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

Supporting Information

Self-assembly of Polyoxometalates, Pt Nanoparticles and Metal-Organic Frameworks in a Hybrid Material for Synergistic Hydrogen Evolution

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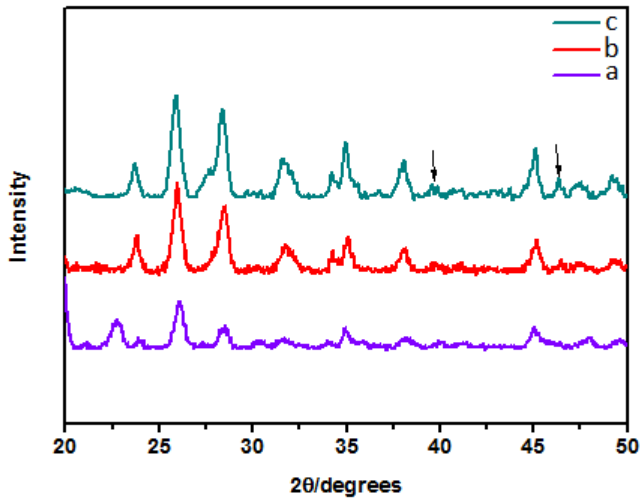


Fig S1. PXRD patterns of a) MIL-53 (purple), b) NH_2-MIL-53 (red) and c) **PNPMOF** (green) in the 20°-50° range showing the small peaks at 39.6° and 46.3° which are indexed to be the [111] and [200] planes of Pt NPs.

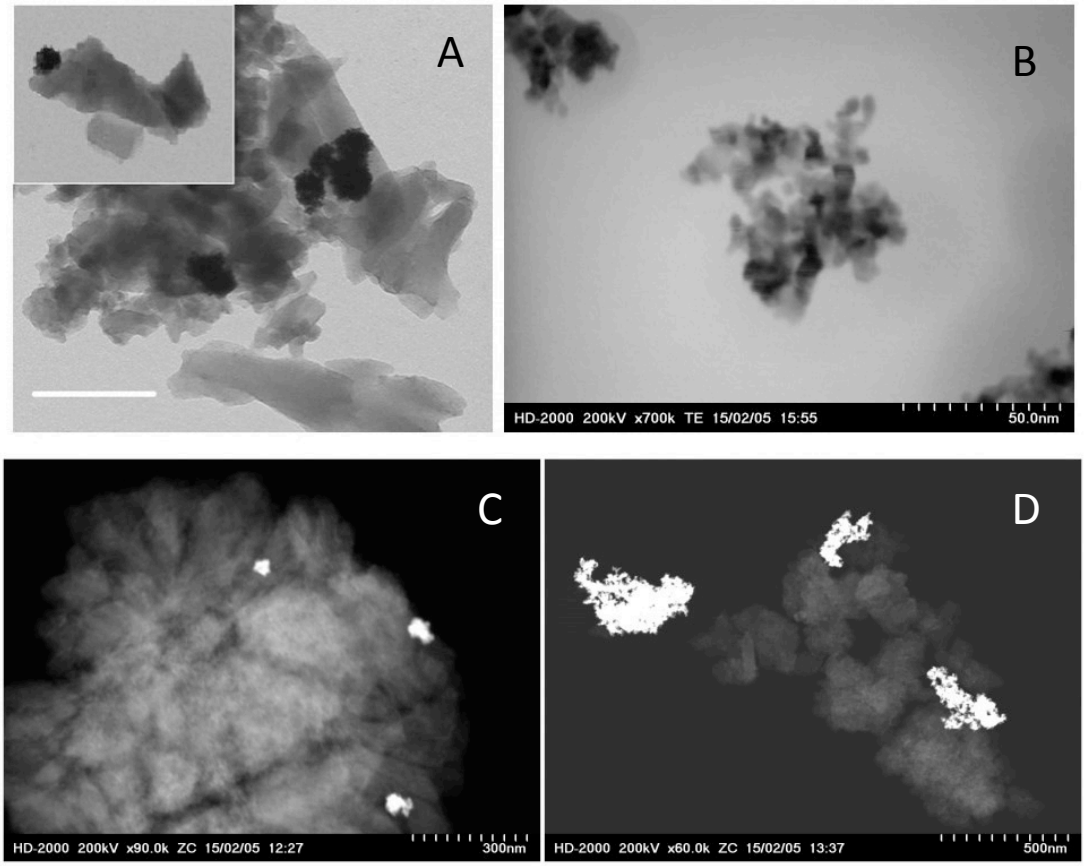
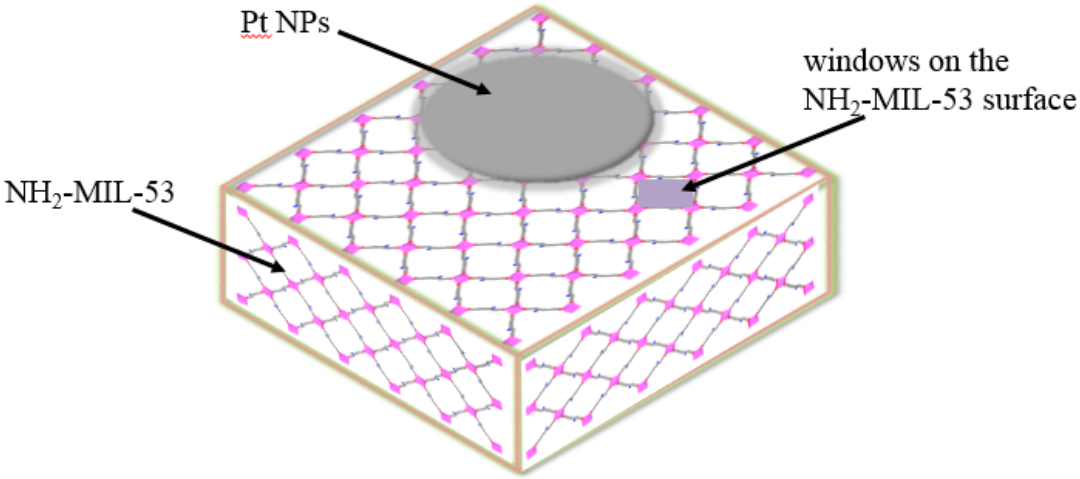


