Supplementary Information

Site-isolated Manganese Carbonyl on Bipyridine-Functionalities of Periodic Mesoporous Organosilicas: Efficient CO_2 Photoreduction and Detection of Key Reaction Intermediates

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I. Characterization

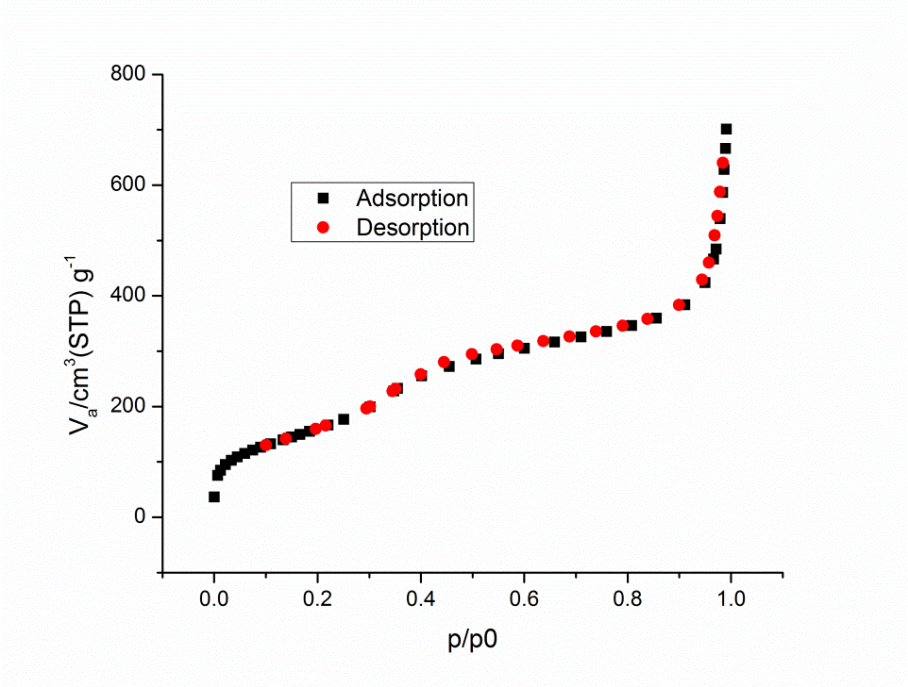


Figure S1. N_2 Adsorption/Desorption isotherm for **bpy-PMO**.

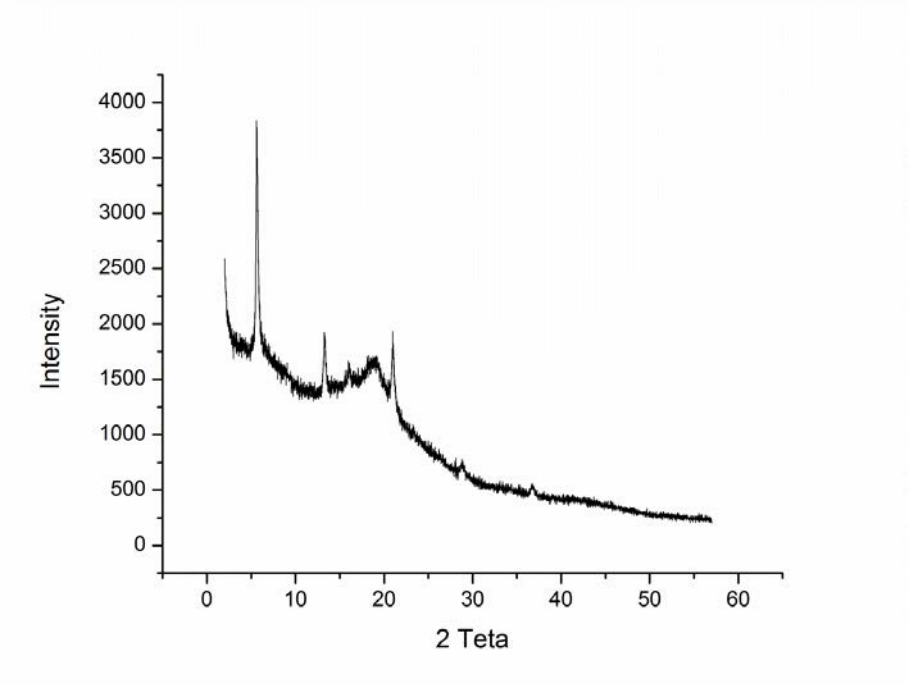


Figure S2. Powder-XRD spectrum of **bpy-PMO**.

