Post synthetic exchange in zirconium metal-organic framework for effective photoreduction of CO_2 to formate.

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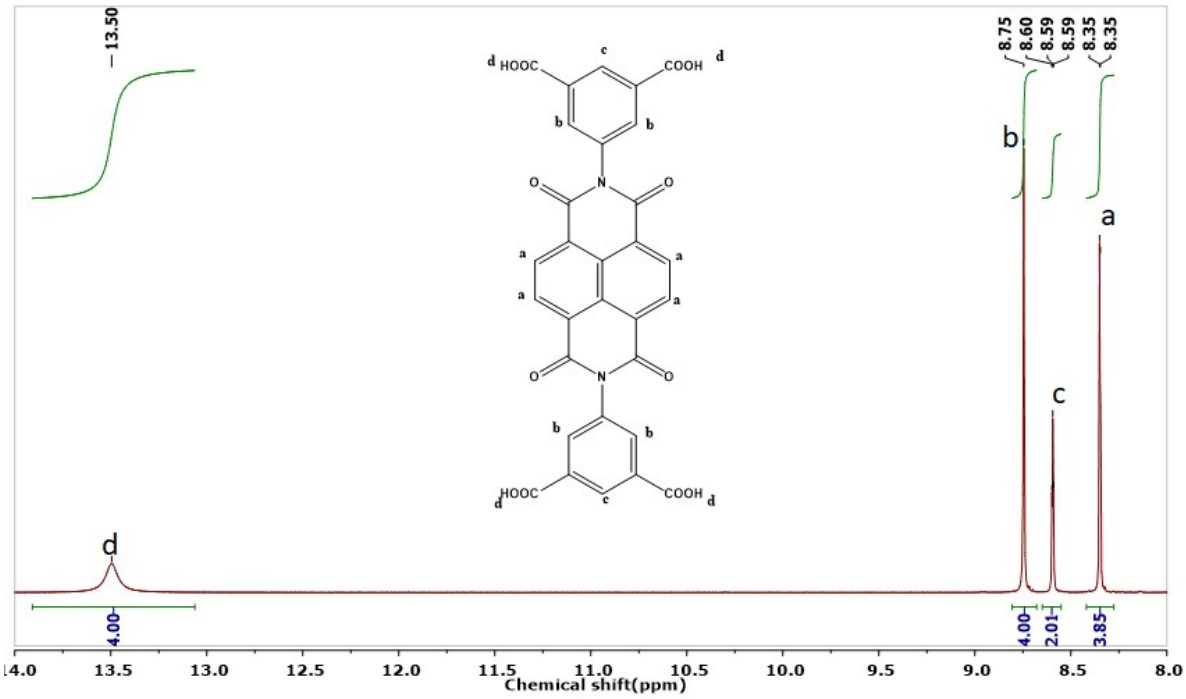


Figure S1. Proton NMR spectra of TNDI ligand.

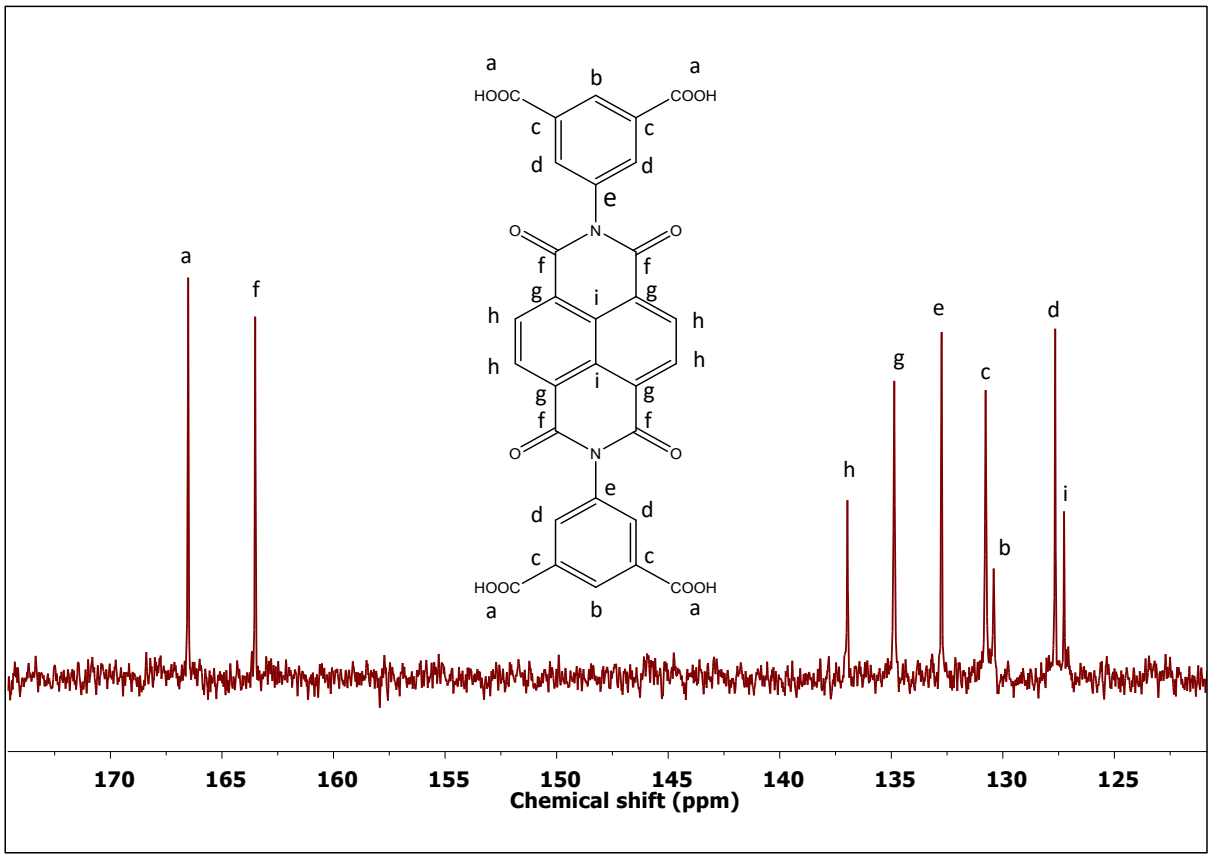


Figure S2. 13C NMR spectra of TNDI ligand.

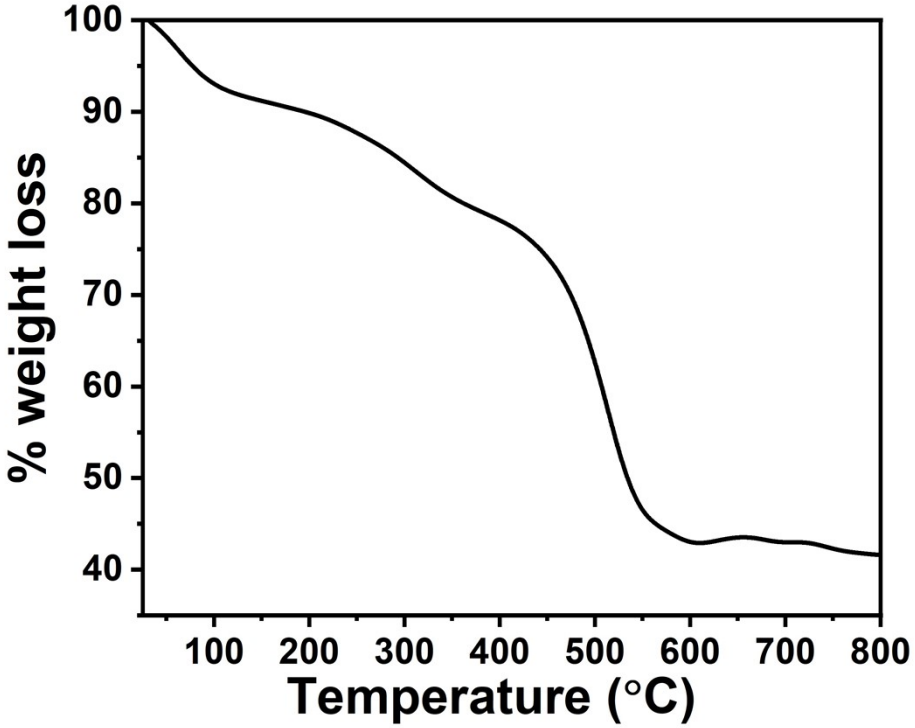


Figure S3. TGA profile of the pristine MOF **1**.

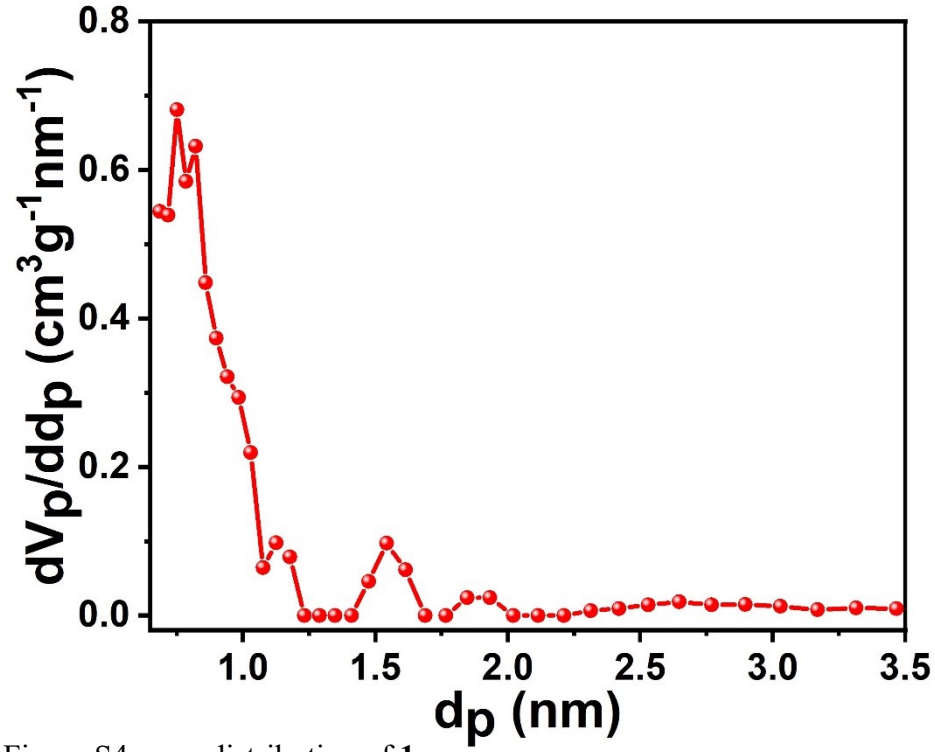
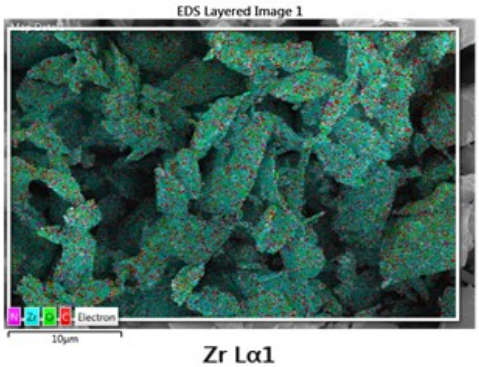
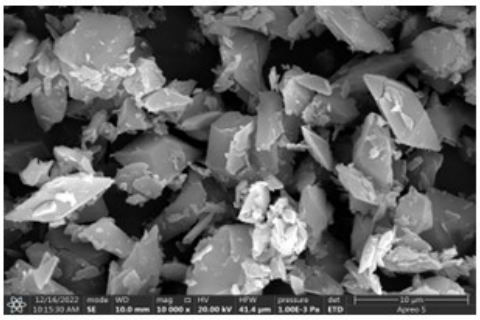