Fig S2 A): TEM images of POM-Pt NPs@NH_2-MIL-53 (**PNPMOF**). The large

dark approximately spherical particles are the POM-capped Pt NPs. The scale bar in the graph corresponds to 200 nm. B): TEM image of POM-stabilized Pt NPs. C) Z-contrast TEM image of **PNPMOF**. D) Z-contrast TEM image of NH_2-MIL-53 mixed with the commercial Pt black.

Scheme S1. Illustration of the Pt NPs and the windows on the NH_2-MIL-53 surface



Based on the weight percent of Pt NPs (0.38 %) and the average size of Pt NPs (80 nm), the number of Pt NPs loaded onto the surface of NH_2-MIL-53 is calculated to be 2.0×10^{17} in a 100 g sample, and the number of NH_2 groups in this same sample is calculated to be 1.4×10^{23}. Considering the pore window of NH_2-MIL-53 (0.7 nm × 0.7 nm), the number of windows on the NH_2-MIL-53 surface that are covered by the Pt NPs is estimated to be: $3.14\times(40\text{nm})^2\times2.0\times10^{17}/(0.7\text{nm}\times0.7\text{nm}) = 2.05\times10^{21}$. Each window has four NH_2 groups, therefore, the number of NH_2 groups that are connected with each Pt NP is estimated to be: $4\times2.05\times10^{21} = 8.2\times10^{21}$. Therefore, about 6% ($= 8.2\times10^{21}/1.4\times10^{23}$) of the total NH_2 groups are connected to Pt NPs. See Scheme S1 graphical illustrations.

