

Electronic Supplementary Information

Covalent Lindqvist Polyoxometalate-Cubic Polyhedral Oligomeric Silsesquioxane Hybrid Material: Enhancing Photocatalytic Antibacterial Activity and Hydrogen Production as a Heterogeneous Catalyst

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Synthesis of tetrabutyl ammonium hexamolybdate [LPOM(Mo)]

2.5 g (10mmol) of sodium molybdate dehydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in 10 ml of water with 2.9 ml of 2N HCl (17.4mmol) stirred in 50 ml of RB flask at room temperature on one minute. A solution of 1.21g (3.7mmol) tetrabutylammonium bromide in 2 ml of water was added with vigorous stirring to cause the immediate formation of a white precipitate. The resulting residue was heated at 75 to 80°C with stirring until 45 minutes in this period, the white solid slowly turned to yellow. This crude product was washed using the suction filter with 20ml of water three times. The Air-dried crude product crystallized by dissolving in hot acetonitrile and cooled -20°C. After 24 hours, the yellow crystalline product was collected with suction filtration, washed twice with a 20 ml portion of diethyl ether, and dried using a vacuum. Yield: 1.82g (72.8%). FT-IR (KBr, 500-1000 cm^{-1}) 590.97(m), 738.83(m), 793.15(s), 881.02(m), 951.01(s). ^1H NMR (500 MHz, CDCl_3 , TMS, ppm): δ = 0.98 (t, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.38 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.62 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.11 (t, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

Synthesis of heptaisobutylpropylamine-T8-Silsesquioxane (POSS-NH₂)

To a solution of 1,3,5,7,9,11,14-Heptaisobutyl tricyclo [7.3.3.1] heptasiloxane-endo-3,7,14-triol (2g, 2.53mmol) in dichloromethane (20mL), (3-Aminopropyl) trimethoxysilane (0.5ml, 2.79mmol) in dichloromethane (20 mL) was added under nitrogen atmosphere at RT. The reaction mixture was stirred for 48 hours, and the colourless solution evaporated under a vacuum to a colourless solid (POSS-NH₂). Yield: 2.23g (89%). FT-IR (KBr, cm^{-1}): 3390(br), 2955(s), 1579(br), 1465(m), 1332(w), 1231(m), 1113(s), 956(m), 837(m), 745(s), 687(w), 560(w), 482(m). ^1H NMR (500 MHz, CDCl_3 , TMS, ppm): δ = 0.58 (t, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 0.60(d, 14H,-

CH₂inⁱBu), 0.95 (dd, 42H, -CH₃), 1.55 (m, 2H, -CH₂CH₂CH₂NH₂), 1.85 (septet, 7H, -CH), 2.67 (t, 2H, -CH₂CH₂CH₂NH₂). ¹³C NMR (100 MHz, CDCl₃, TMS, ppm): δ = 44.9, 27.3, 25.8, 24.0, 22.6, and 9.3 (aliphatic-carbons). ²⁹Si NMR (79.30 MHz, CDCl₃, TMS, ppm): δ = -67.8, -67.6, -67.2. Positive ion ESI-Mass m/z = 874.20 [POSS-NH₂].

