

Site Specific Supramolecular Heterogeneous Catalysis by Optically Patterned Soft Oxometalate - Porous Organic Framework (SOM-POF) Hybrid on a Chip

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Supplementary Information for characterization of SOM-POF composites in Journal of Materials Chemistry A

1. Zeta Potential measurements

SOM-POF composite dispersions were prepared namely SOM-PAF1, SOM-JUC-Z2 and SOM-JUC-Z5, by varying the SOM:POF mole ratio from 10 to 50 and zeta potential experiments were done on each one of them. The zeta potential values were negative indicating that the stable dispersions were negatively charge stabilized. (Figure S1)

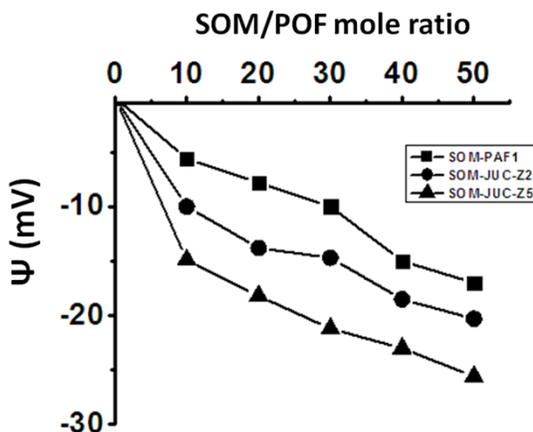


Figure S1: Zeta potential versus SOM:POF ratio plot of SOM-PAF1, SOM-JUC-Z2 and SOM-JUC-Z5.

2. Fourier Transform-Infrared Spectroscopy of SOM-POF composites and their components.

The IR spectra of dried samples of SOM, PAF1, JUC-Z2, JUC-Z4, JUC-Z5, SOM-PAF1, SOM-JUC-Z2, SOM-JUCZ4 and SOM-JUC-Z5 were recorded. The spectra showed characteristic

peaks of both SOM and the constituting POF for the composite thus confirming the formation of each of the composites. (Figure S2) For instance, the peak at 1400 cm^{-1} intensifies in the composites with slight blue shifts as compared to that of ammonium heptamolybdate SOM. This peak is attributed to the bending mode ($\delta_{\text{N-H}}$) of N-H vibration and it is intensified in the composites due to the condensation of NH_4^+ counterions around the composite. (Figure S2)

