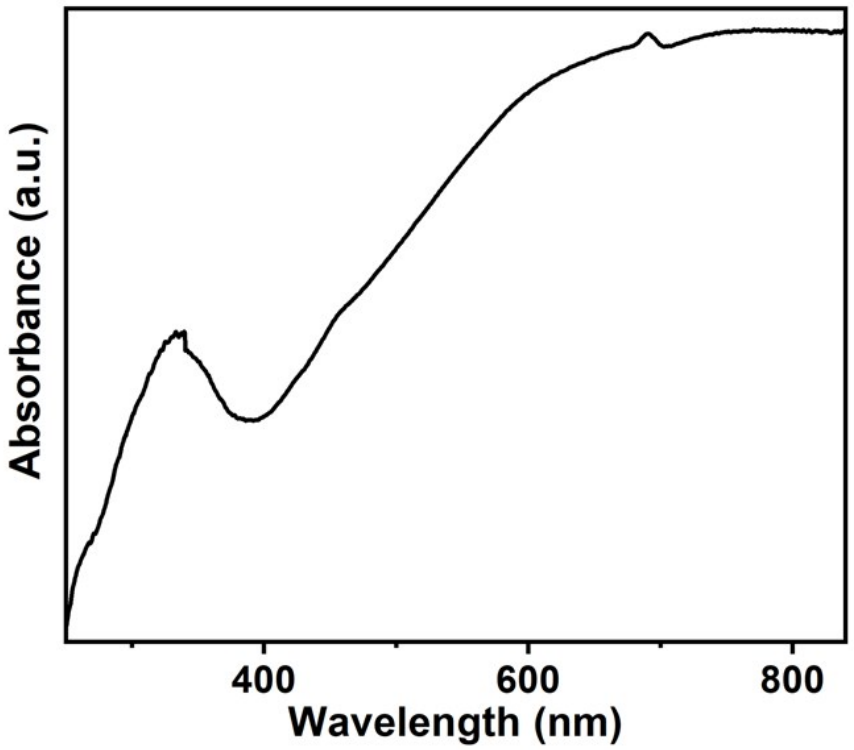

Figure S7. DRS spectrum of $\{Mo_{154}\}$ taken from the solid powder of the same.

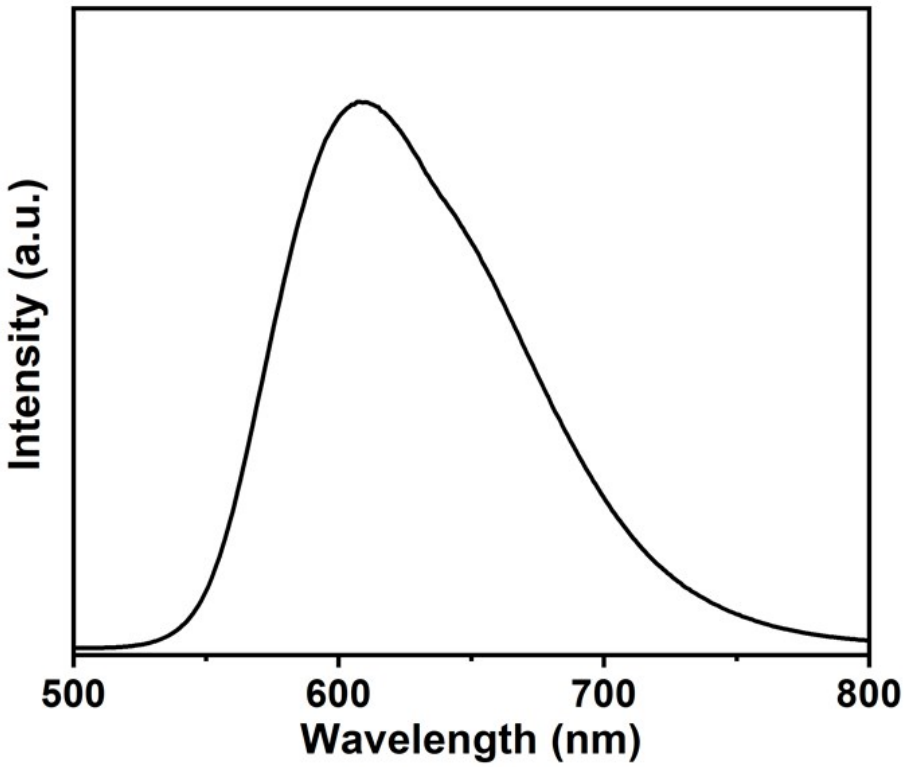

Figure S8. Photoluminescence spectrum of Rubpy dissolved in water.