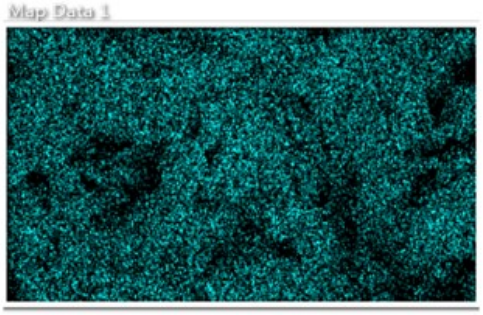
Figure S4. pore distribution of **1**



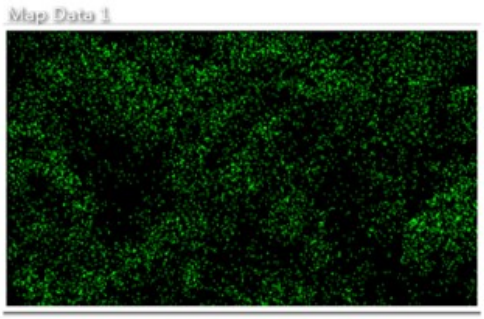


Zr Lα1

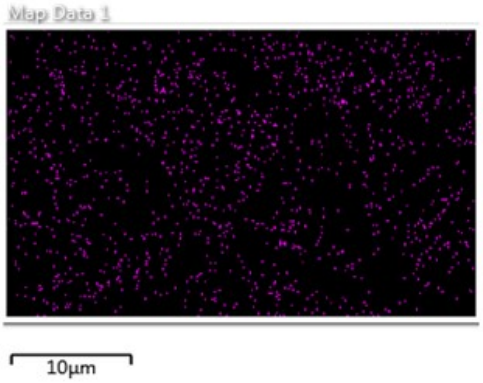
O Kα1

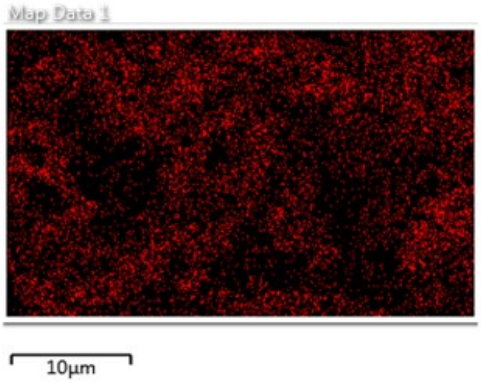


N Kα1_2



C Kα1_2





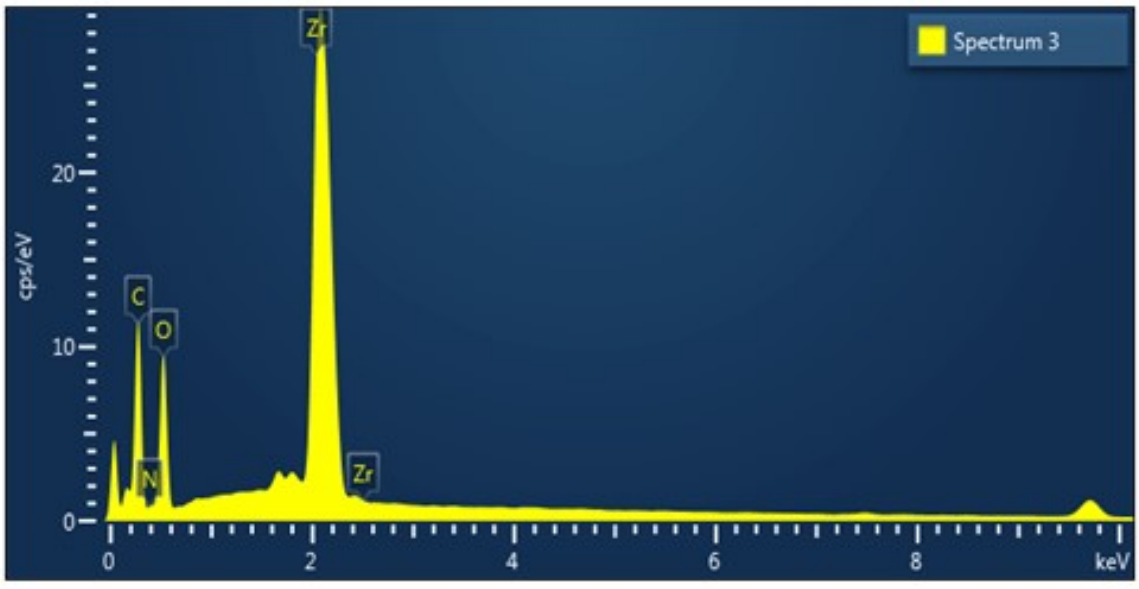


Figure S5. The percentage composition of the elements constituting the intergrown rod-shaped morphology is studied through Elemental mapping. The table below gives the atomic percentage of elements obtained from EDS mapping.

Table S1. Atomic percentage distribution of MOF 1.

Element	Atomic percentage
C	50.69
N	7.07
O	36.25
Zr	5.99

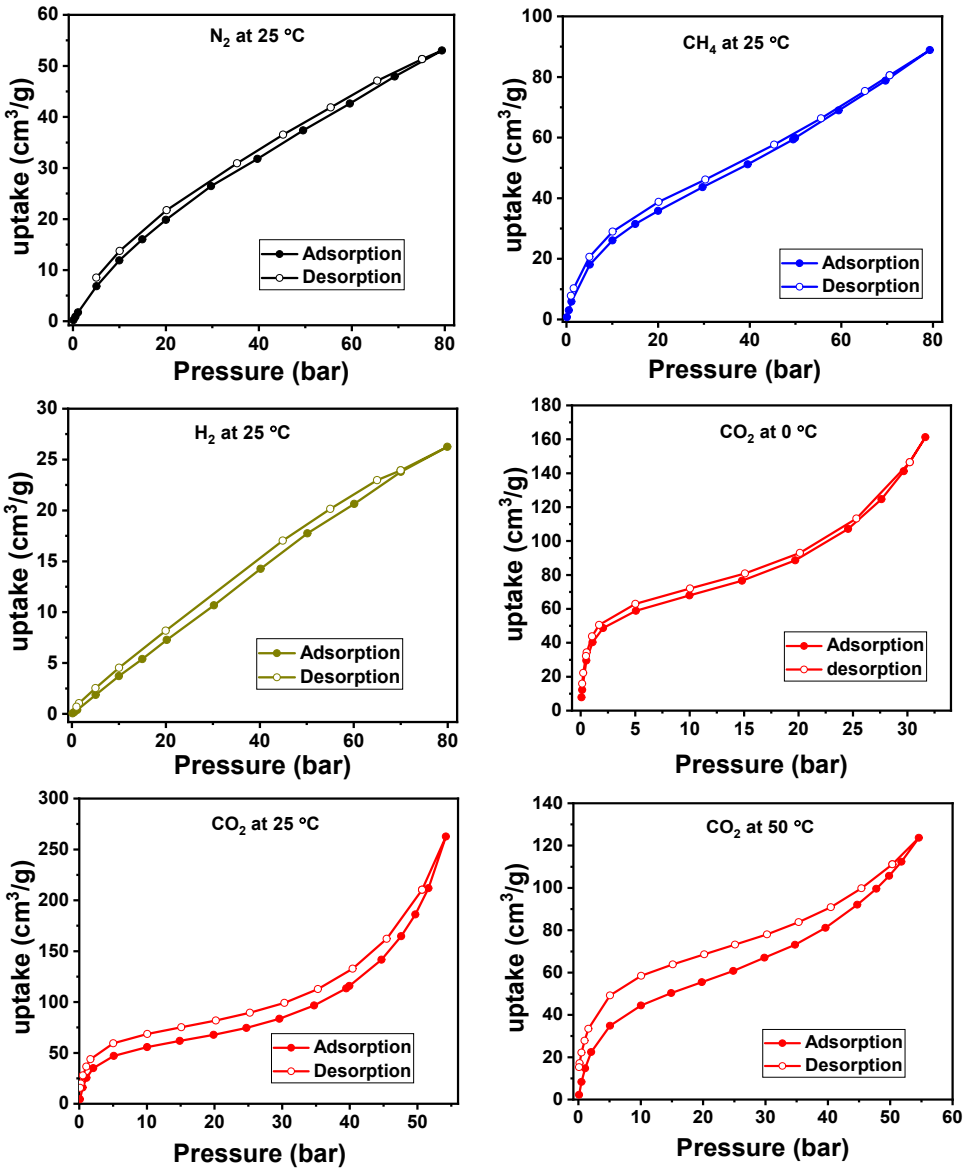


Figure S6. Adsorption behavior of the MOF for different gases at different temperatures and pressures.