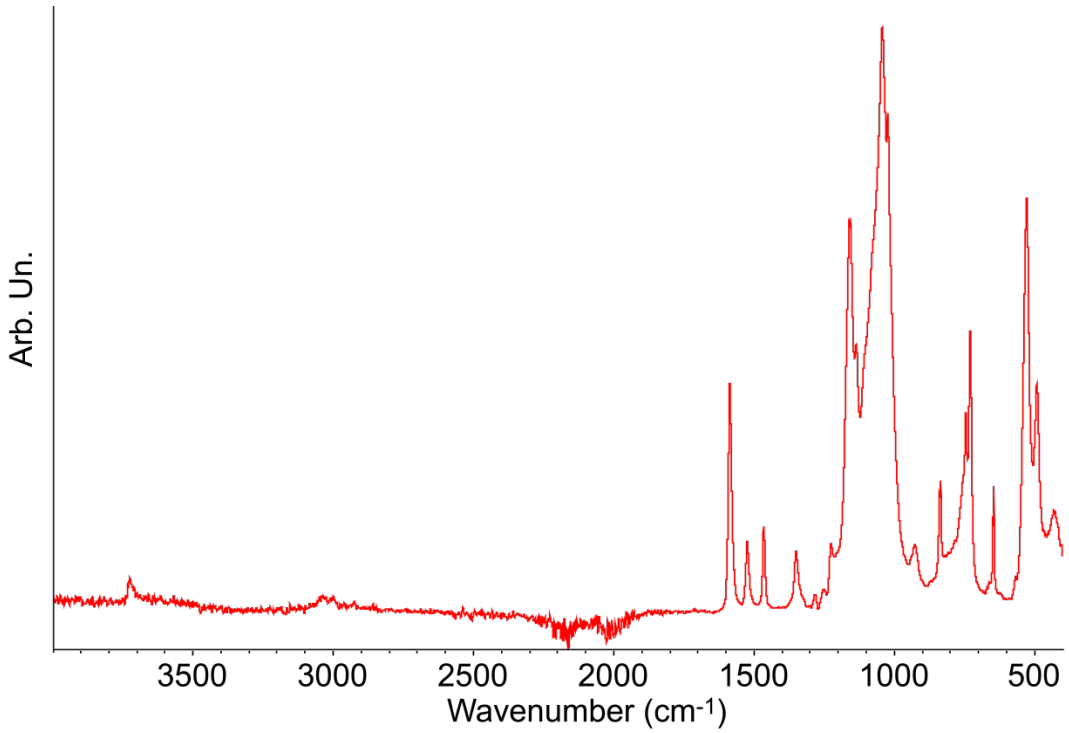


Figure S3. Fourier Transform Infrared (FT-IR) spectrum of **bpy-PMO**.

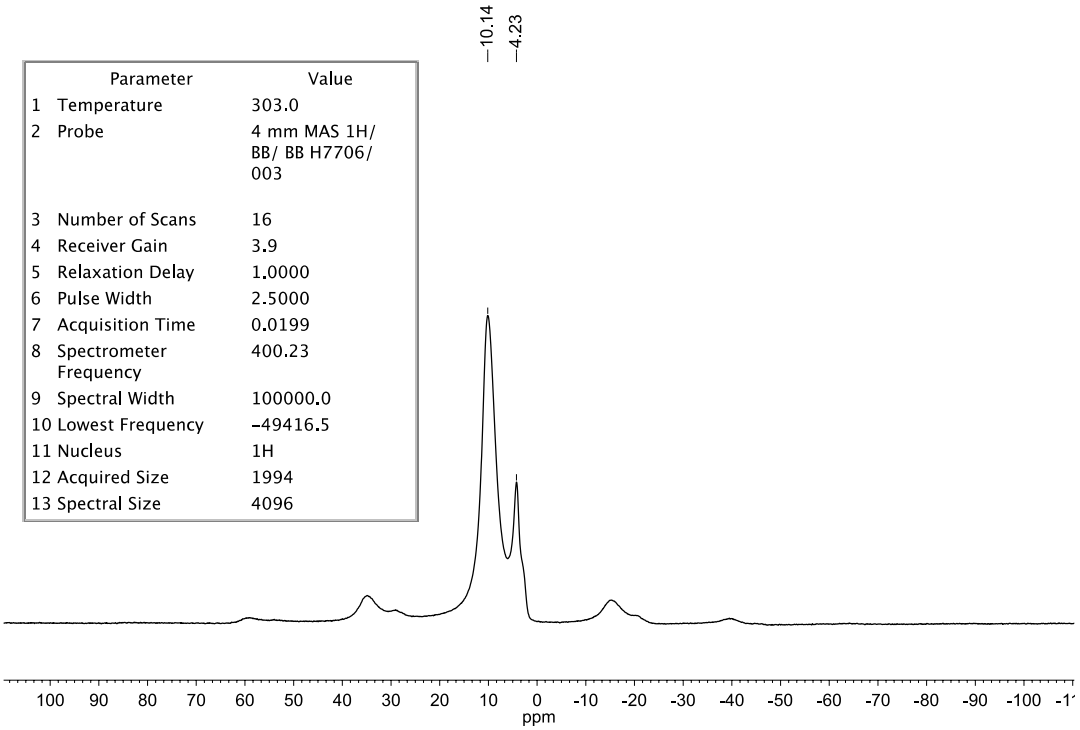


Figure S4. ^{1}H MAS NMR spectrum of **bpy-PMO**.