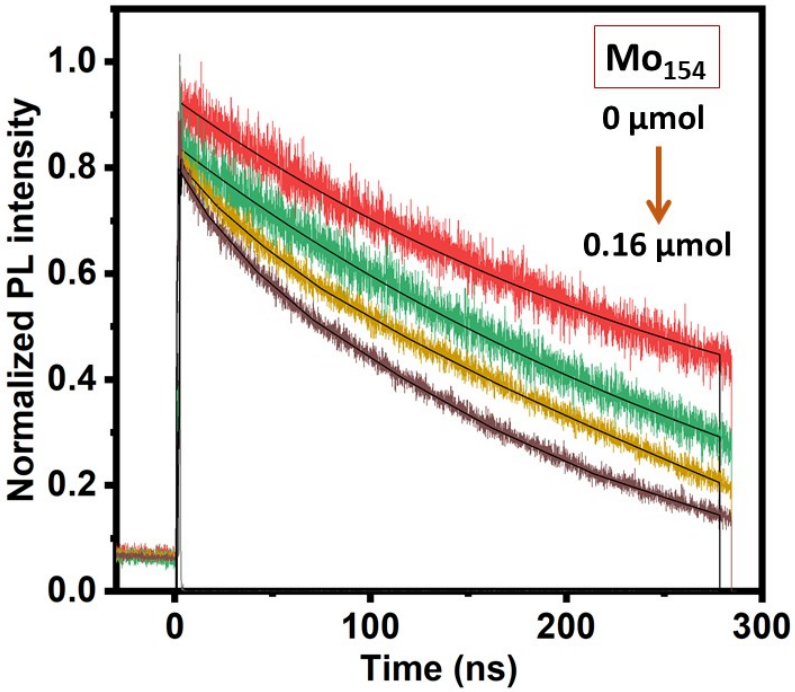

Figure S9. Time correlated single photon counting (TCSPC) luminescence decay of $[Ru(bpy)_3]^{2+}$ (2.3 µmol) after the addition of $\{Mo_{154}\}$ (upto 0.16 µmol) in water.

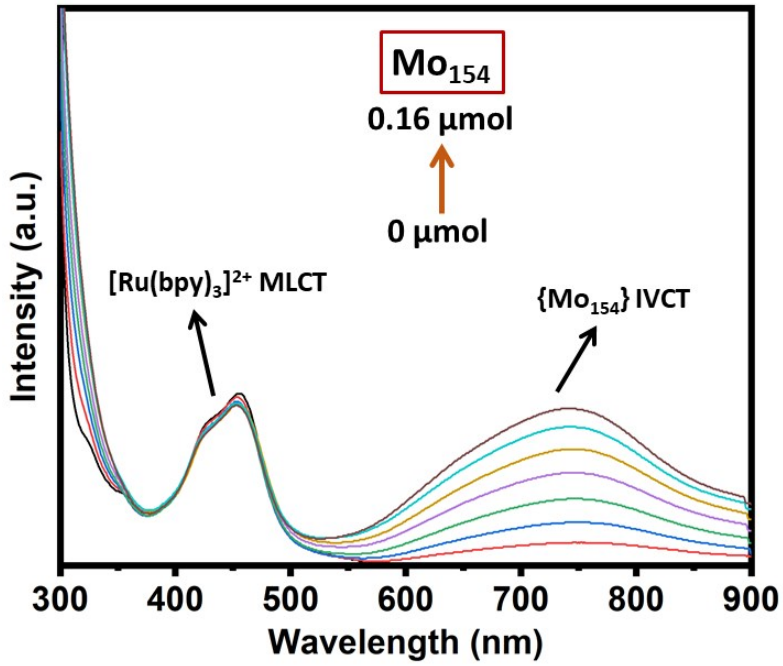

Figure S10. UV-Vis spectra of the solution containing $[Ru(bpy)_3]^{2+}$ and $\{Mo_{154}\}$ in water.