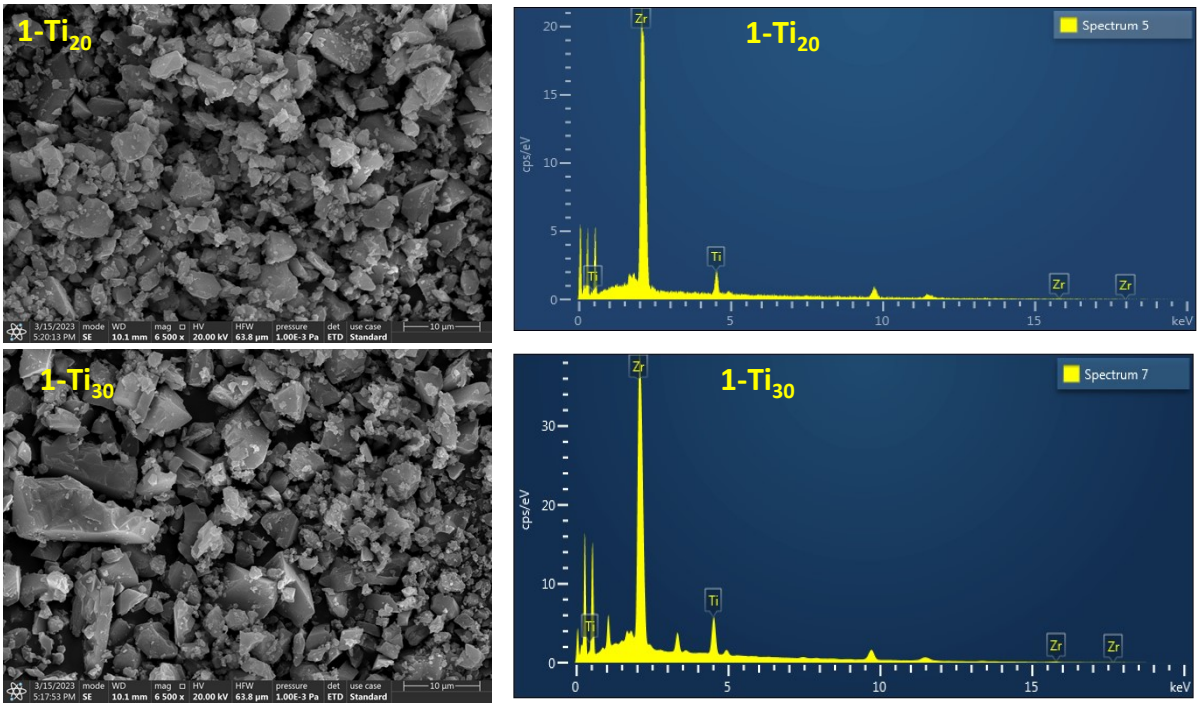


Figure S7. SEM images of the Titanium metal exchanged MOF and their elemental composition.

Table S2. Comparison values of percentage titanium exchanged using different methods for **1-Ti$_{20}$** and **1-Ti$_{30}$.**

Technique	Zr atomic percentage in **(1-Ti$_{20}$)/(1-Ti$_{30}$)**	Ti atomic percentage **(1-Ti$_{20}$)**	Ti atomic percentage **(1-Ti$_{30}$)**
SEM	82% /73%	18%	27%
Xray Fluorescence	80%/70%	20%	30%
ICP-OES	83%	17%	

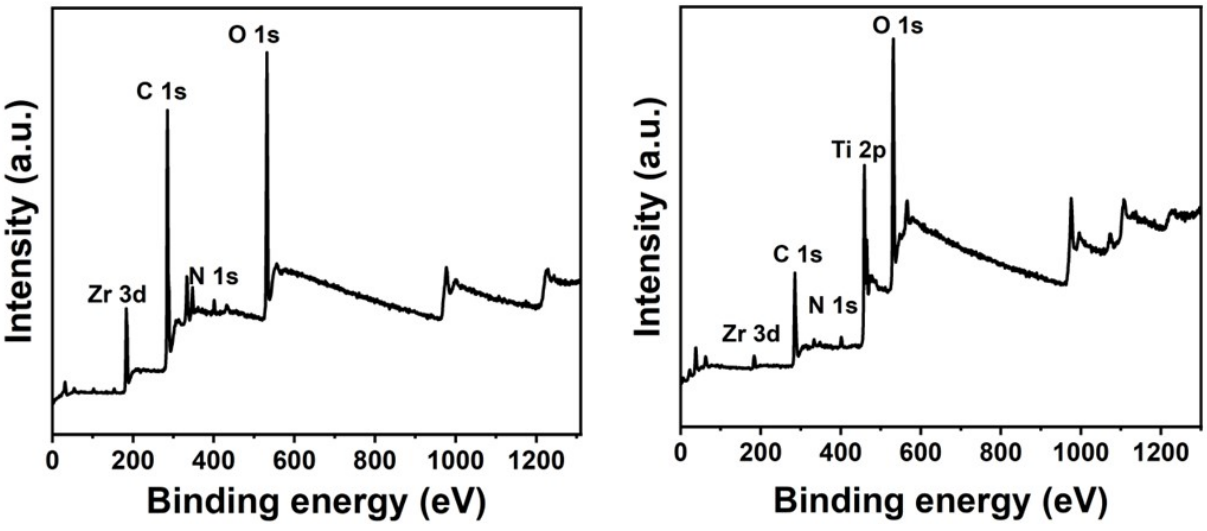


Figure S8. XPS survey spectra of pristine MOF **1** and b) Ti exchanged MOF.

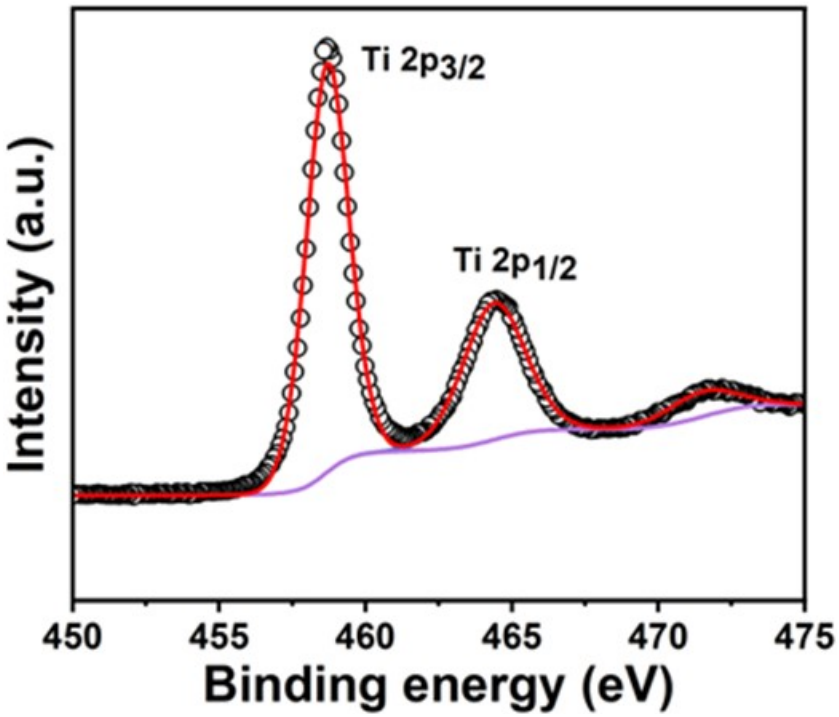


Figure S9. Titanium deconvoluted spectra obtained from the post-synthetically exchanged MOF (**1-Ti$_{20}$**).

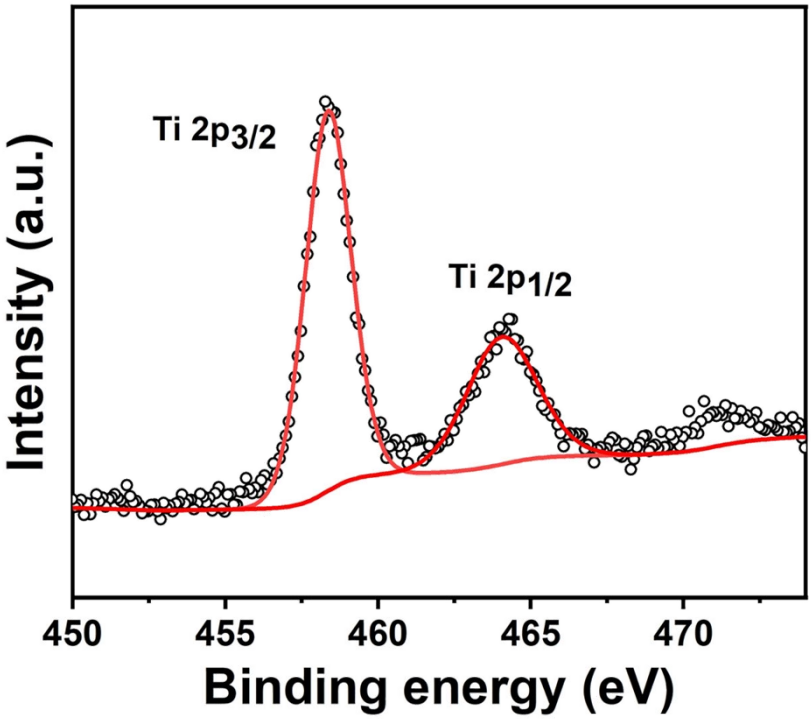


Figure S10. Titanium deconvoluted spectra obtained from the post-synthetically exchanged MOF (**1-Ti$_{30}$**).