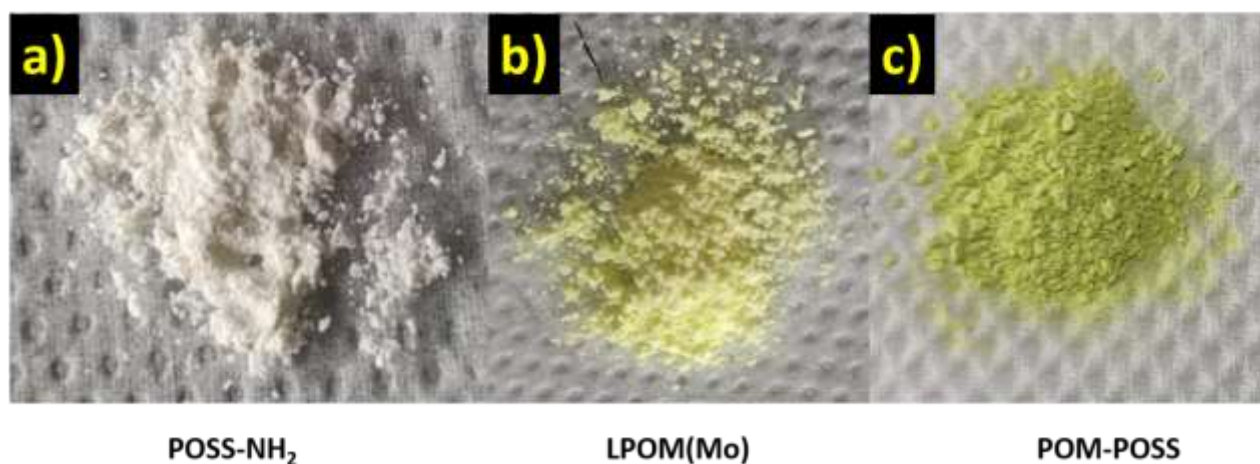


Fig. S1. Photographs of synthesized (a) POSS-NH₂, (b) LPOM(Mo) and (c) POM-POSS hybrid material.