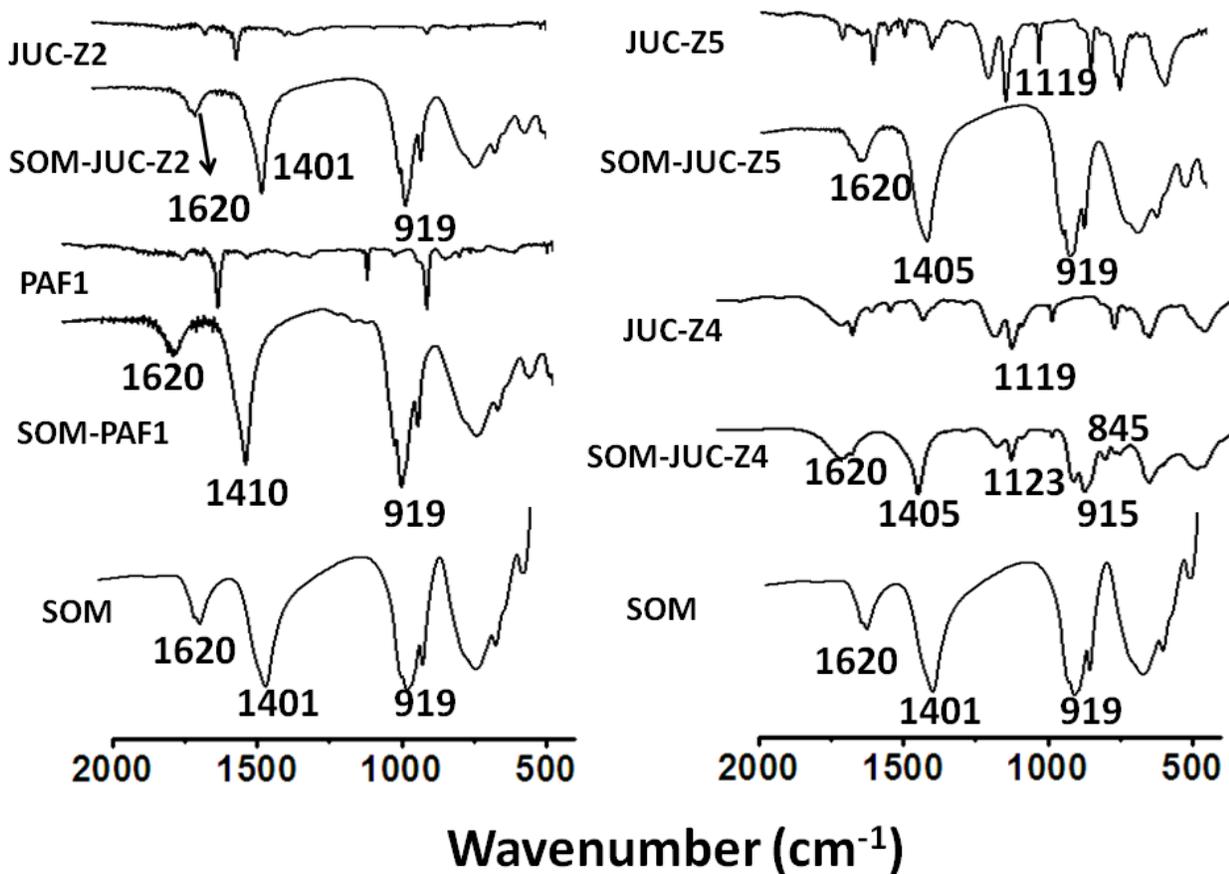


Figure S2: IR spectra of SOM, different POF materials and their corresponding SOM-POF composites.

A sharp band at 1620 cm^{-1} corresponds to the bending vibration of the hydrogen bonded $-\text{OH}$ group in water molecules. The bending mode ($\delta_{\text{C-H}}$) of C-H vibration is blue shifted in case of SOM-JUC-Z4 composite at 845 cm^{-1} as compared to their corresponding POF materials i.e., JUC-Z4. This indicates that the aromatic C-H bonds of the benzene rings of POF are getting stiffened due to the restriction brought about by the surrounding heptamolybdate clusters. The peaks between 1000 cm^{-1} and 900 cm^{-1} are ascribed to the $\text{Mo}=\text{O}$ characteristic stretching vibration of the hexagonal phase of ammonium heptamolybdate SOM. We also observe a slight blue shift in the band around 1123 cm^{-1} for SOM-JUC-Z4 composite. This is attributed to the

stretching mode (ν_{C-P}) of C-P vibration in the SOM-POF composite and occurs due to electron donation from heptamolybdate to positive centre of phosphorous of POF which in turn strengthens the C-P bond. Interestingly it is not observed in the SOM-JUC-Z5 composite.

3. Thermogravimetric Analysis of SOM-POF composites and their components.

The TGA measurements of different SOM-POF materials showed greater decomposition temperature for the composites as compared to their corresponding POF precursors. The decomposition temperature for each of the composites is increased by almost 200-300 °C owing to introduction of soft oxometalates. (Figure S3) The heptamolybdate based soft-oxometalate has a high decomposition temperature around 800°C which is reflected in the decomposition temperatures of SOM-POF composites. (Figure S3) For instance, PAF1 decomposes around 400 °C whereas SOM-PAF1 composite decomposes around 700 °C. Similarly while JUC-Z2, JUC-Z4 and JUC-Z5 decompose around 400 °C, 500 °C and 400°C, respectively, SOM-JUC-Z2, SOM-JUC-Z4 and SOM-JUC-Z5 decompose around 700°C, 600 °C and 650 °C respectively.