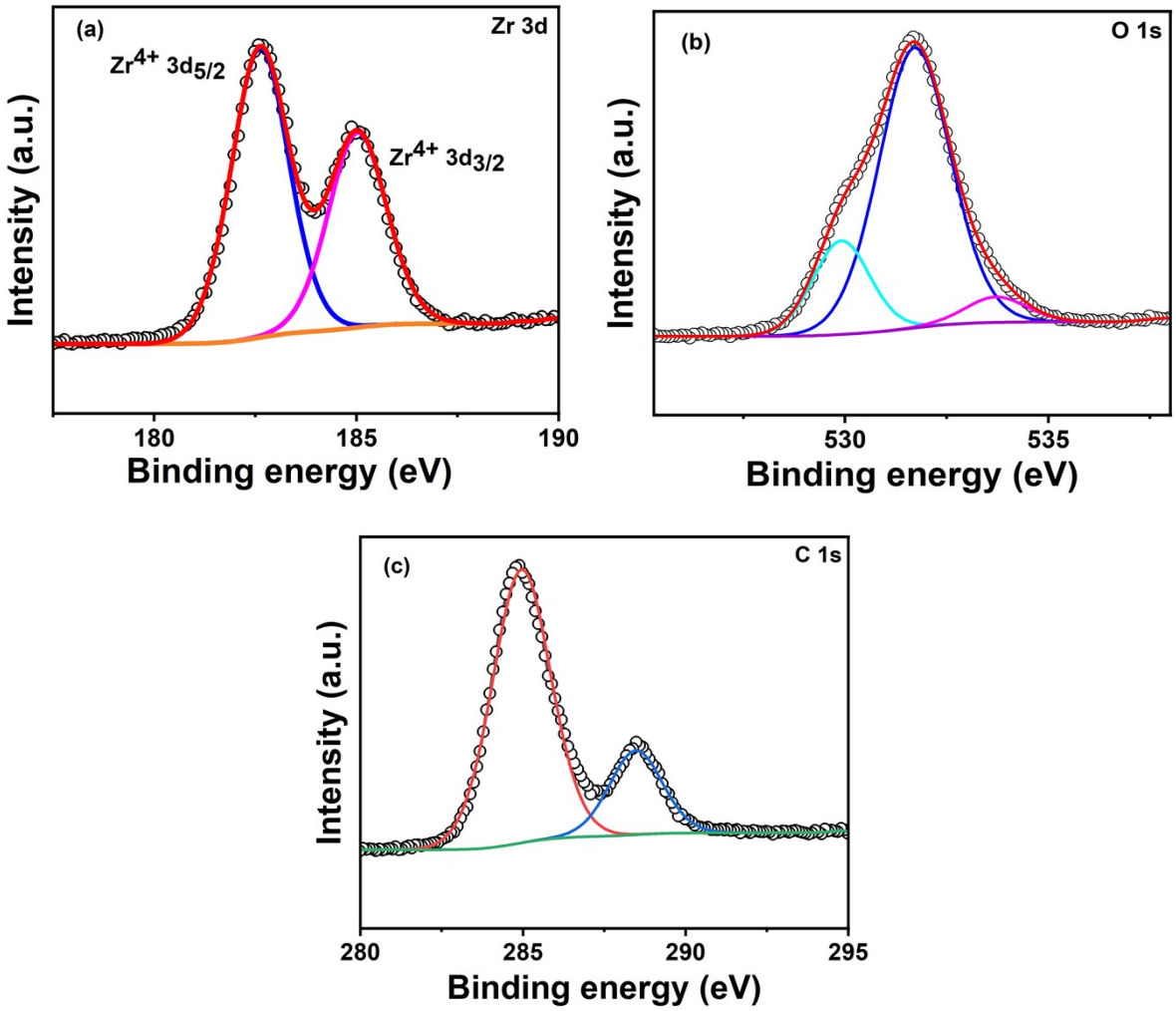


Figure S11. XPS deconvoluted spectra of Zr 3d, O1s, and C1s of the MOF **1**.

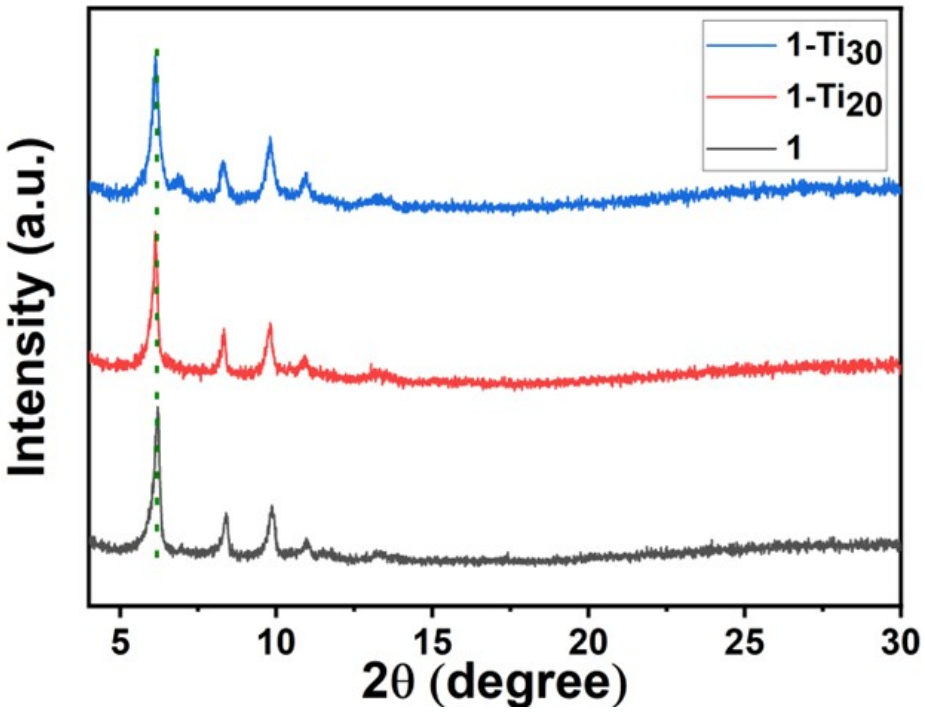


Figure S12. Comparison of PXRD pattern of the pristine MOF and titanium exchanged MOFs.

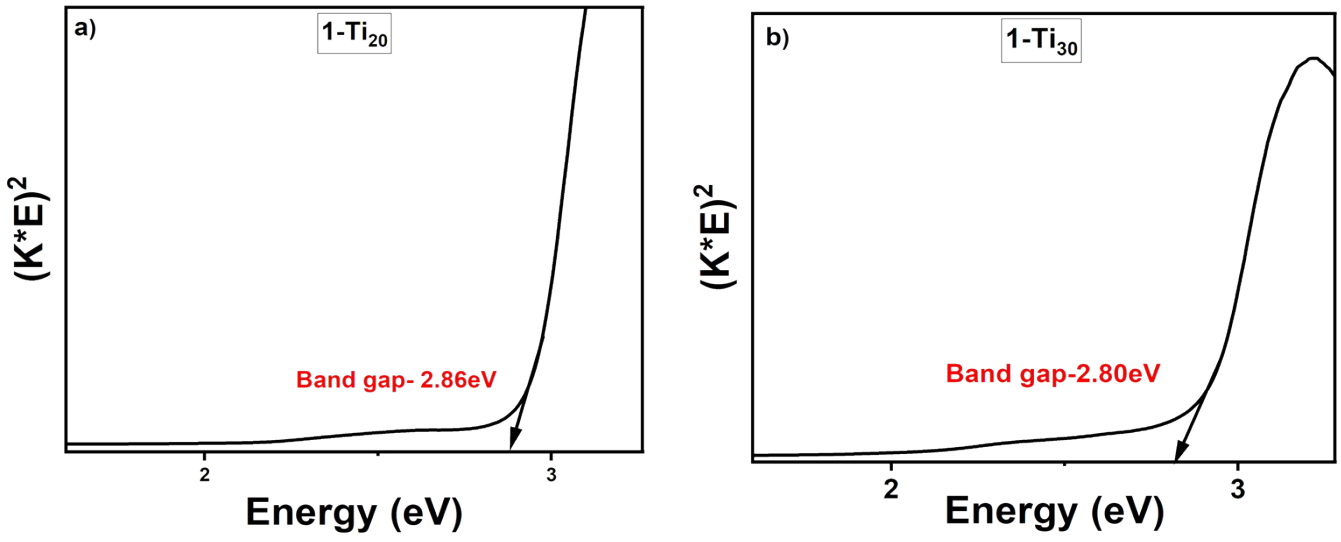


Figure S13. Kubelka Munk plot for a) **1-Ti$_{20}$** and b) **1-Ti$_{30}$**

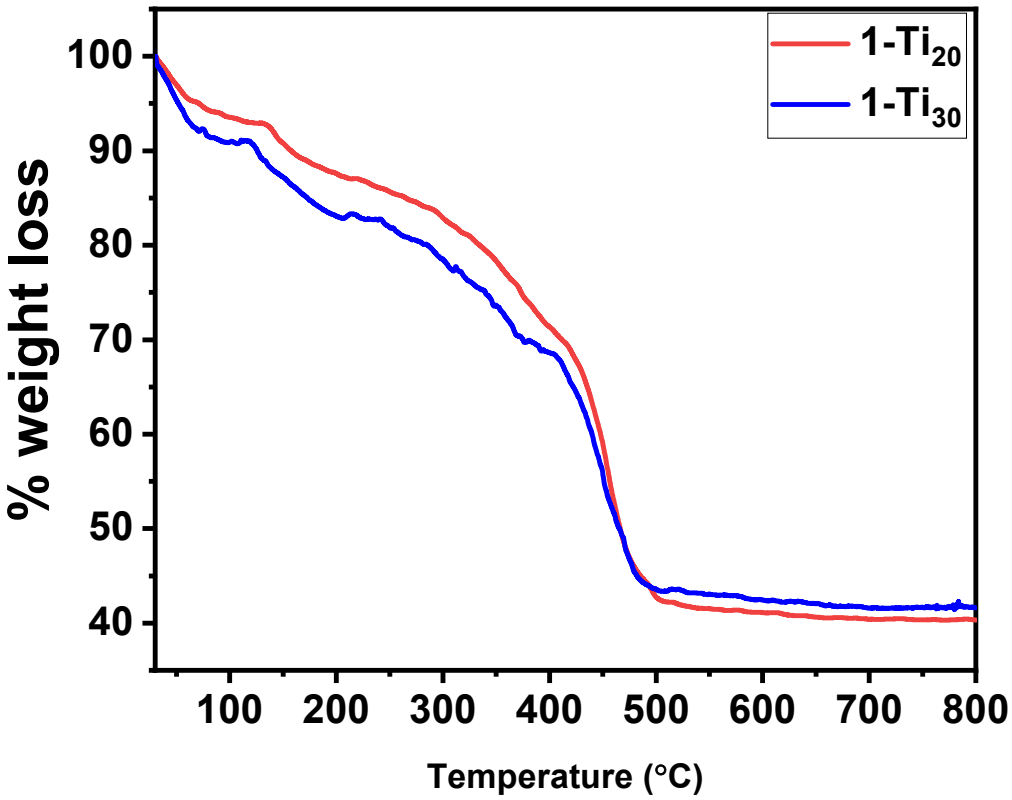


Figure S14. TGA profiles of the Ti exchanged samples from RT to 800 °C at a heating rate of 10 °C min^{-1}.