Spinning rate = 10 kHz

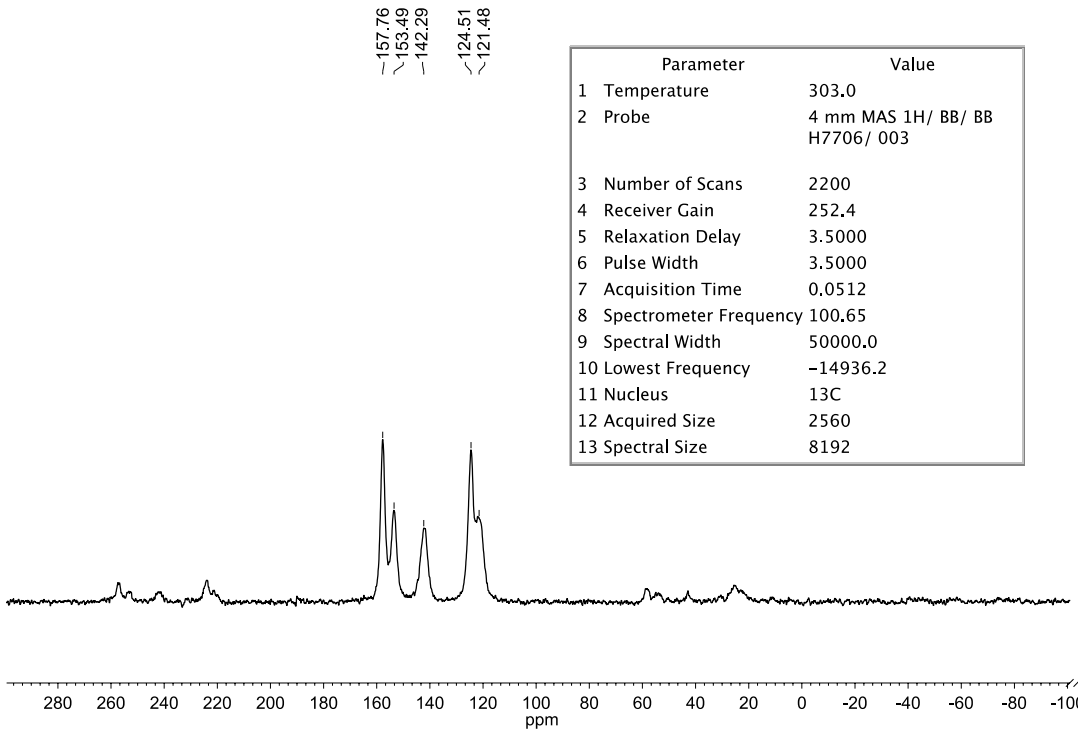


Figure S5. CP MAS ^{13}C NMR spectrum of **bpy-PMO**.