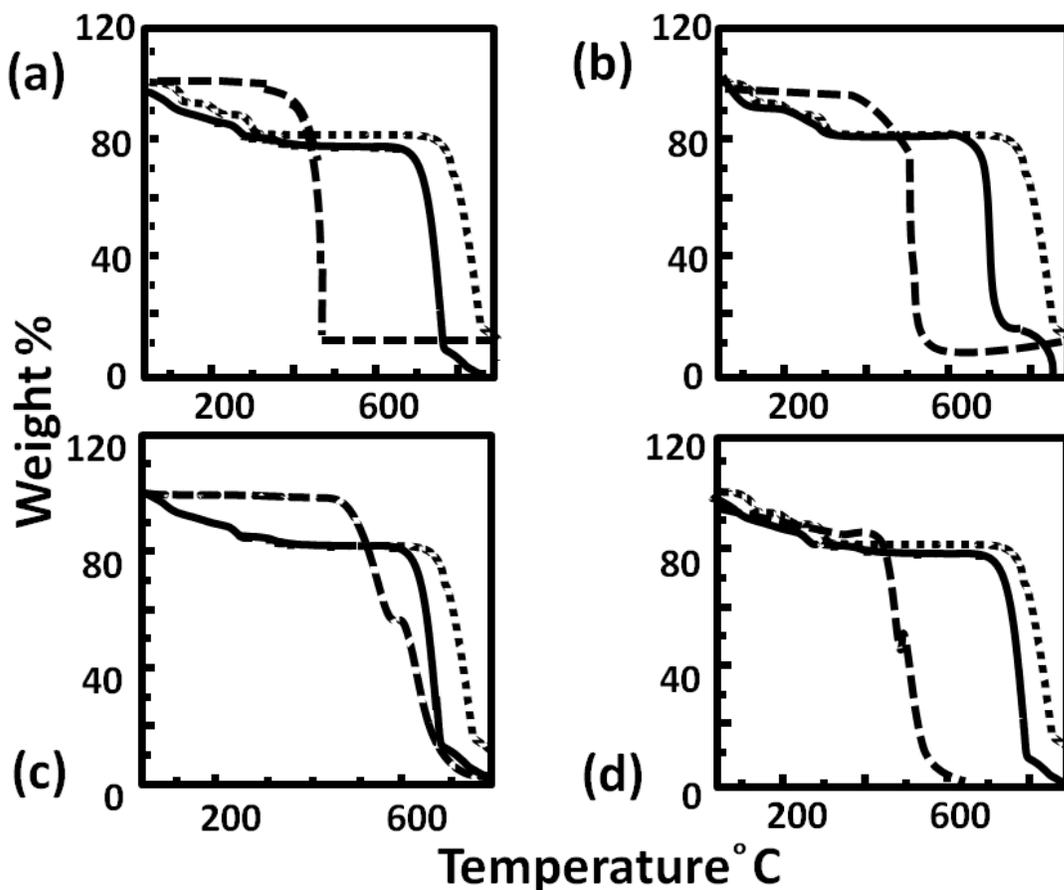


Figure S3: TGA plot of a) Ammonium heptamolybdate SOM (dotted line), PAF1 (dashed line) and SOM-PAF1 (solid line). b) Ammonium heptamolybdate SOM (dotted line), JUC-Z2 (dashed

line) and SOM-JUC-Z2 (solid line). c) Ammonium heptamolybdate SOM (dotted line), JUC-Z4 (dashed line) and SOM-JUC-Z4 (solid line). d) Ammonium heptamolybdate SOM (dotted line), JUC-Z5 (dashed line) and SOM-JUC-Z5 (solid line).

4. N₂ Adsorption isotherm measurements for POFs and SOM-POF composites.

N₂ measurement of the composites were done to estimate the BET surface areas of the SOM-POF composites and also to compare them with the surface areas of their POF precursors (Figure S4). This has been depicted in Table S1. It was observed that the surface areas of the SOM-POF composites were extremely less than their POF precursors. This could be due to impregnation of the ammonium heptamolybdate soft-oxometalate in the pores of each of the porous organic frameworks.