Redox titration:

Redox titration was done using a solution of Ce^{4+} with a conc. of 0.005 M in 0.5 M H_2SO_4. A 50 ml solution containing 11.5 µmol of $[Ru(bpy)_3]^{2+}$ and 0.8 µmol of Mo_{154} was titrated with the Ce^{4+} solution. The end point of the titration was determined to be 6.93 ml of Ce^{4+} for before the reaction and 7.76 ml of Ce^{4+} for during the reaction. The theoritical value of Ce^{4+} required for the titration of 11.5 µmol of $[Ru(bpy)_3]^{2+}$ and 0.8 µmol of Mo_{154} is 6.8 ml (1 Ru^{2+} centre per $[Ru(bpy)_3]^{2+}$ and 28 Mo^{5+} centres per Mo_{154}). From the excess amount of Ce^{4+} required for the reaction mixture during CO_2 reduction, the average number of reduced center per Mo_{154} cluster is calculated to be 6.

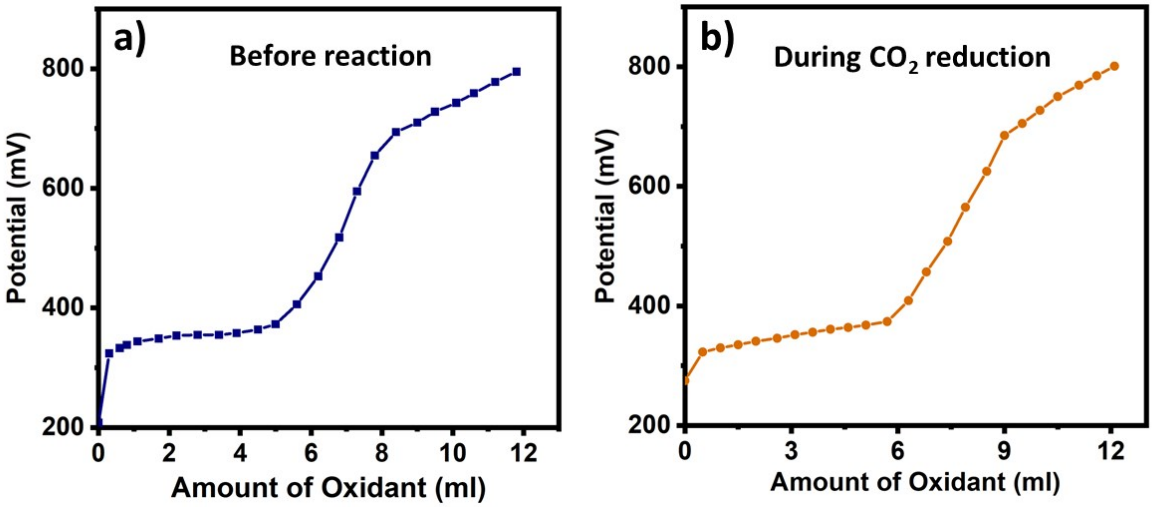

Figure S11. Redox titration of solution containing $[Ru(bpy)_3]^{2+}$ and Mo_{154} (50 ml solution containing 11.5 µmol of $[Ru(bpy)_3]^{2+}$ and 0.8 µmol of Mo_{154}) a) before the CO_2 reduction and b) in-situ during the CO_2 reduction reaction with Ce^{4+} (0.005 M) in 0.5 M H_2SO_4.