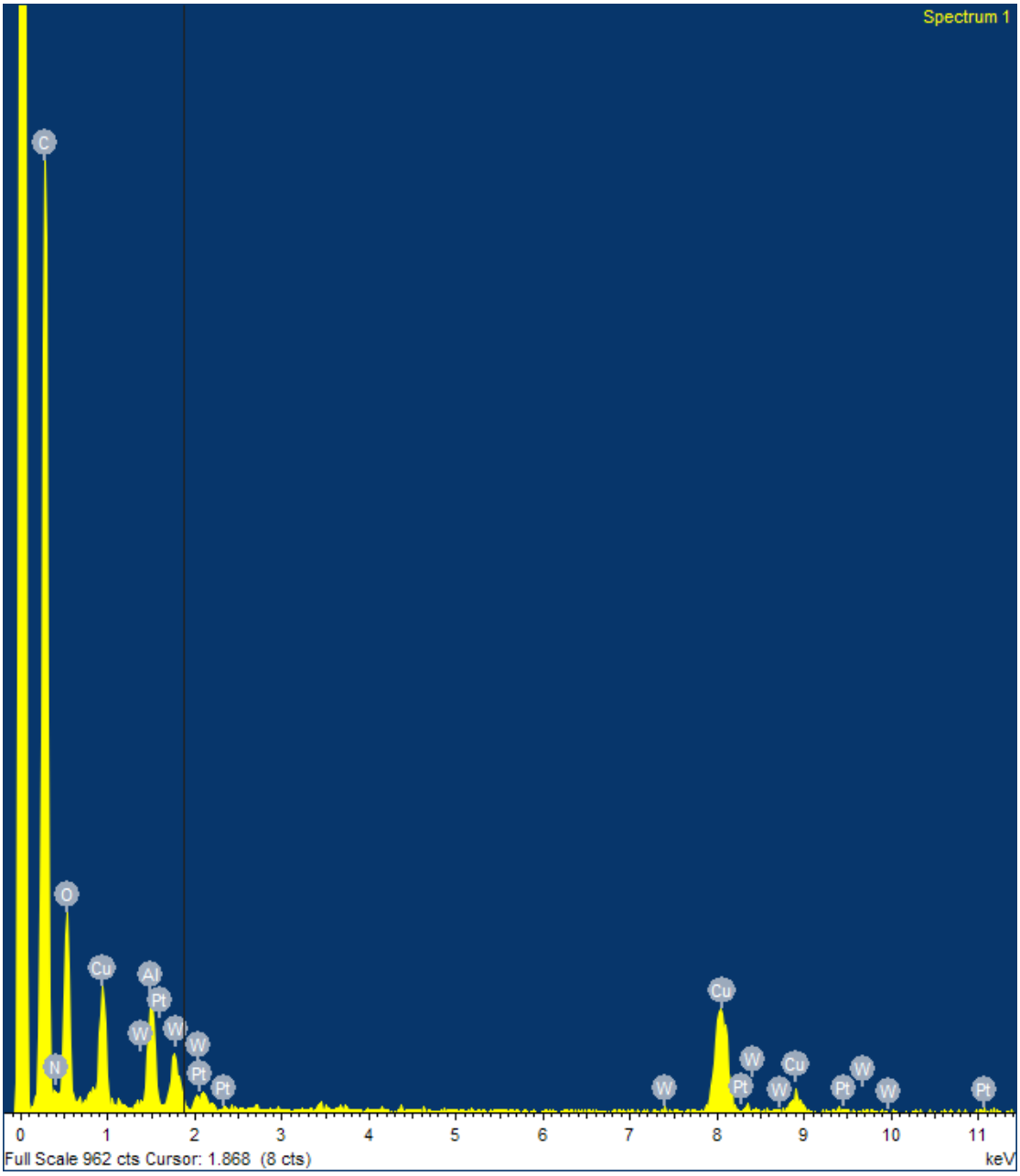


Fig S3. EDX analysis of **PNPMOF**

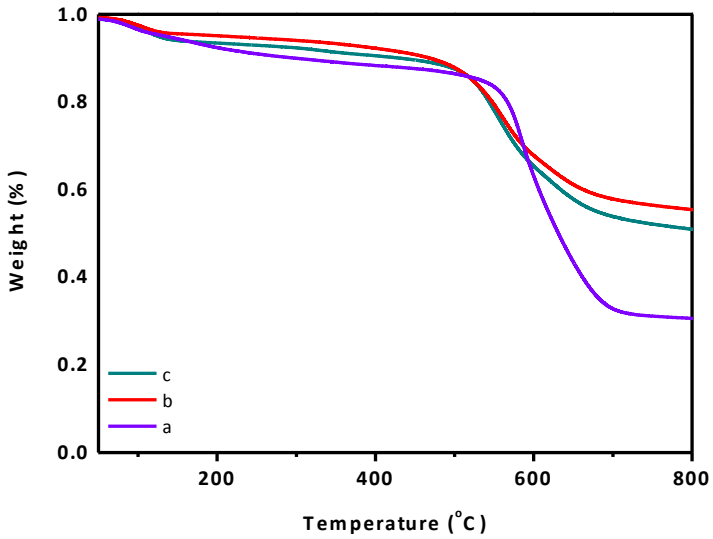


Fig S4. TGA of a) MIL-53 (purple), b) NH_2-MIL-53 (green) and c) **PNPMOF** (red). **PNPMOF** shows a similar thermal behavior to that of NH_2-MIL-53. Both are stable up to 500 °C.

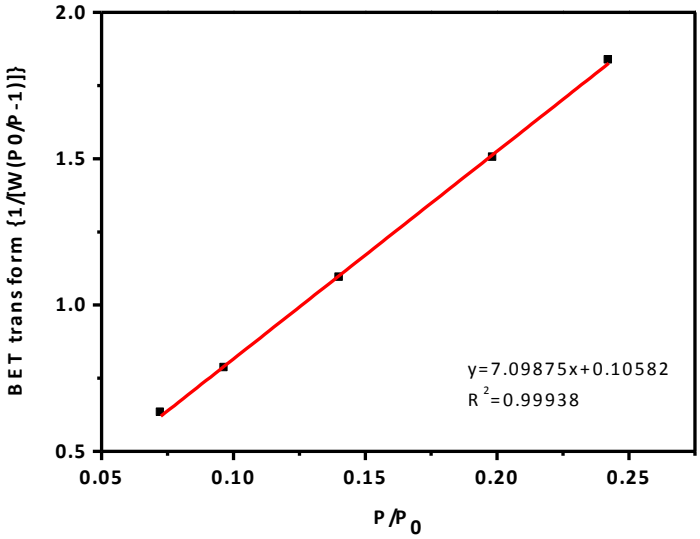