Spinning rate 10 kHz, contact time 600 μs

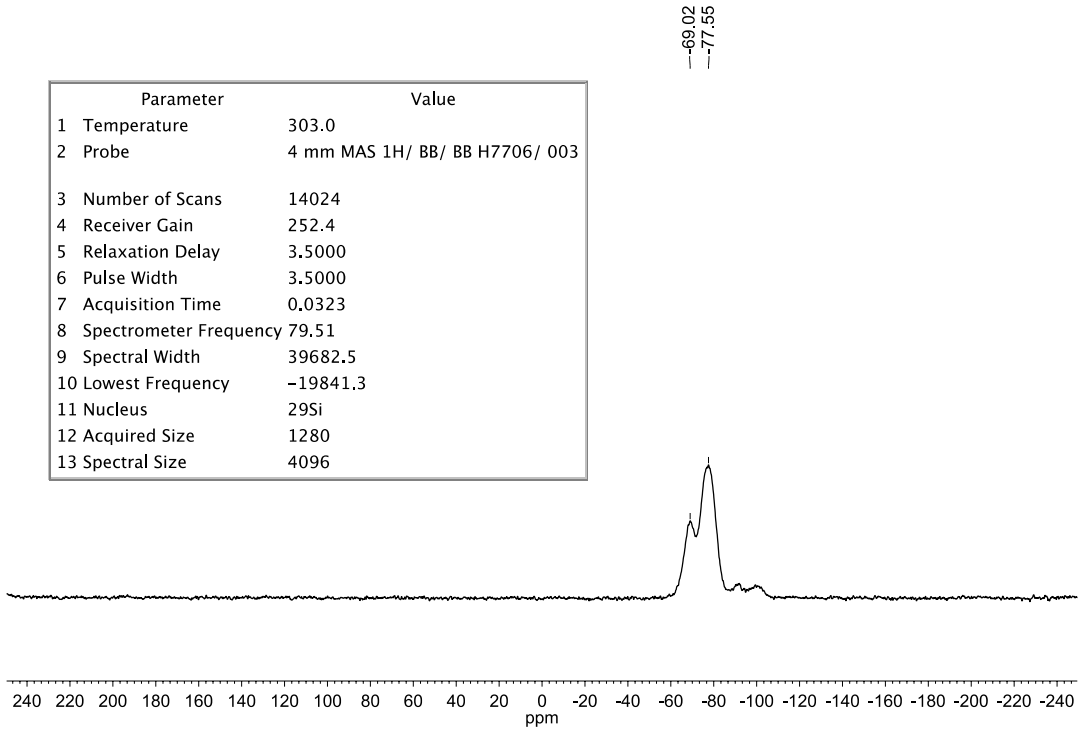
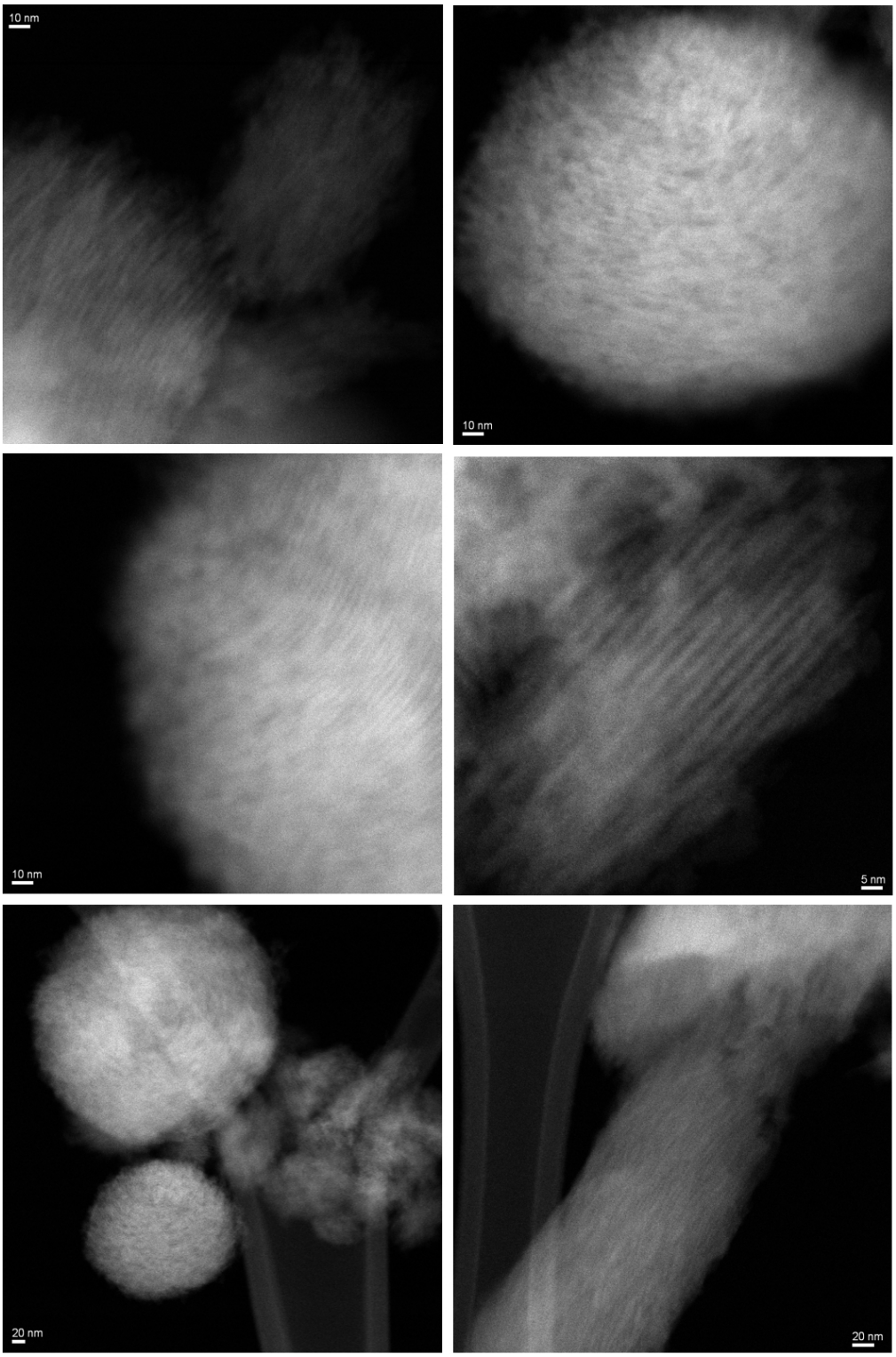