Table S1. Yield of formic acid for different sized nanospheres

Size of the Mo_{154} nanosphere (nm)	Internal HCOOH (µmol)	External HCOOH (µmol)
24	53	1
43	49	4
75	40	14
90	34	19
118	27	34

Table S2. Yield of benzyl formate from the reaction of benzyl alcohol and external HCOOH

Size of the Mo_{154} nanosphere (nm)	Benzyl formate (μmol)
24	52
43	48
75	40
90	33
118	27

Table S3. Yield of ethyl formate from the reaction of ethanol and internal HCOOH

Size of the Mo_{154} nanosphere (nm)	Ethyl formate (μmol)
24	1
43	4
75	14
90	19
118	34

Stability of the catalyst. The electronic absorption spectrum of the catalyst solution and the TEM images of the same show that catalyst mixture retains its molecular integrity and the morphology. Moreover TBA salt of $\{Mo_{154}\}$ was analyzed with TGA, XRPD and XPS analyses to check the catalytic stability.

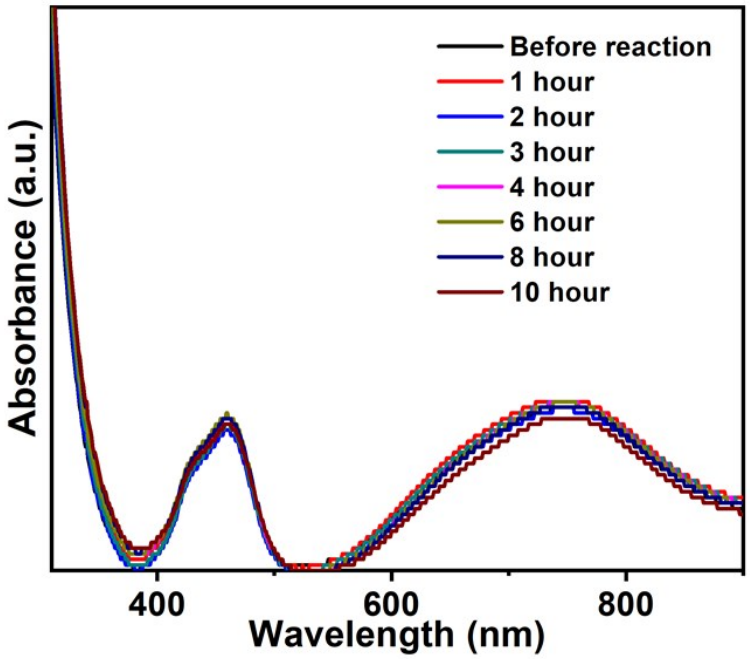

Figure S12. The electronic absorption spectrum of the catalyst solution throughout the span of the reaction.

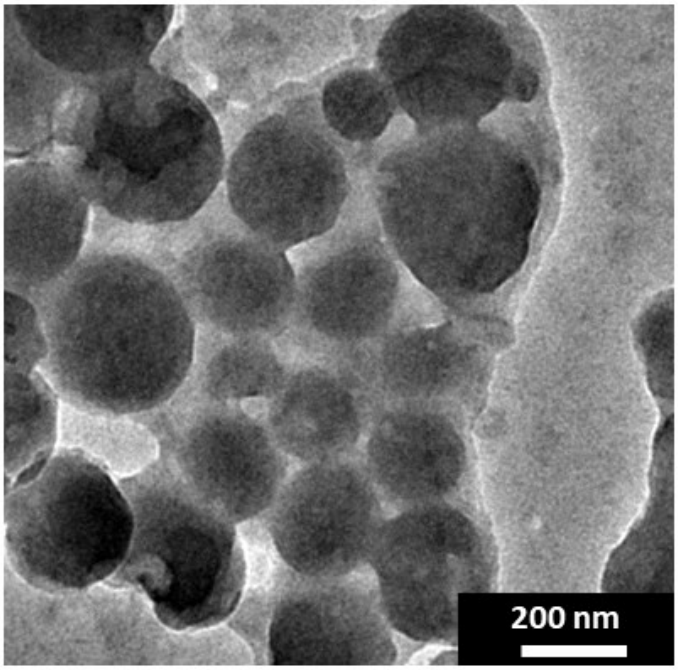

Figure S13. TEM image of the catalyst solution after the photocatalytic CO_2 reduction for 10 h.