Fig S5. BET fitting curve for MIL-53. (MIL-53 surface area = 1174 m^2/g).

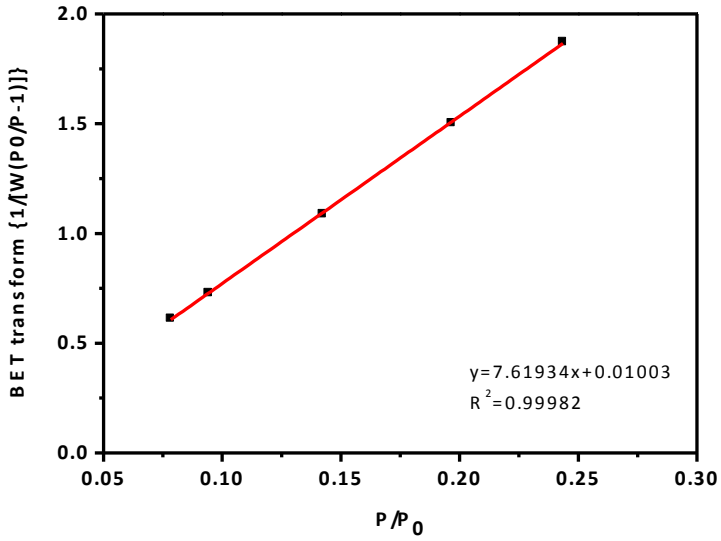


Fig S6. BET fitting curve for NH_2-MIL-53. (NH_2-MIL-53 surface area = 912 m^2/g). This is lower than that of MIL-53 (1174 m^2/g) because NH_2 groups partially block the pores of NH_2-MIL-53. These BET surface areas of 912 and 1174 m^2/g are consistent with previously reported literature values.[1]