Figure S6. CP MAS ^{29}Si NMR spectrum of **bpy-PMO**.

Spinning rate 10 kHz, contact time 5 ms

1)



2)

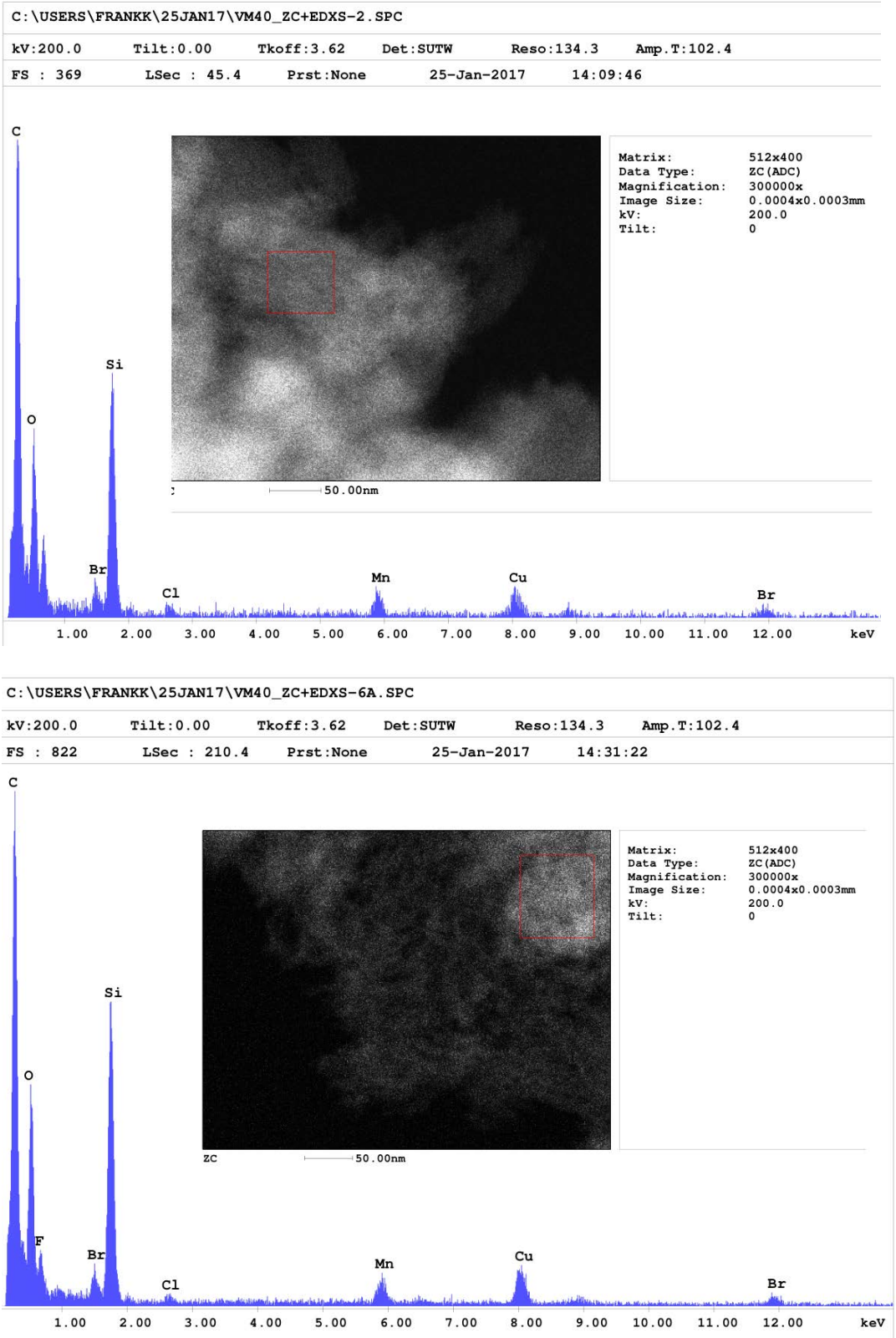


Figure S7. STEM-HAADF (1) and EDXS (2) images of material **2**. The significant Cu signal originates from the copper TEM grid used.

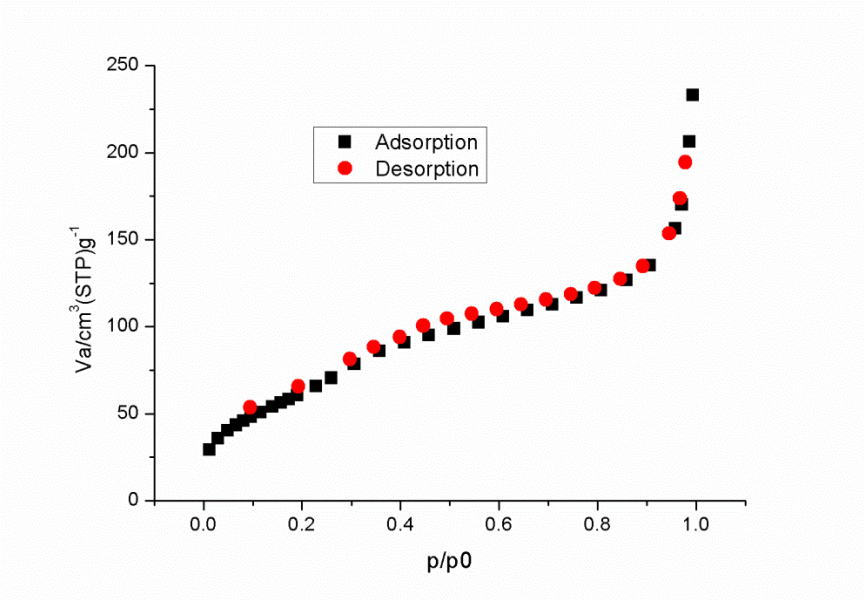


Figure S8. N_2 Adsorption/Desorption isotherm for **2**.

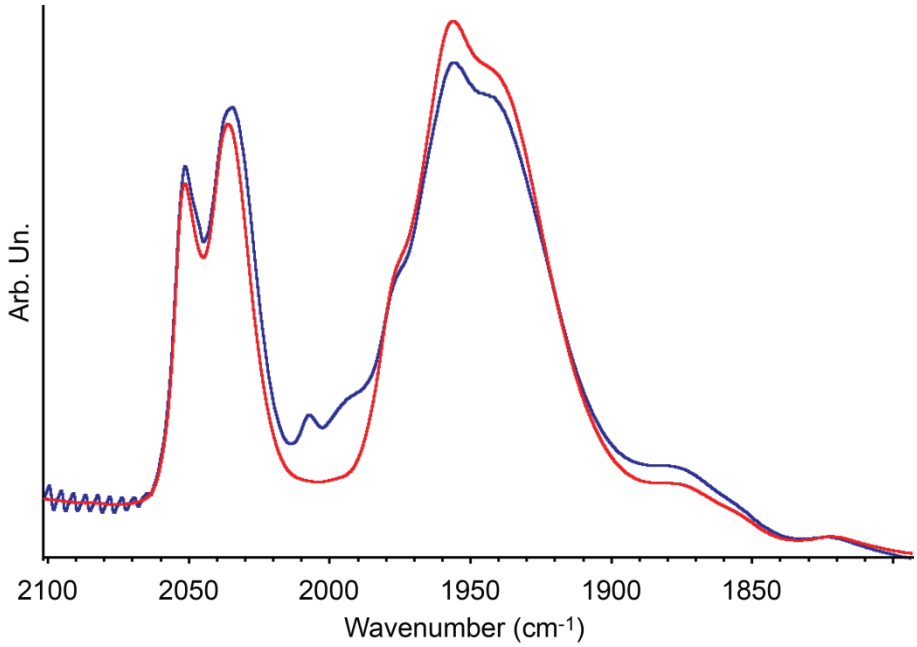


Figure S9. IR spectrum of **2** after 30 min irradiation in 300 mBar of CO atmosphere (blue) and after consequent evacuation to 10^{-5} mBar for 2 min (red).
Disappearance of bands from $[Mn^{+}(bpy_{PMO}^{\bullet-})(CO)_4]$ species is observed.