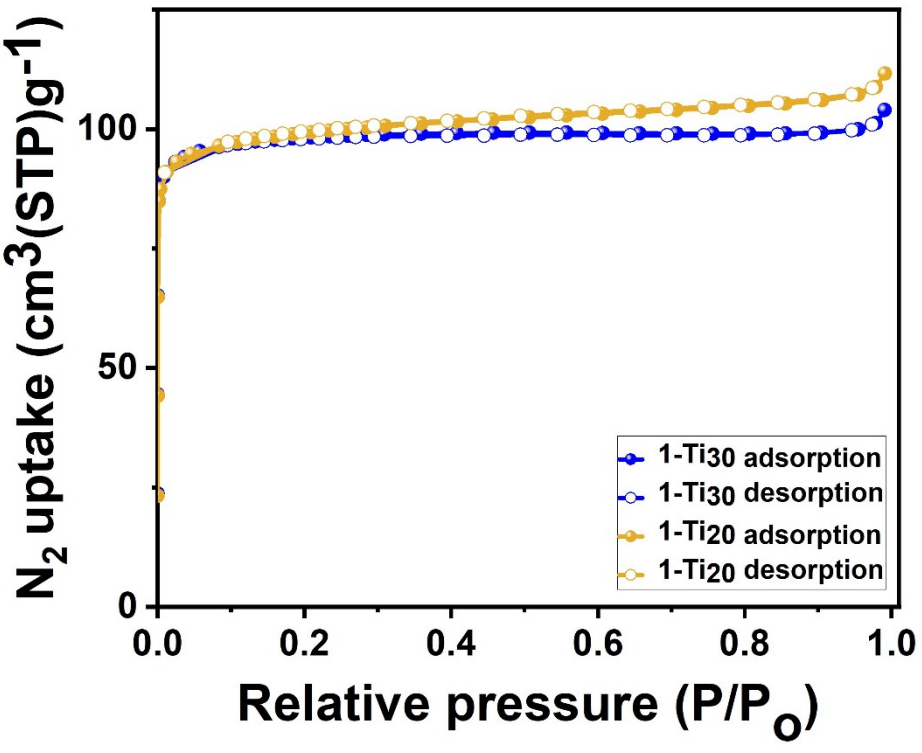


Figure S15. N_2 adsorption isotherm of titanium exchanged samples.

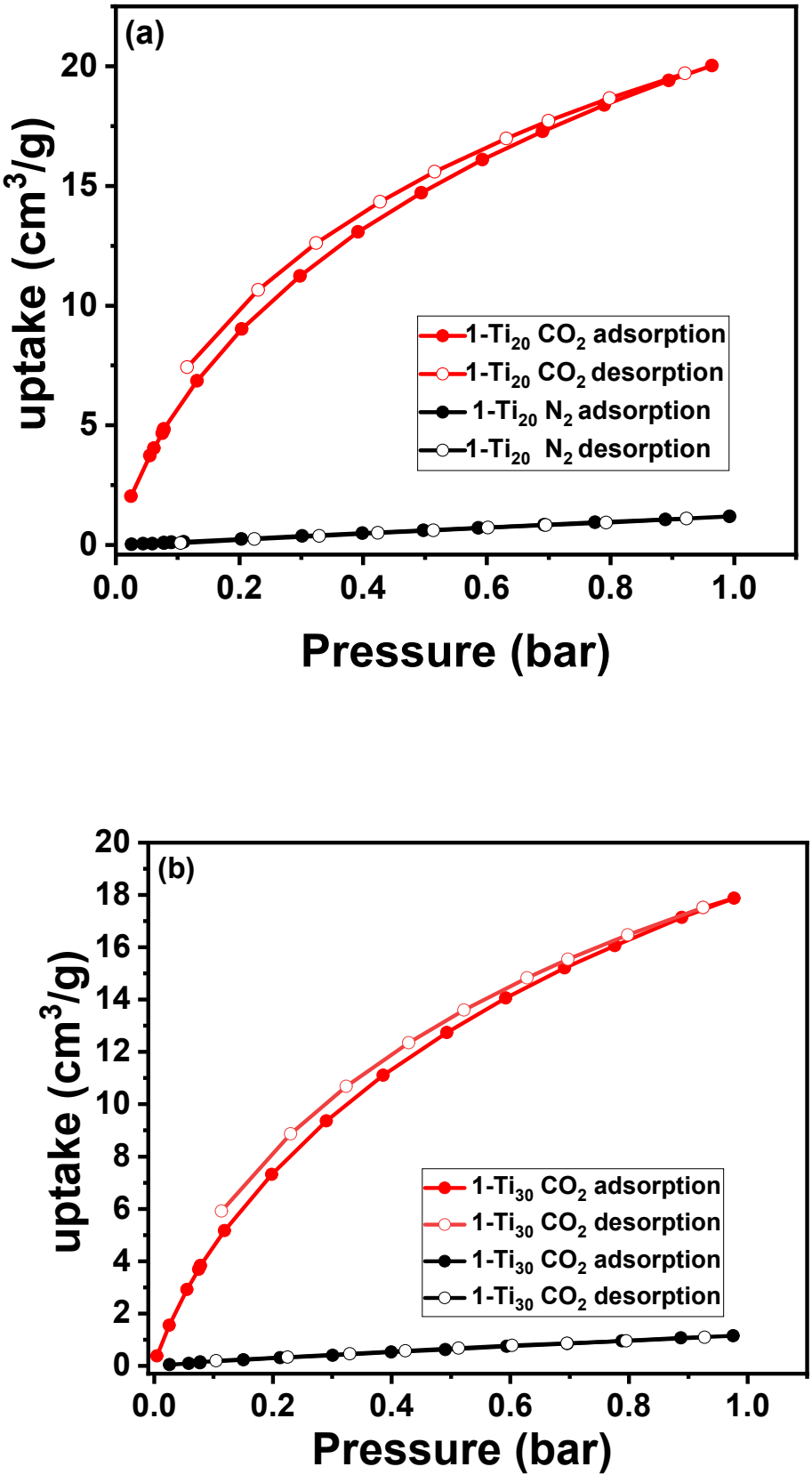


Figure S16 CO_2 and N_2 adsoption isotherms of exchanged samples at RT a) **1-Ti$_{20}$** b) **1-Ti$_{30}$**

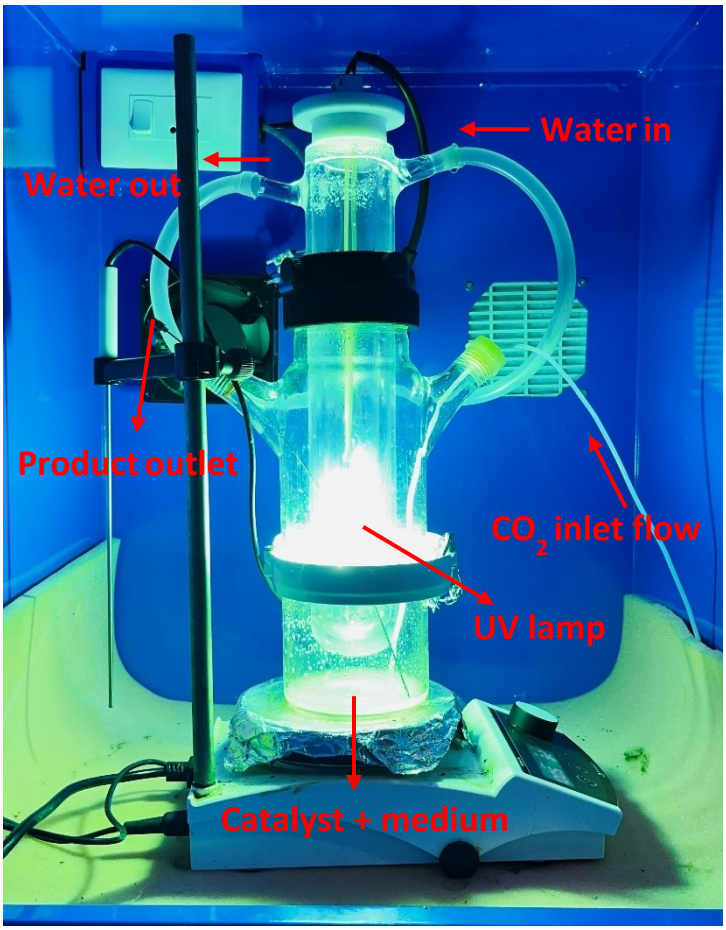


Figure S17. Experimental setup used for photocatalytic reduction of CO_2. The reaction mixture containing the catalyst is placed below the medium-pressure mercury vapor lamp allowing stirring throughout the reaction. Ice water is circulated to the light source to prevent overheating of the lamp. CO_2 is purged into the reaction mixture at a rate of 5cc/min. Each hour the product is collected through the outlet.

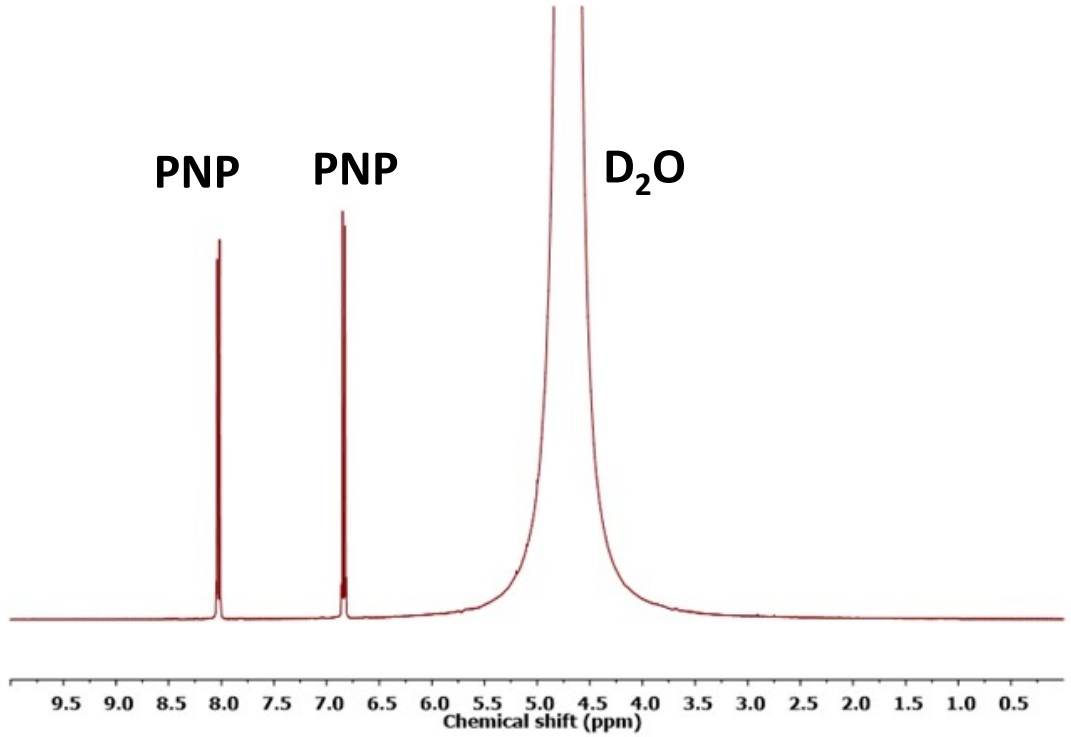


Figure S18. Dark reaction without light irradiation. Internal standard and reference peaks are shown. No further peak indicates the absence of the product.