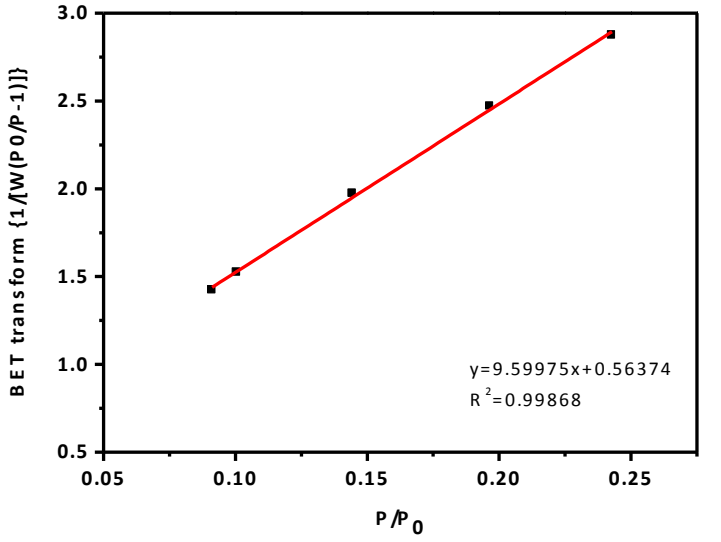


Fig S7. BET fitting curve for **PNPMOF**. (**PNPMOF** surface area = 684 m^2/g).

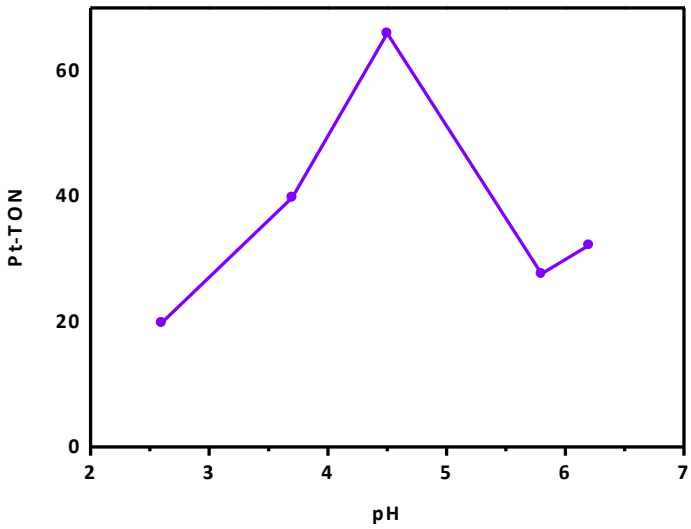


Fig S8. pH dependence of hydrogen evolution by **PNPMOF** using ascorbic (AA) as sacrificial electron donor. The amino group in NH_2-MIL-53 is assumed to have a similar pK_a to that of 3-nitroanilinium cation, which is 2.5.[2] Therefore, at pH 4.5, about 1% of NH_2 groups are protonated; the remaining unprotonated NH_2 groups function as light absorbers.

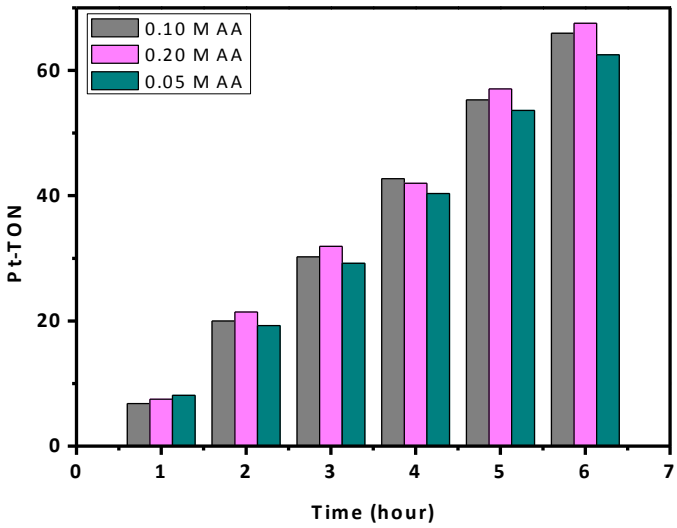


Fig S9. Time-dependent hydrogen evolution curves for **PNPMOF** using different concentrations of AA.