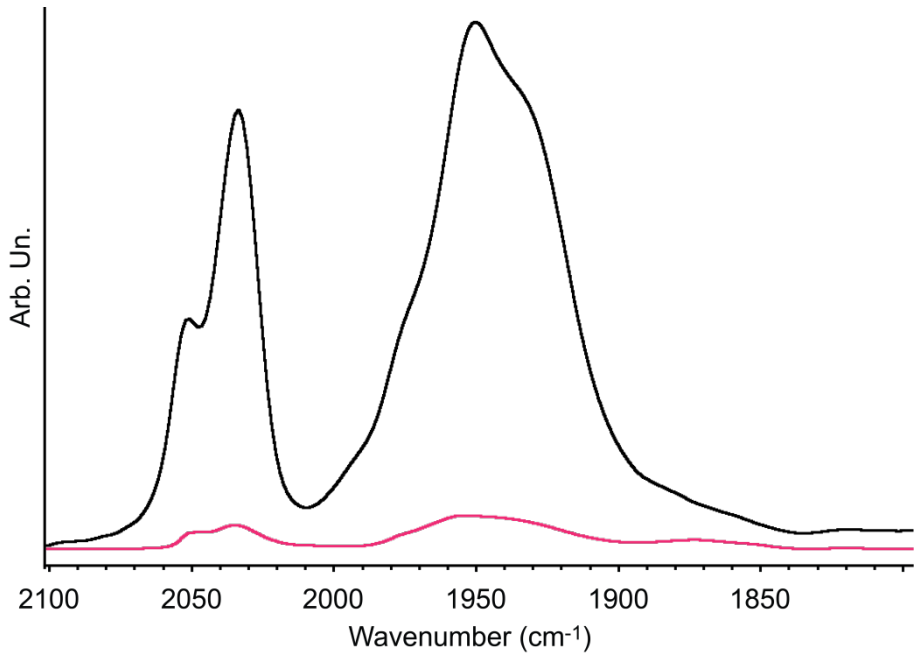


Figure S10. IR spectrum of **2** before (black) and after (pink) 24 h irradiation under high vacuum (10^{-5} mBar).

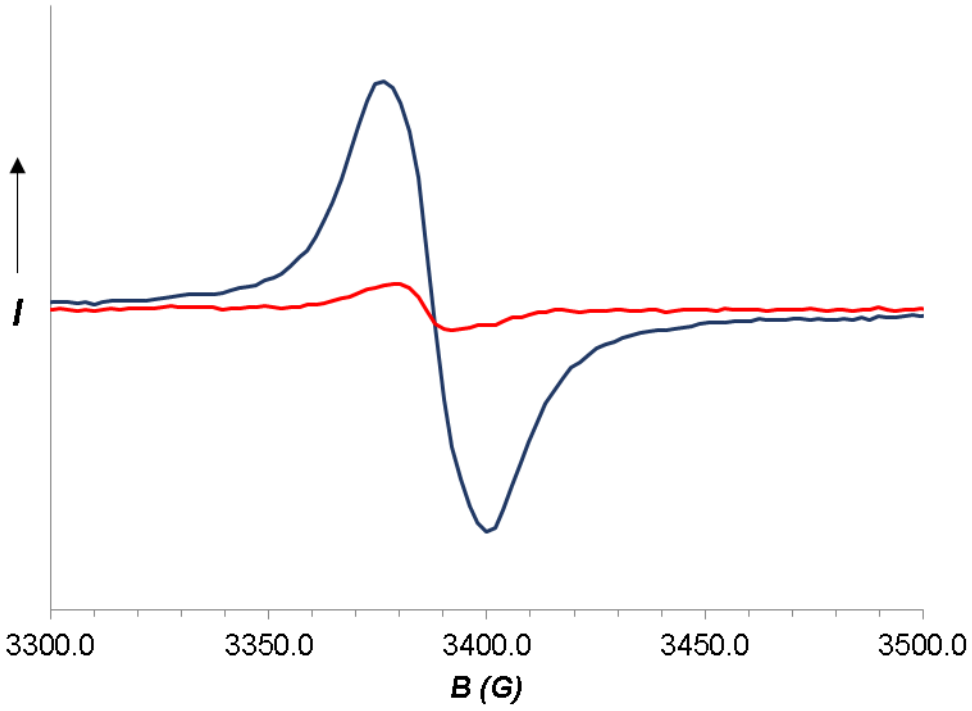


Figure S11. Low temperature (100 K) cw X-band EPR spectra of **2** collected before (red) and after 30 min irradiation (blue).

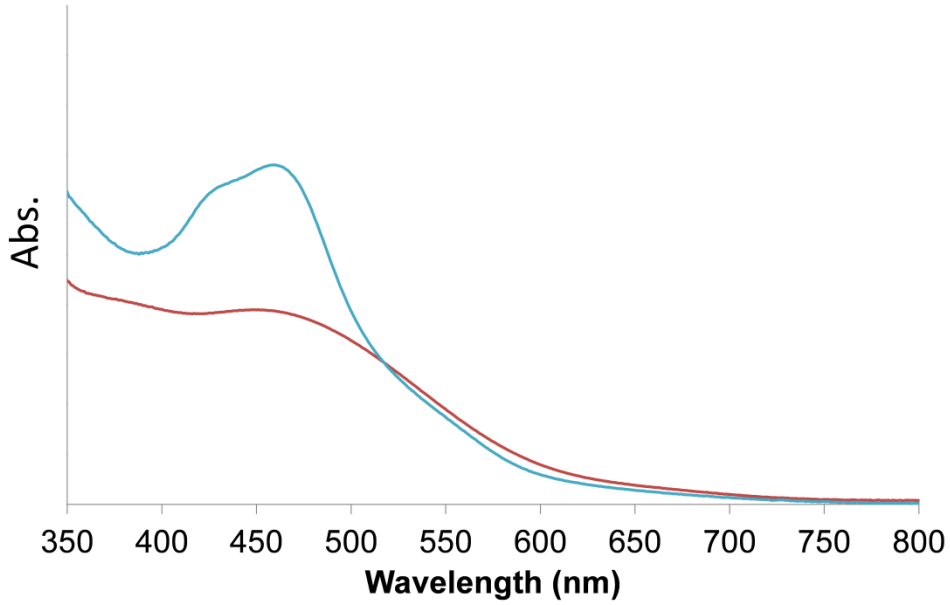


Figure S12. UV-diffuse reflectance spectra of **2** before (red) and after 3 h catalytic test conditions under light irradiation (blue).