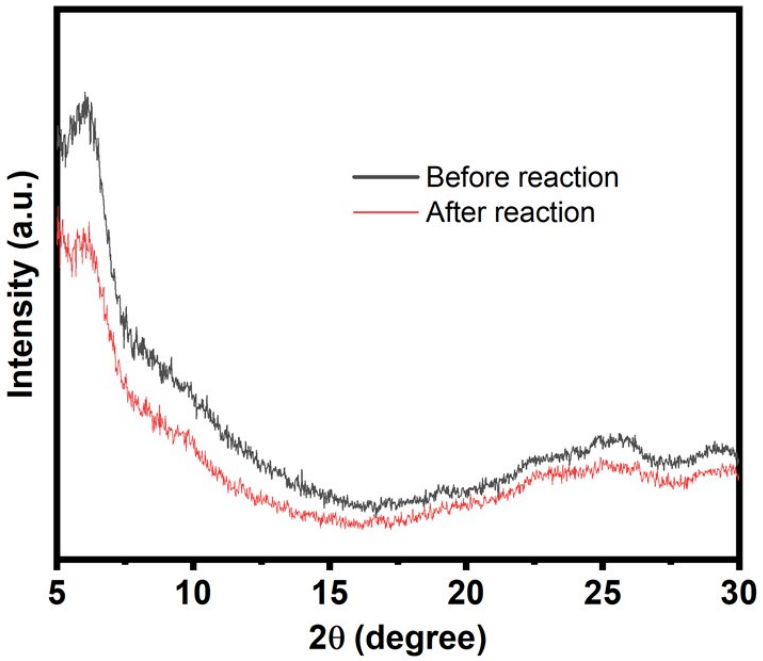

Figure S14. Comparison of powder XRD pattern of TBA salt of {Mo_{154}} before and after the CO_2 reduction.

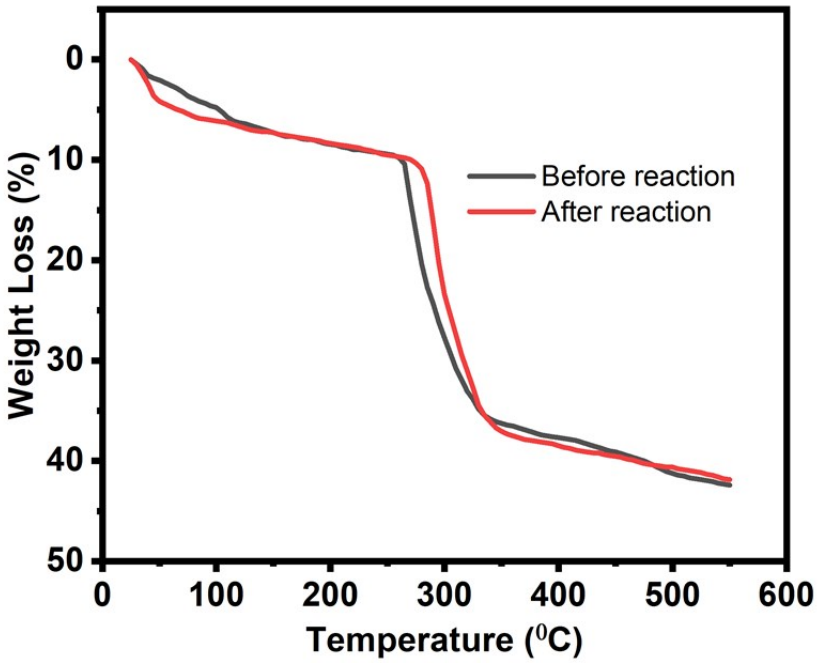

Figure S15. Thermogravimetric analysis (TGA) of TBA salt of Mo_{154} before and after the CO_2 reduction.