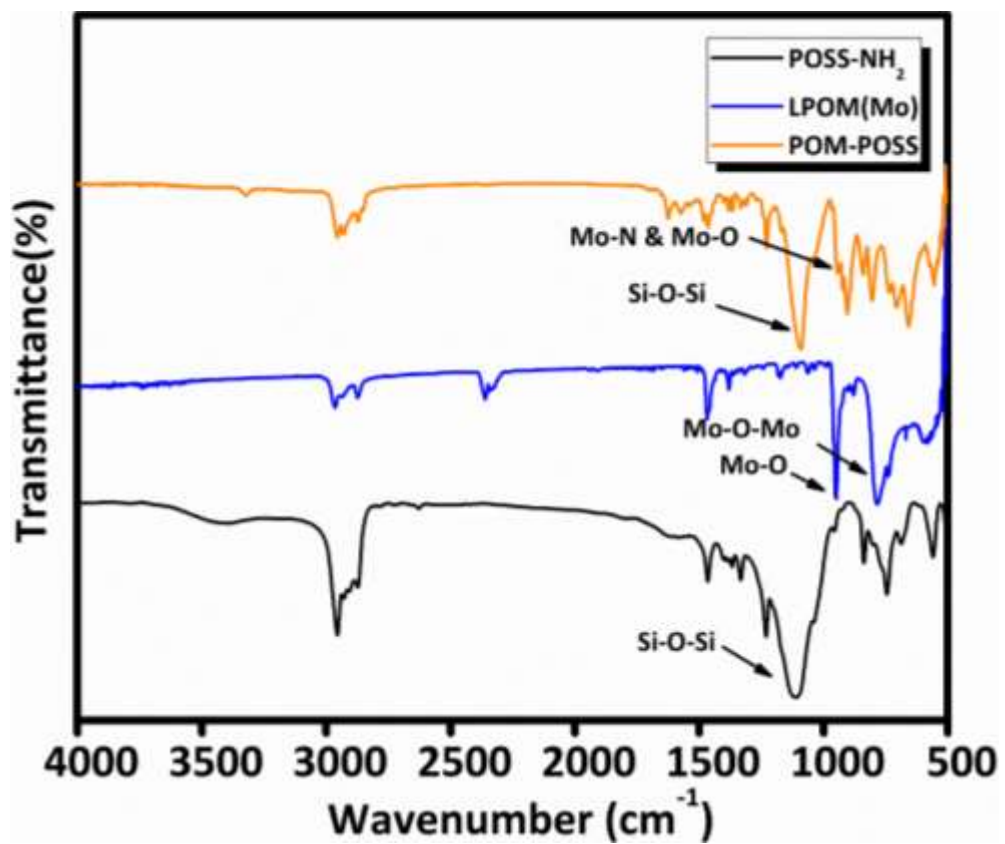


Fig. S2. FT-IR spectra of POSS-NH₂, LPOM(Mo) and POSS-POM hybrid materials

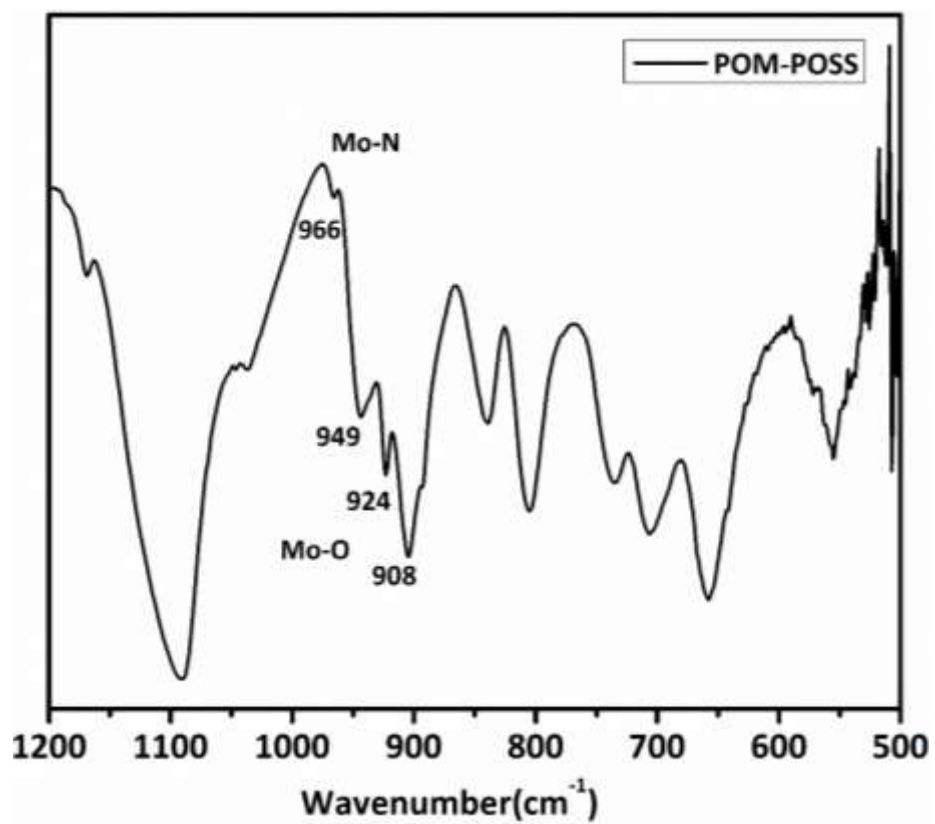


Fig. S3. Enlarged FT-IR spectra of POM-POSS hybrid materials