Due to a larger amount of material required for UV-DRS studies with respect to typical catalytic test, the test was here scaled up to 5 mL of CO_2-saturated MeCN/TEOA (5:1, v:v) solvent mixture, using 1 µmol/mL of material **2**, 10 mM $[Ru(bpy)_3]Cl_2$ and 20 mM of BIH: Solvent: MeCN/TEOA 5 mL.

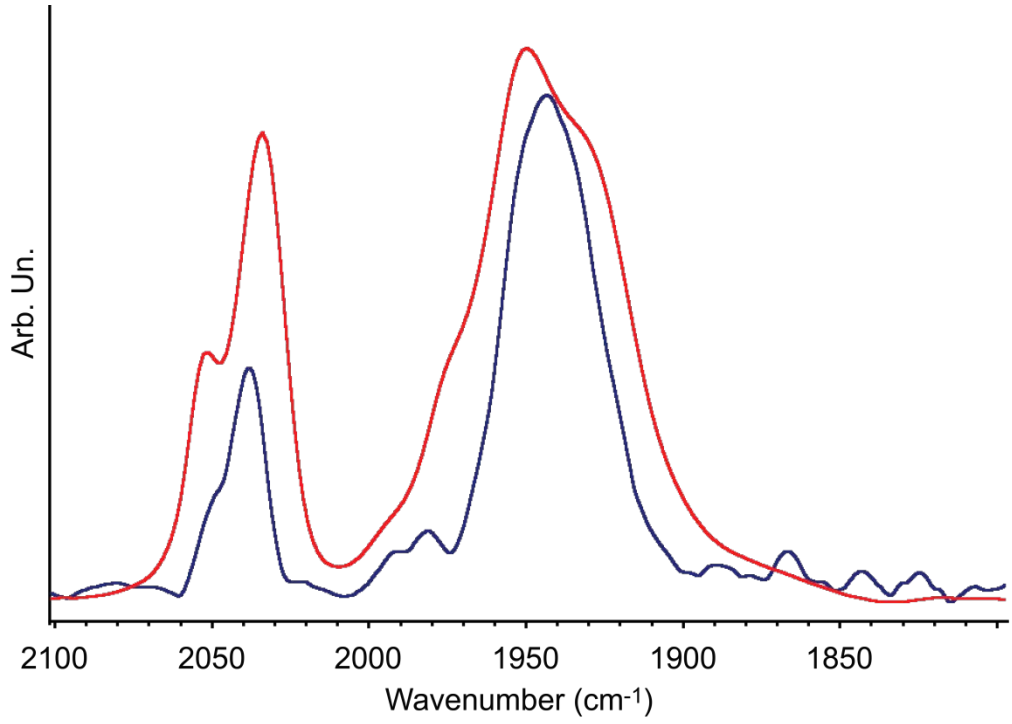


Figure S13. FTIR spectra of **2** before (red) and after 3 h catalytic test conditions under light irradiation (blue).Reaction conditions are described in Figure S12.

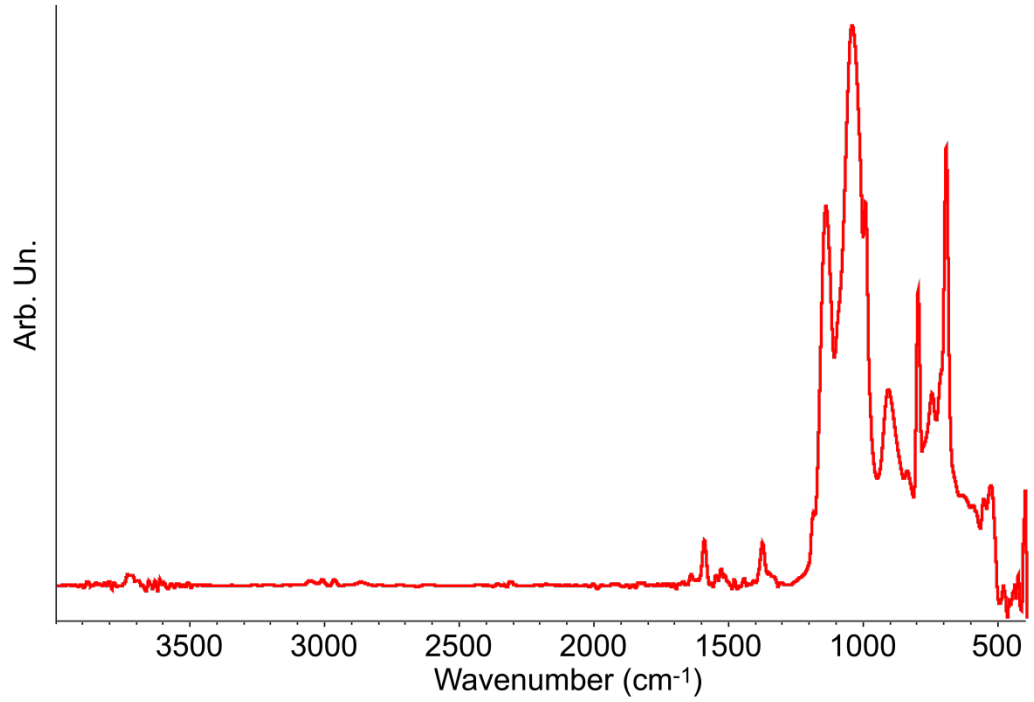


Figure S14. FTIR spectra of **biph-PMO²** after reaction with $[Mn(CO)_5Br]$.