Table S1: BET surface area of SOM-POF composites and their POF precursors

S. No.	Compound	BET Surface Area $S_{\text{BET}}(\text{m}^2\text{g}^{-1})$
1.	PAF1	5640
2.	JUC-Z2	2081
3.	JUC-Z5	242
4.	SOM-PAF1	9.61
5.	SOM-JUC-2	4.93
6.	SOM-JUC-Z5	14.69

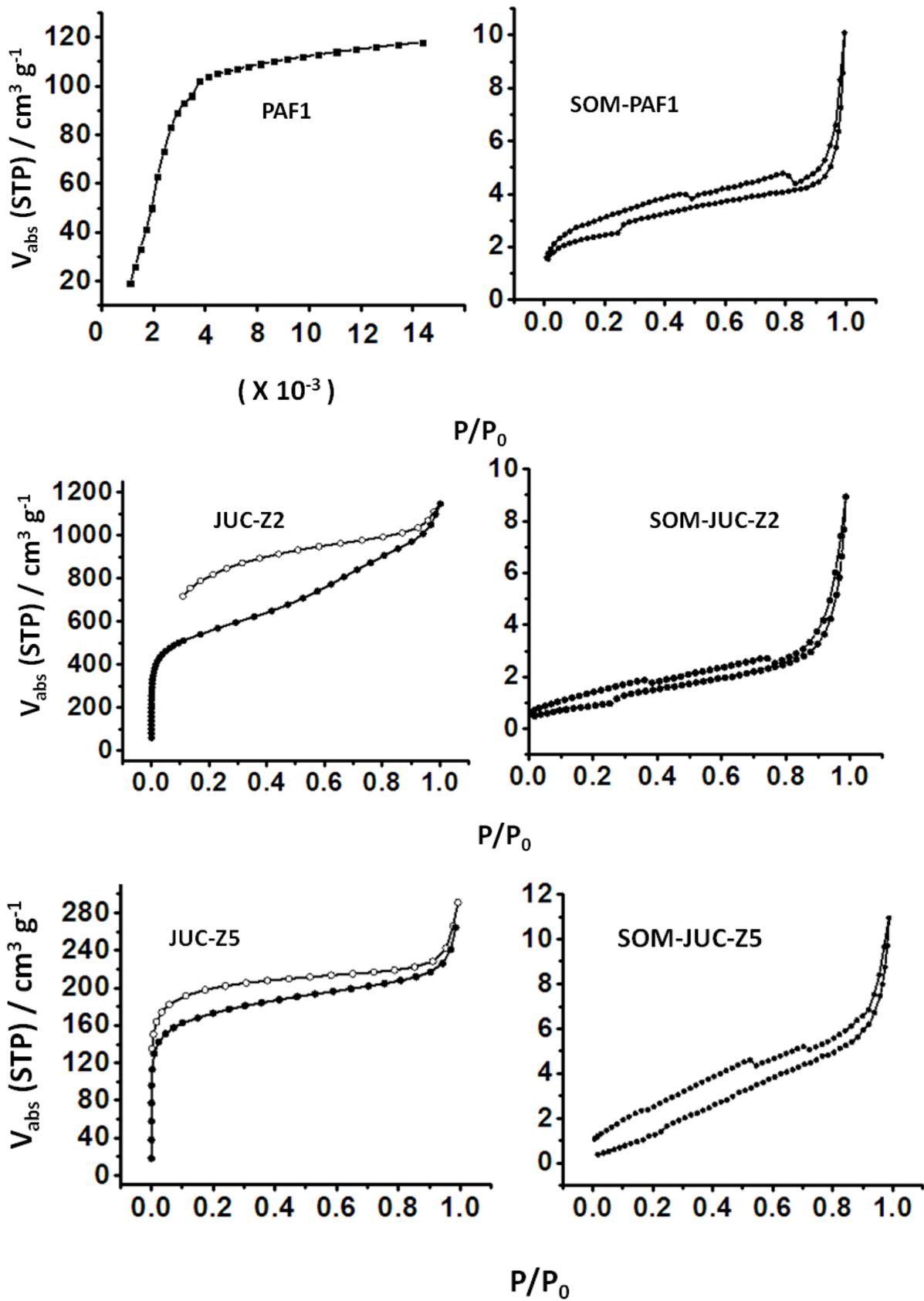


Figure S4: N_2 Adsorption Isotherms of SOM-POF composites and their corresponding POF precursors.