Table S1. Control experiments for photocatalytic hydrogen evolution under standard conditions after 6 hours.

Entry	Catalyst	TON with respect to Pt

1	MIL-53	< 1% (limit of detection)
2	NH_2-MIL-53	< 1% (limit of detection)
3	**PNPMOF**	66
4	$(n\text{-BuN})_3PW_{12}O_{40}$	< 1% (limit of detection)
5	POM-stabilized Pt NPs	< 1% (limit of detection)
6	H_2PtCl_6	< 1% (limit of detection)
7	NH_2-MIL-53 with $H_3PW_{12}O_{40}$	< 1% (limit of detection)
8	Without the addition of AA	< 1% (limit of detection)
9	**PNPMOF** in 0 ^oC	58
10	**PNPMOF** in 25 ^oC	58
11	**PNPMOF** in 50 ^oC	59

Table S2. Average lifetimes[a] for different samples from time-resolved fluorescence decay measurements.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Average life-time (ns)
2-Aminoterephthalic acid	0.71	49	3.5	51	3.0
NH_2-MIL-53	0.2	79	2.6	21	2.1
PNPMOF	0.14	79	1.0	21	0.7

[a]Average lifetime of $\tau = (A_1\tau_1^2+A_2\tau_2^2)/((A_1\tau_1+A_2\tau_2)$.

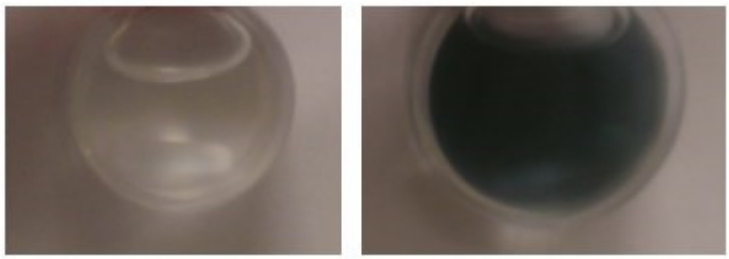


Fig S10. Oxidation of 2-aminoterephthalic acid by $H_3PW_{12}O_{40}$. When 50 μM 2-aminoterephthalic acid was mixed with 0.1 M $H_3PW_{12}O_{40}$ in distilled water in the dark purged with Ar, the color of the solution changes from light yellow (left) to dark blue (right) (a characteristic color for reduced $H_3PW_{12}O_{40}$) after 1 hour indicating that the 2-aminoterephthalic acid is oxidized by $H_3PW_{12}O_{40}$.

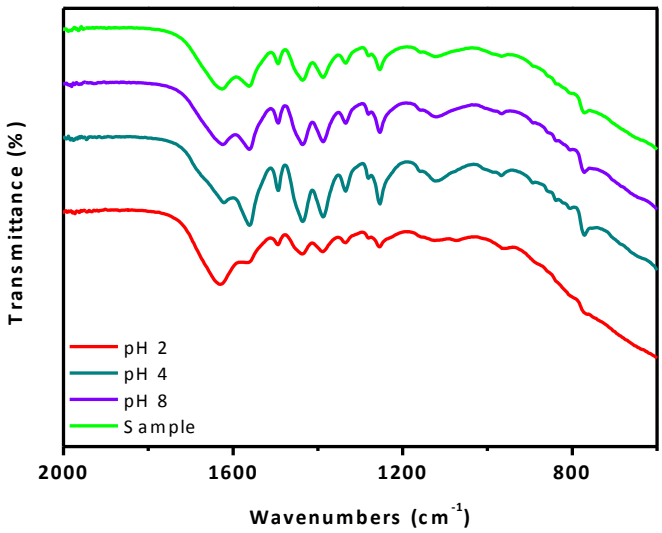


Fig S11. ATR-IR spectra of **PNPMOF** at different pH values. The "sample" is for **PNPMOF** with no additional added acid.