The following conditions were used: in a Ar glovebox, the material **biph-PMO** (10 mg, 0.038 mmol biphenyl moieties) was charged into a flask and suspended in Et_2O (10 mL). A solution of $[Mn(CO)_5Br]$ (1.7 mg, 3.8 nmol) in Et_2O (2 mL) was added to this suspension. The suspension was stirred for 4 h. The suspension was centrifuged and the solid part was then washed by Et_2O (4 x 4 mL). The material was subsequently dried under CO flow to give a colorless material (**control-biph-PMO**).

II. Photolytic experiments

1. Performance of electron donors in photocatalytic CO_2 reduction

Table S1. Photolytic CO_2 reduction in the presence of different electron donors

		Products (μmols)		
Entry[a]	Electron donor	CO	formate	H_2
1	TEOA	0	0	0
2	BNAH (0.1 M)	0	1	0
3	BIH (0.1 M)	49	70	33

[a] samples containing 1 μmol of catalyst **2** and 10 μmol of $[Ru(bpy)_3]Cl_2$ in 1 mL CO_2-saturated MeCN/TEOA (5:1, v:v) solvent mixture upon 16 hours irradiation.

2. Control experiments

Table S2. Photolytic CO_2 reduction experiments

			Products (μmols)		
Entry [a]	Catalyst (μmol)	PS (μmol)	CO	formate	H_2
1[b]	**2** (1)	$[Ru(bpy)_3]Cl_2$ (10)	49	70	33
2[b]	**2** (1)	/	0.65	0.19	0
3[b]	/	$[Ru(bpy)_3]Cl_2$ (10)	1.96	3.12	0.99
4[b]	**2** (0.1)	$[Ru(bpy)_3]Cl_2$ (1)	5.3	10.6	2.2
5[b]	/	$[Ru(bpy)_3]Cl_2$ (1)	0.92	1.20	0.30
6[b]	**2** (0.01)	$[Ru(bpy)_3]Cl_2$ (0.1)	0.29	1.42	0.39
7[b]	**3** (0.01)	$[Ru(bpy)_3]Cl_2$ (0.1)	1.68	2.92	0.72
8[b]	**bpy-PMO**[c]	$[Ru(bpy)_3]Cl_2$ (0.1)	0.13	0.40	0.95
9[b]	/	$[Ru(bpy)_3]Cl_2$ (0.1)	0.04	0.35	0.18
10[d]	**3** (0.01)	ZnTPP (0.1)	0.17	0.52	0
11[d]	/	ZnTPP (0.1)	0.04	0.02	0
12[d]	**3** (0.01)	Fluorescein (0.1)	0.11	0.65	0
13[d]		Fluorescein (0.1)	0	0.01	0
14[d]	**control-biph-PMO** (0.01)	$[Ru(bpy)_3]Cl_2$ (0.1)	0.09	0.22	0.29

a: All samples were prepared in 1 mL CO_2-saturated MeCN/TEOA (5:1, v:v) solvent mixture containing 0.1 M of BIH. b: 16 hours irradiation. c: 1.3 mg of **bpy-PMO**. d: 5 hours irradiation.

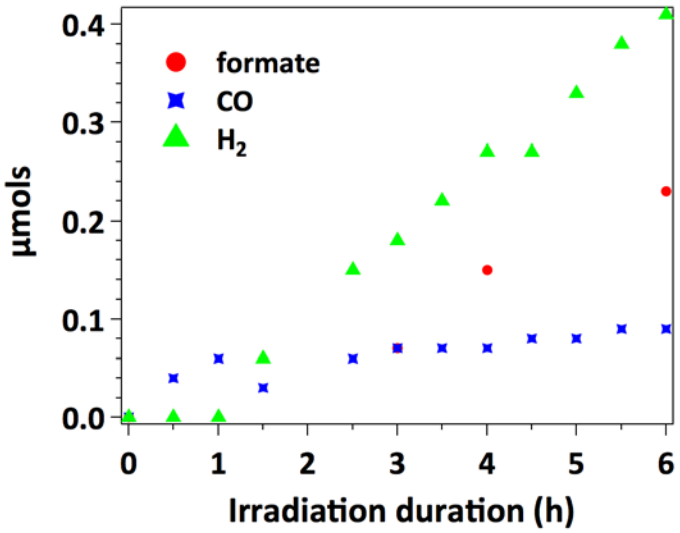


Figure S15. Evolution of the product distribution in the Mn-free control experiment of the kinetic studies presented in Figure 4 of the manuscript.
Reaction mixture contains 1.3 mg of **bpy-PMO**, 0.1 mM of $[Ru(bpy)_3]Cl_2$ and 0.1 M of BIH in 1 mL CO_2-saturated MeCN/TEOA (5:1, v:v).

References:

[1] X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang and J.-P. Cheng, *J. Am. Chem. Soc.*, 2008, **130**, 2501–2516.

[2] (a) M. P. Kapoor, Q. Yang and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 15176–15177. (b) I. Thiel, A. Fedorov, R. Verel, S. Yakunin, M. V. Kovalenko and C. Copéret, *Phys Chem Chem Phys*, 2016, **18**, 13746–13749.