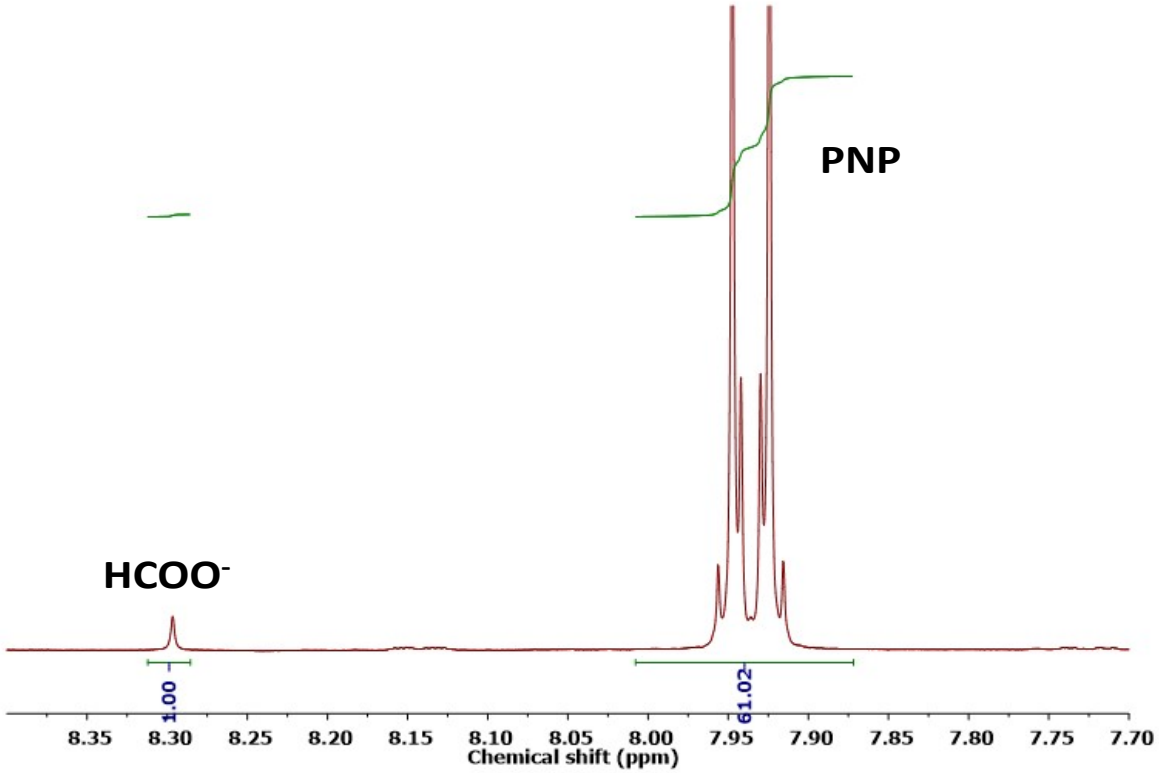


Figure S19. Product peak appears in NMR after light irradiation.

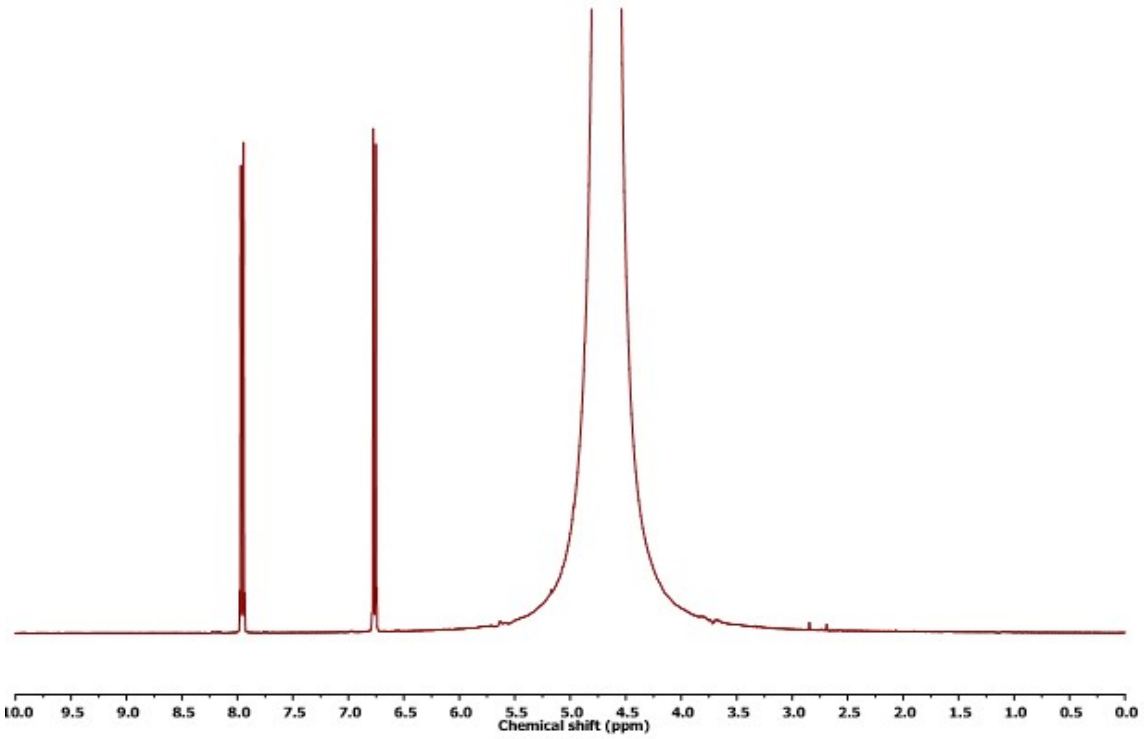


Figure S20. NMR taken after doing catalytic reaction in a water medium to ensure formate is not appearing from the coordinated sites of MOF itself after long exposure to light.

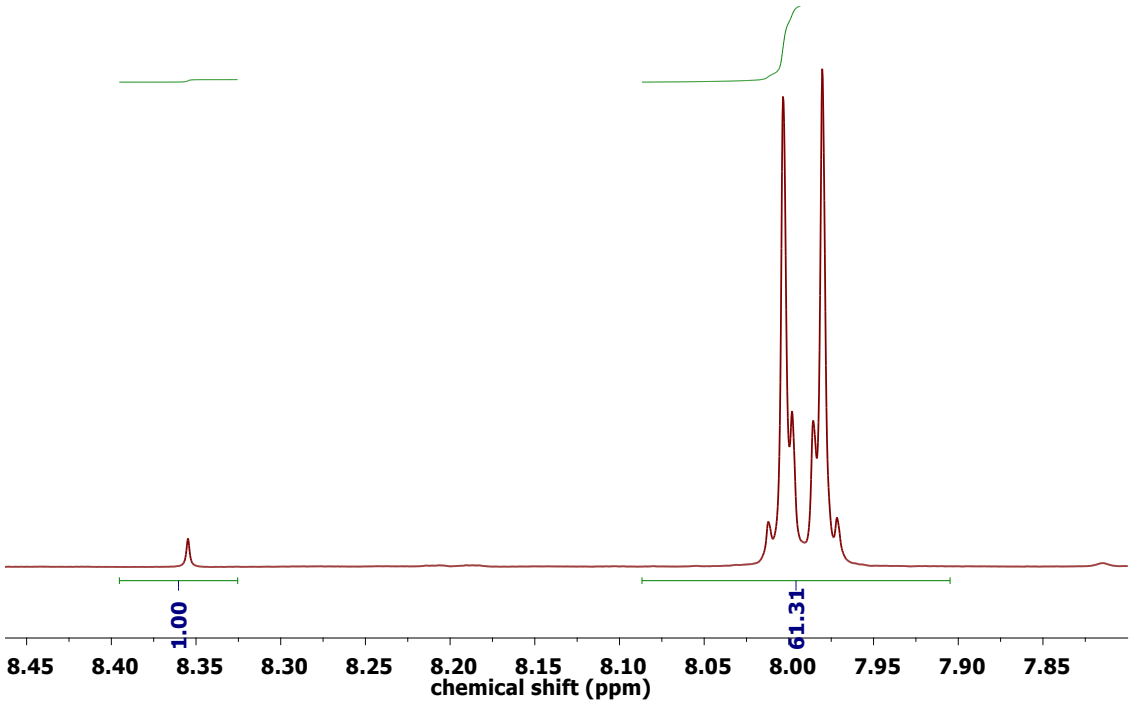


Figure S21. NMR at the first hour of the reaction. Area integrals of the peaks are done to find out the concentration of the products.