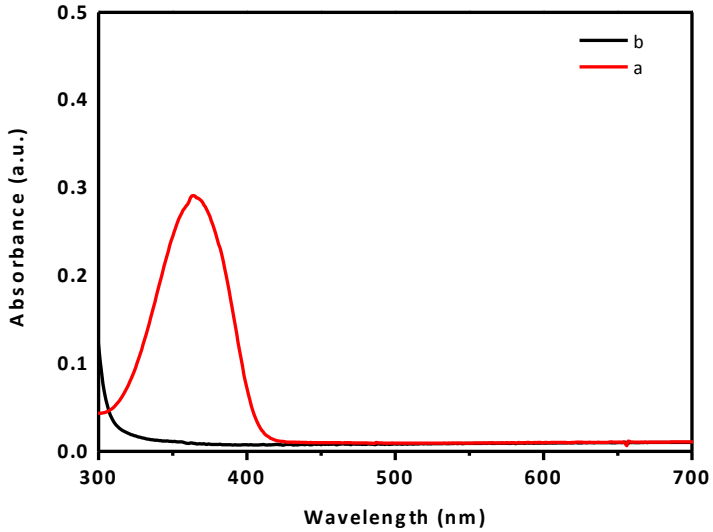


Fig S12. UV-vis spectra of a) 2-aminoterephthalic acid in distilled water (60 μM) and b) the filtrate solution after the first run. The UV-vis spectra of the filtrate solution indicate a negligible amount of organic linker is present arguing strongly that the MOF structure is maintained during the catalytic reactions.

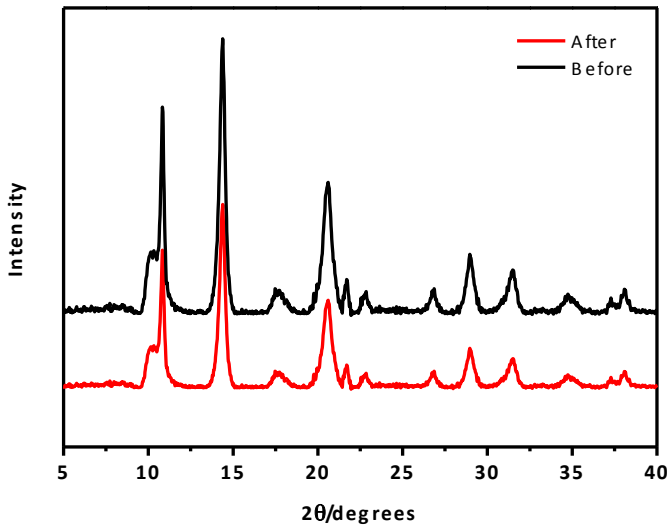


Fig S13. PXRD patterns of **PNPMOF** before and after catalysis.

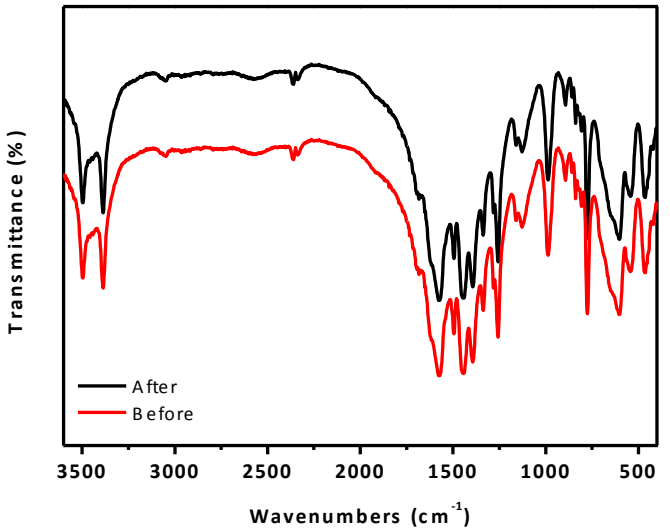


Fig S14. FT-IR spectra of **PNPMOF** before and after catalysis.

(1) Bromberg, L.; Klichko, Y.; Chang, E. P.; Speakman, S.; Straut, C. M.; Wilusz, E.; Hatton, T. A. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4595.

(2) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. In *Organic Chemistry*; 3rd ed.; McGraw-Hill: New York, 1970; Vol. 3, p Chapter 8.