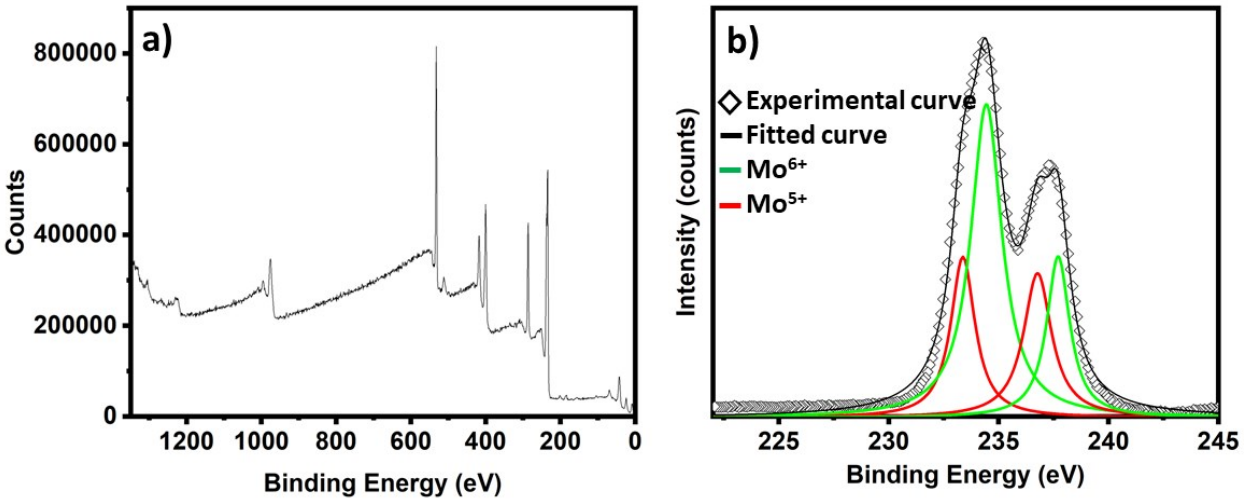

Figure S16. a) XPS survey spectrum and b) deconvoluted Mo 3d spectra of the TBA salt of $\{Mo_{154}\}$ before the reaction.

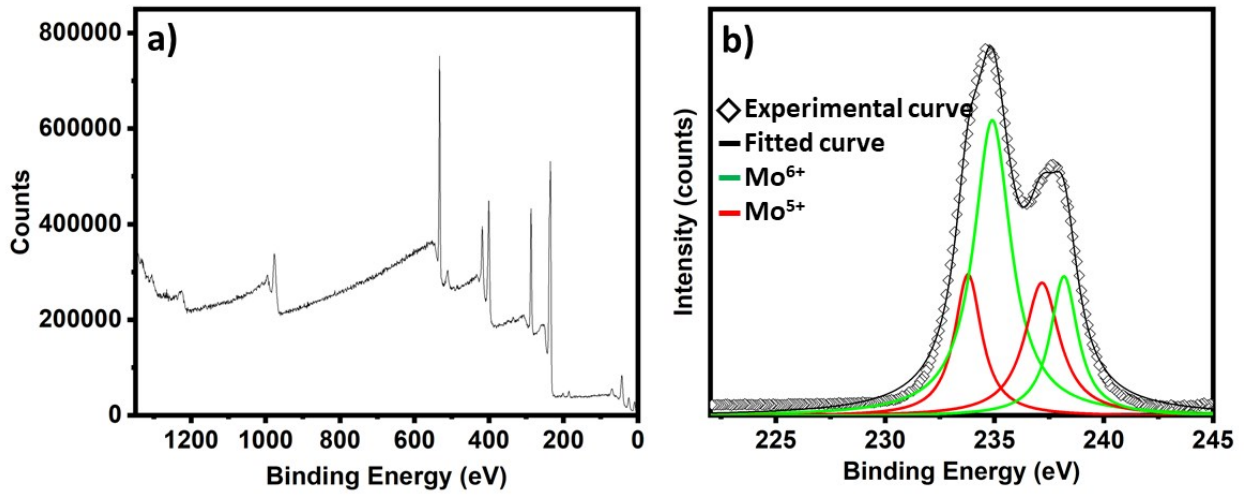

Figure S17. a) XPS survey spectrum and b) deconvoluted Mo 3d spectra of the TBA salt of $\{Mo_{154}\}$ after the reaction.