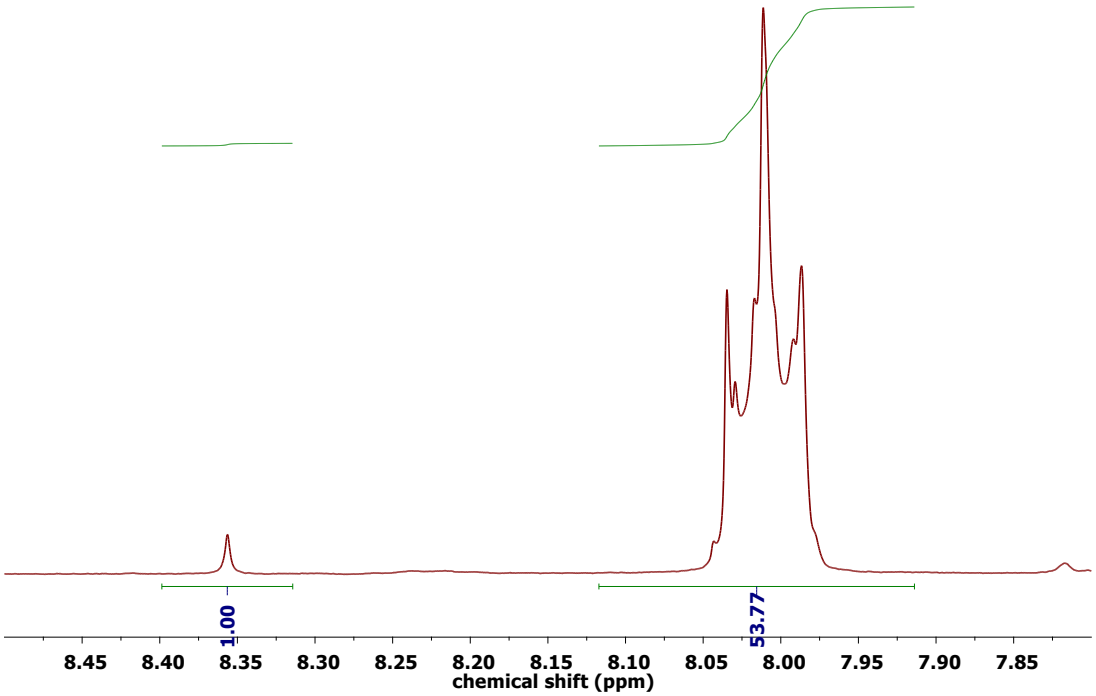


Figure S22. NMR at the second hour of the reaction.

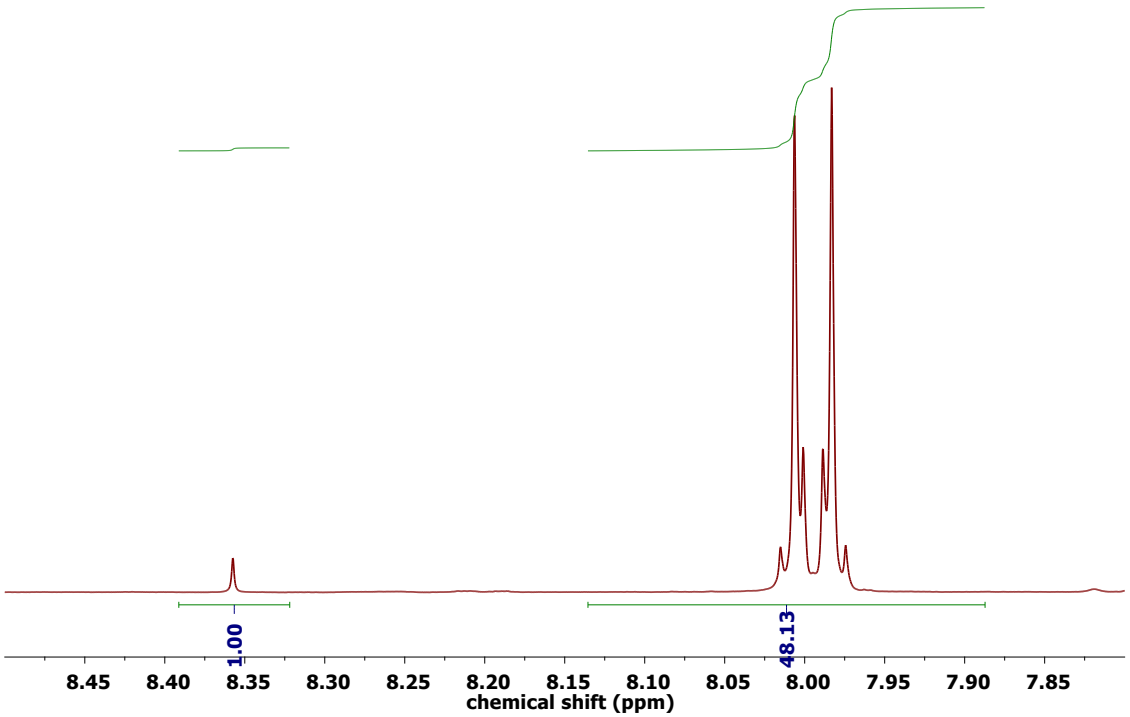


Figure S23. NMR at the third hour of the reaction

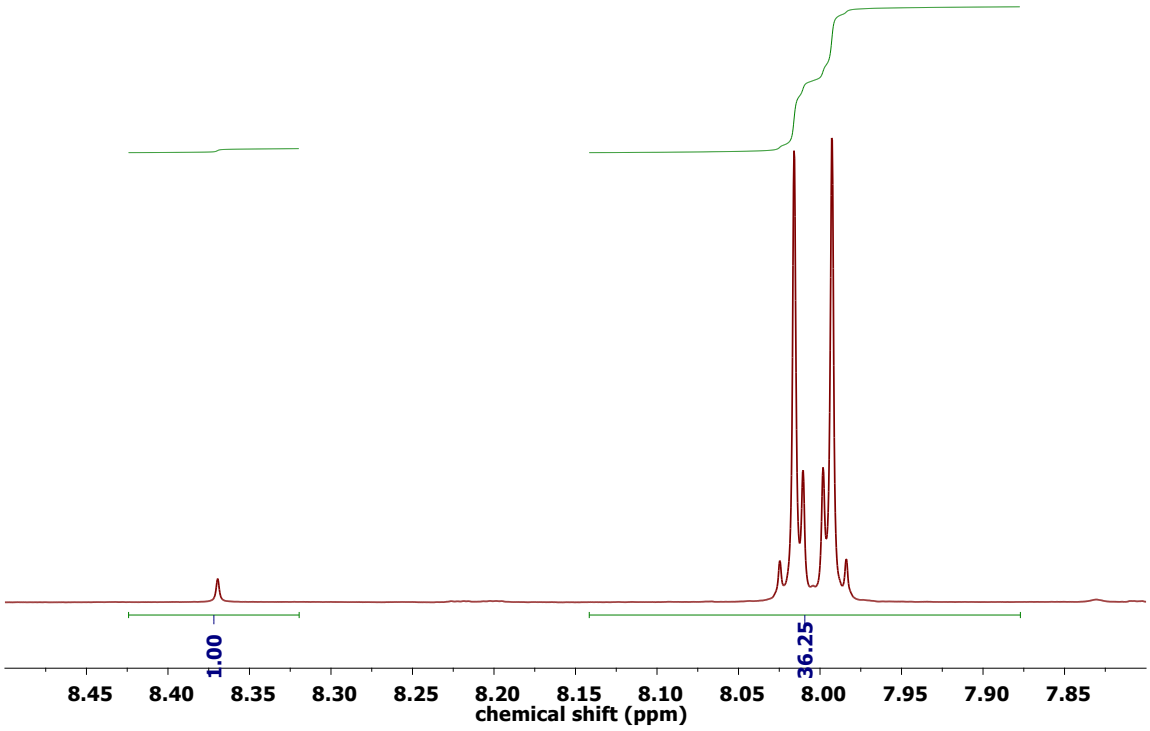


Figure S24. NMR at the fourth hour of the reaction.

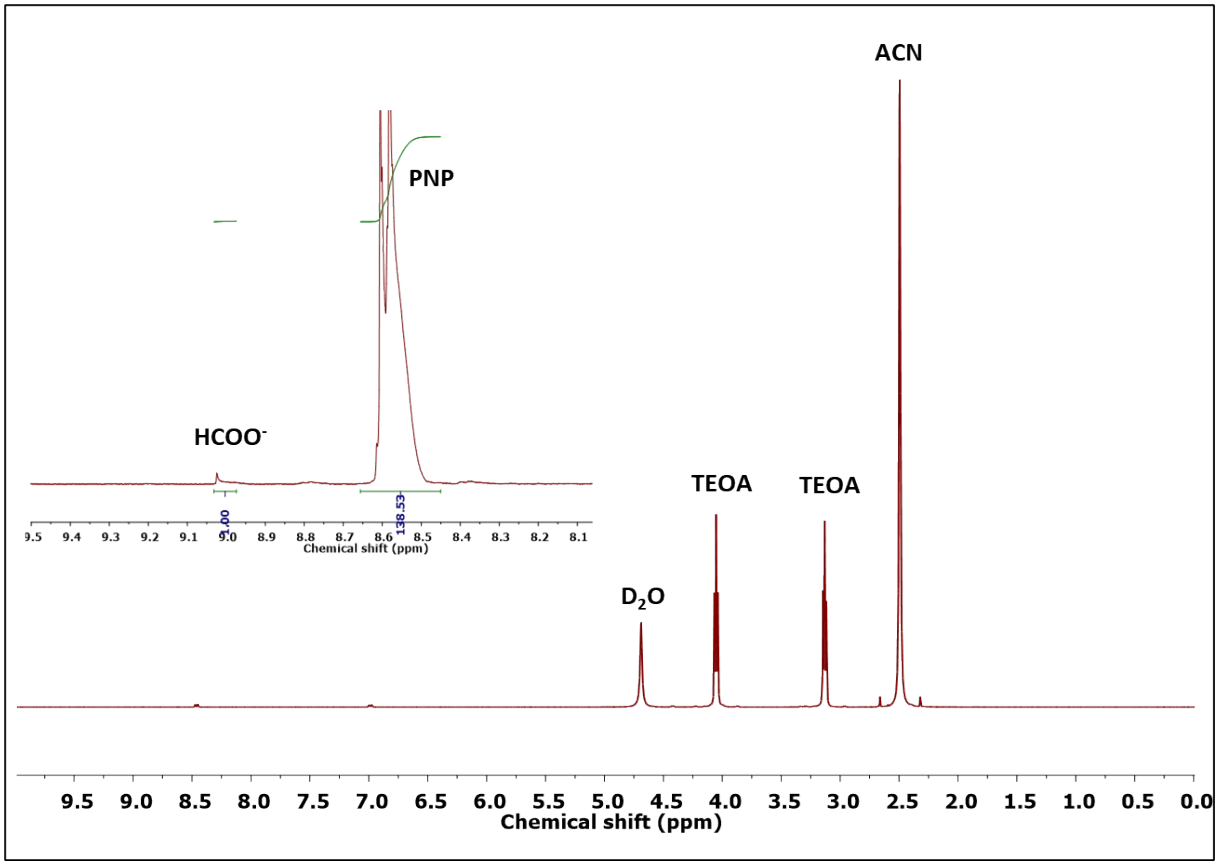


Figure S25. Proton NMR of Photocatalytic experiment carried out in organic medium (ACN/TEOA).