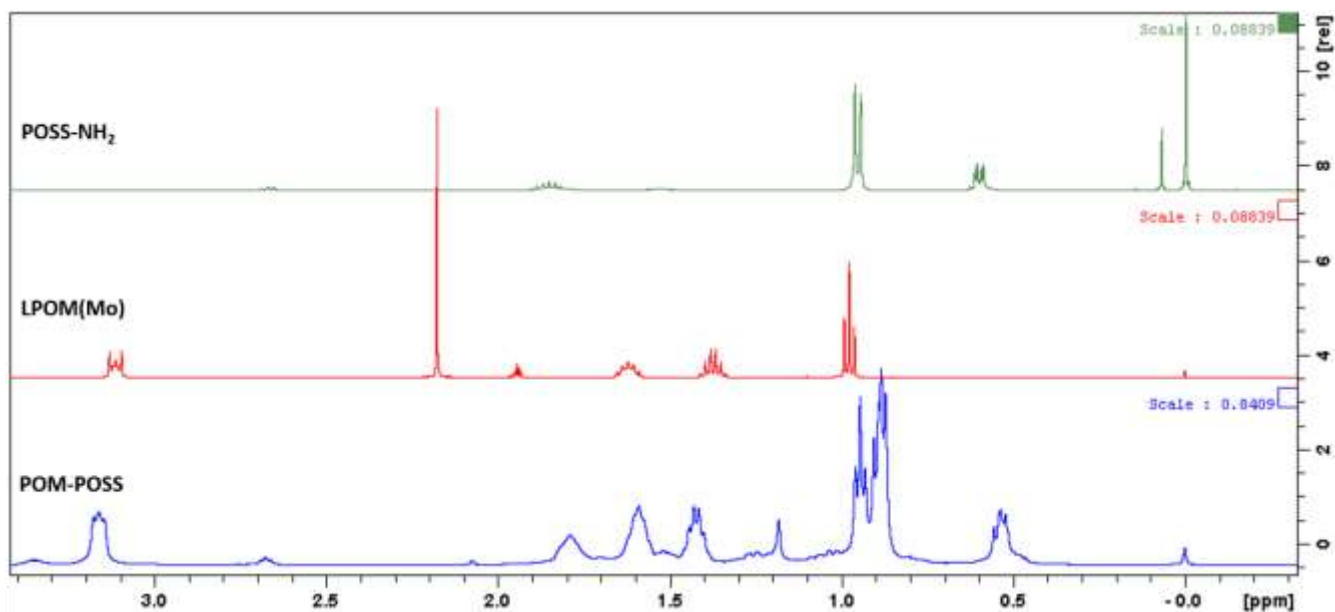


Fig. S4. Combined ^1H NMR spectrum of the POM-POSS, LPOM(Mo) and POSS-NH₂

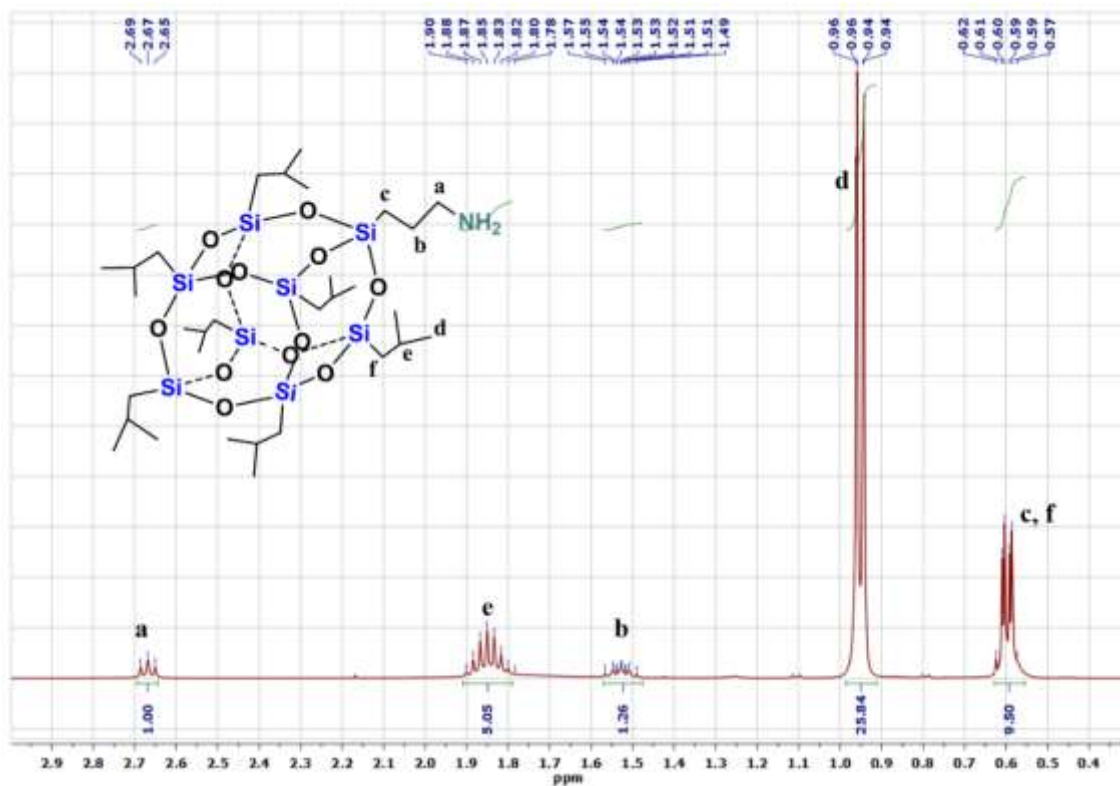


Fig. S5. ^1H NMR spectrum of the POSS-NH₂