5. Comparative study of benzaldehyde oxidation using different oxidants and different composites

A comparative study to understand the effect of different oxidants was also conducted. For this purpose time dependent ^1H NMR studies were done on benzaldehyde oxidation reaction ensemble using different SOM-POF composites in presence of four different oxidants namely hydrogen peroxide, silver(I) oxide, dilute sulphuric acid and dilute nitric acid. In this study dilute sulphuric acid showed maximum product formation followed by hydrogen peroxide, dilute nitric acid and silver (I) oxide. (Figure S5) Note: We believe that a minuscule part of the SOM-POF catalyst is reduced in course of this reaction and aerielly regenerated by a well-known reoxidation process also shown by us and others before. [38] Since SOM-JUCZ4 showed maximum catalysis for benzaldehyde oxidation in dispersion phase, therefore trails of SOM-JUC-Z4 were identical to the

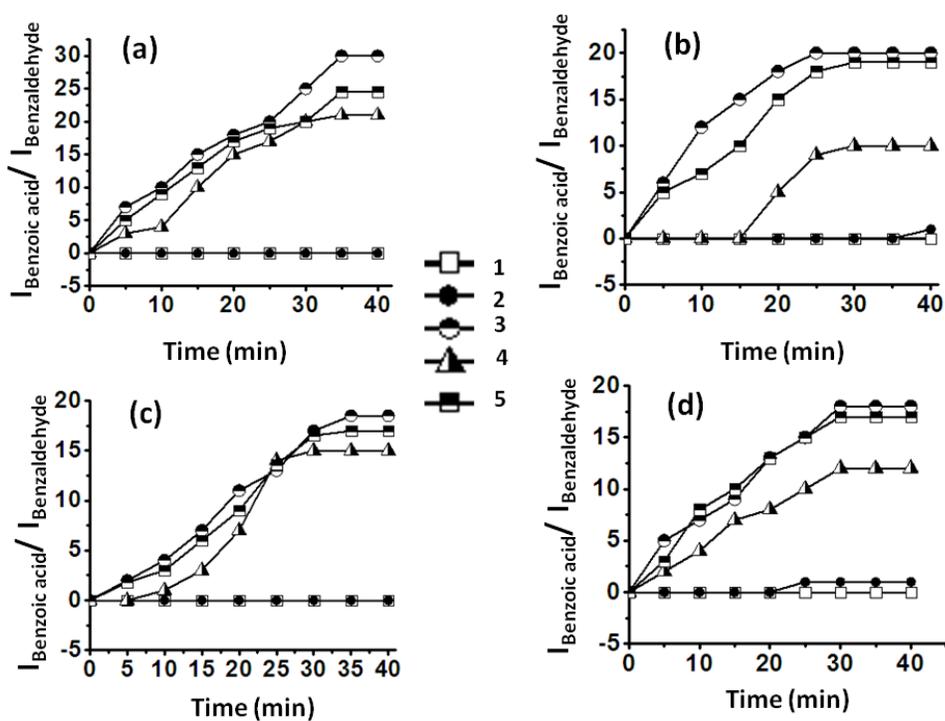


Figure S5: Plot of ratio of intensity of acidic proton of the formed benzoic acid and ratio of the aldehydic proton of the reactant benzaldehyde versus time obtained by time dependent ^1H NMR studies using different SOM-POF composites namely SOM-PAF1 (depicted in Figure as 1), SOM-JUC-Z2 (2), SOM-JUC-Z4 (3), SOM-JUC-Z5 (4) composites and molecular PMo_{12} (5). and a) Dilute sulphuric acid b) Hydrogen peroxide c) Dilute nitric acid and d) Silver (I) oxide as oxidizing agents.