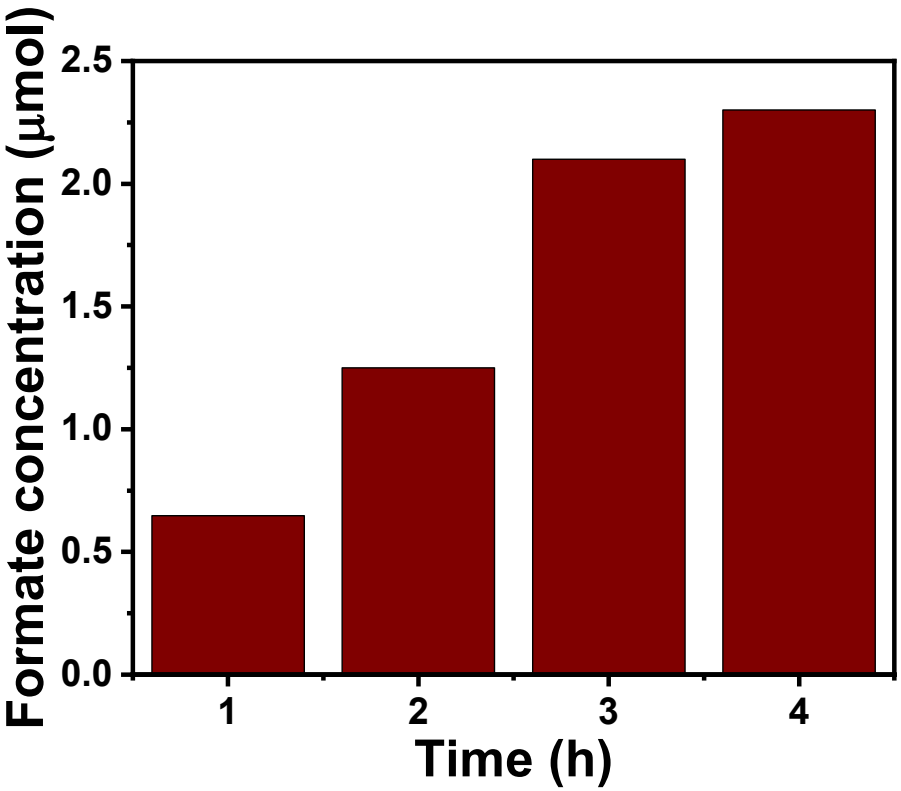


Figure S26. Formate production at different time intervals in the organic medium with the Zr TNDI (**1**) catalyst.

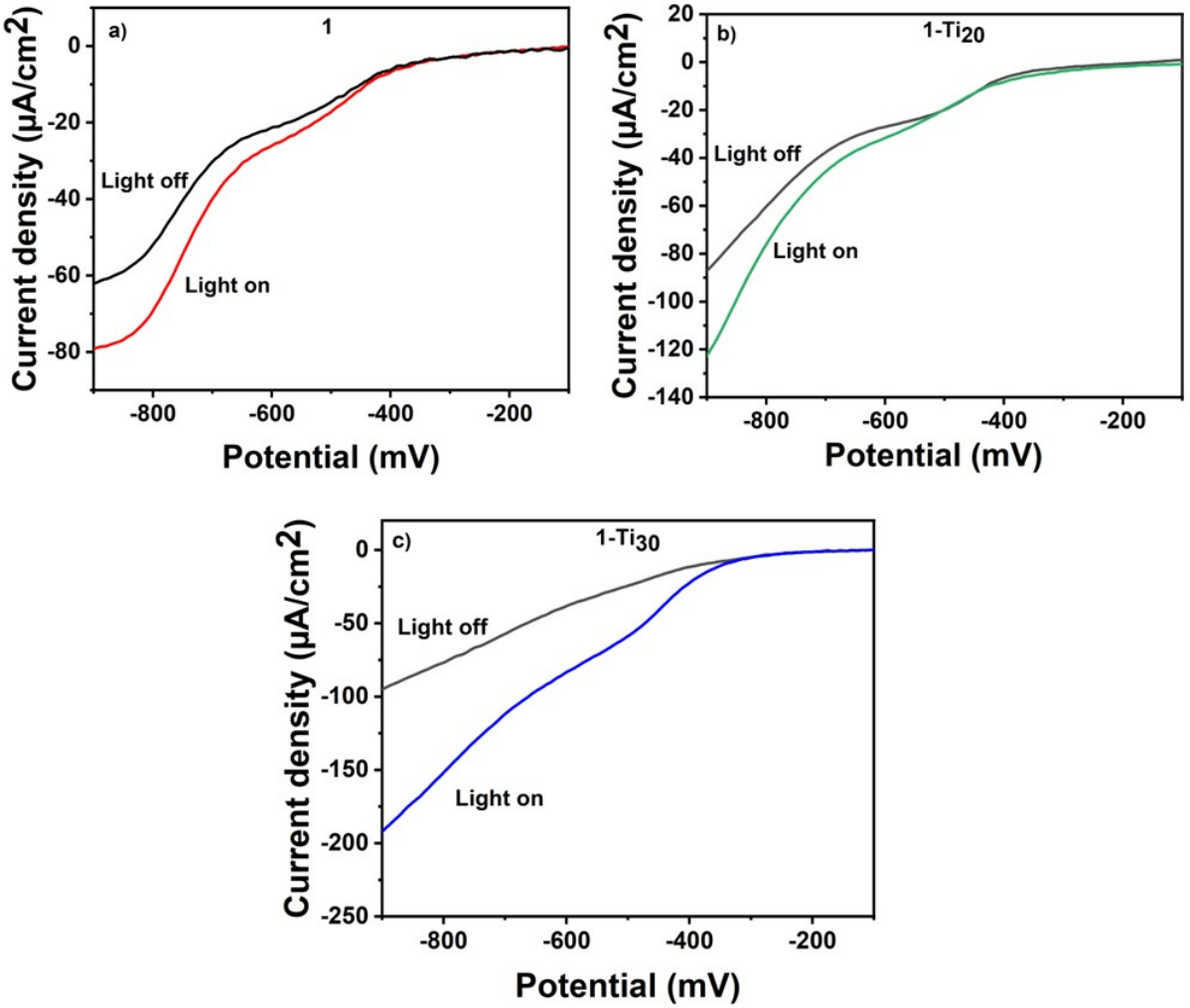


Figure S27. Photocurrent experiment in the CO_2 reduction potential range (cathodic potential) showing current density during light on-off conditions a) **1** b) **1-Ti$_{20}$**, and c) **1-Ti$_{30}$**.

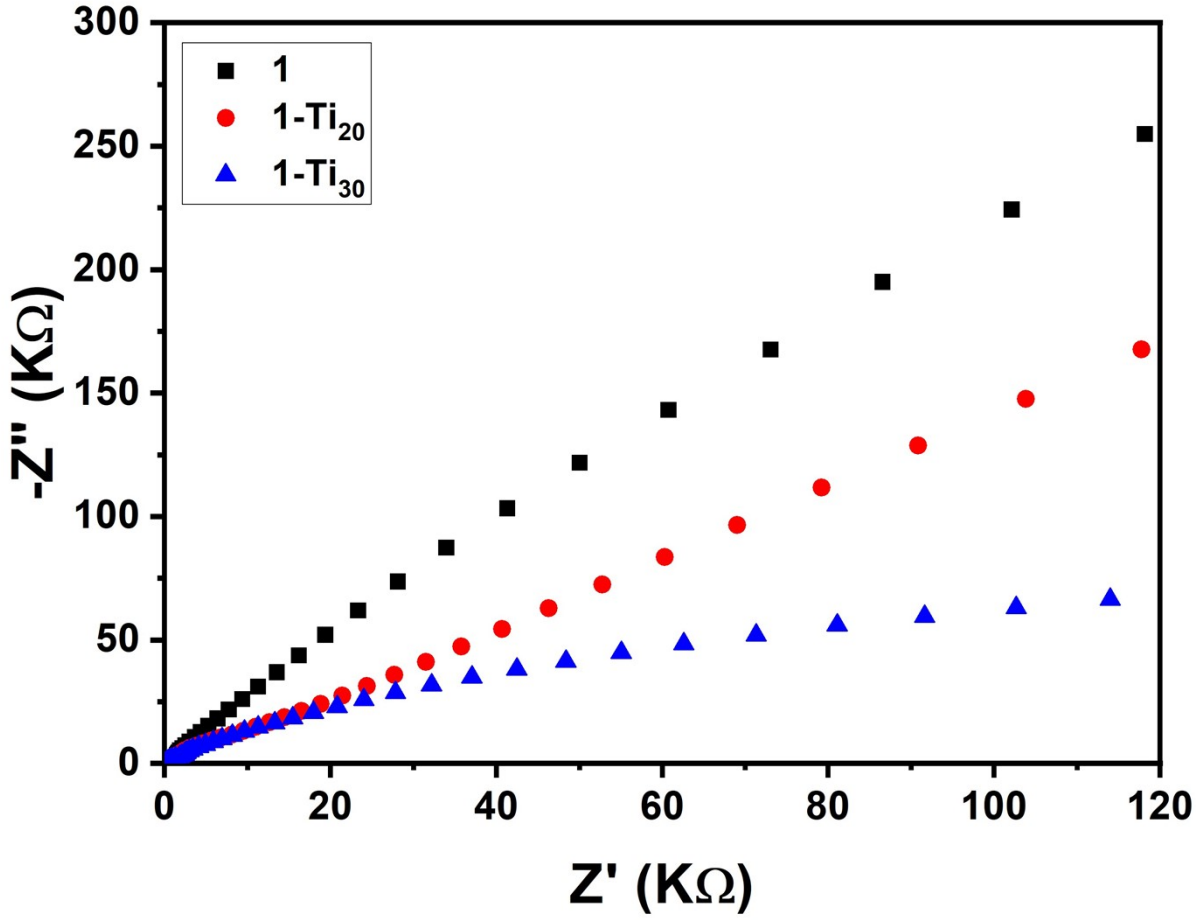


Figure S28. Impedance spectra of **1** and Ti exchanged samples.