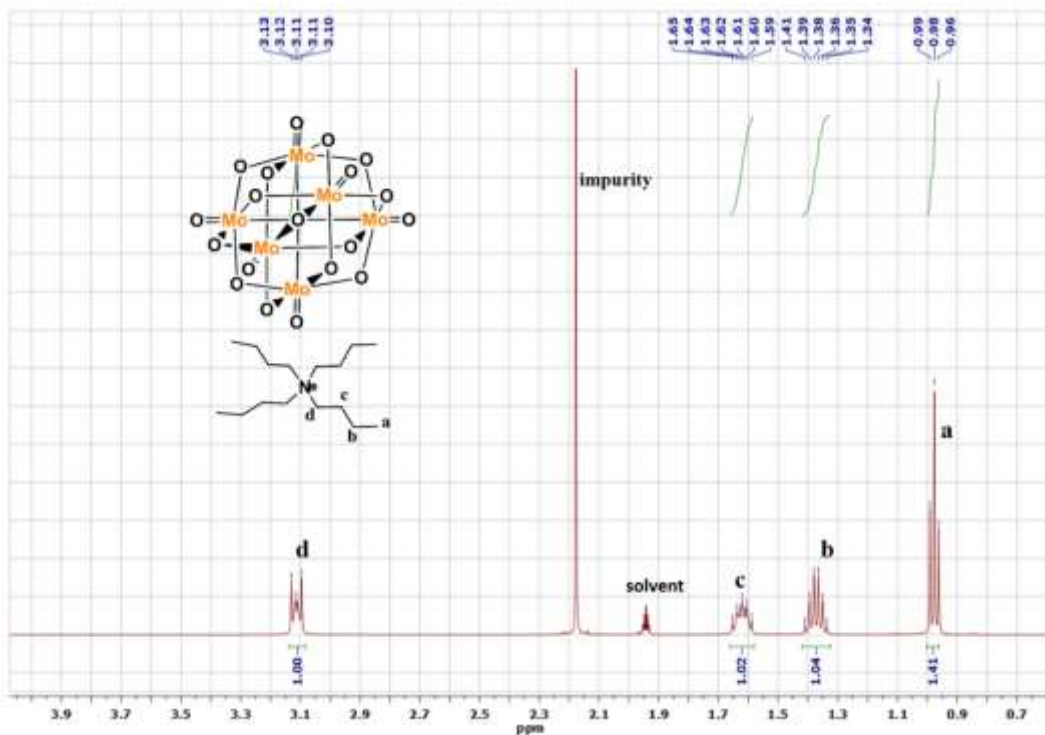


Fig. S6. ¹H NMR spectrum of LPOM(Mo)

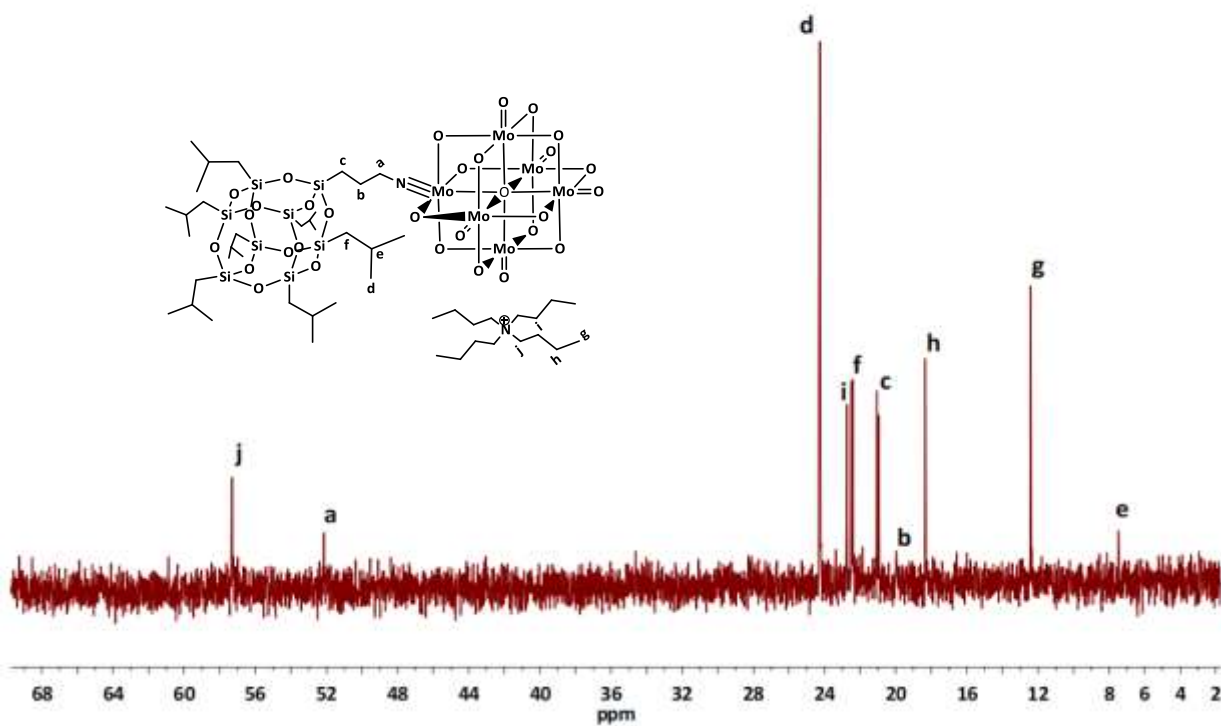


Fig. S7. ¹³C NMR spectrum of the POM-POSS hybrid material.

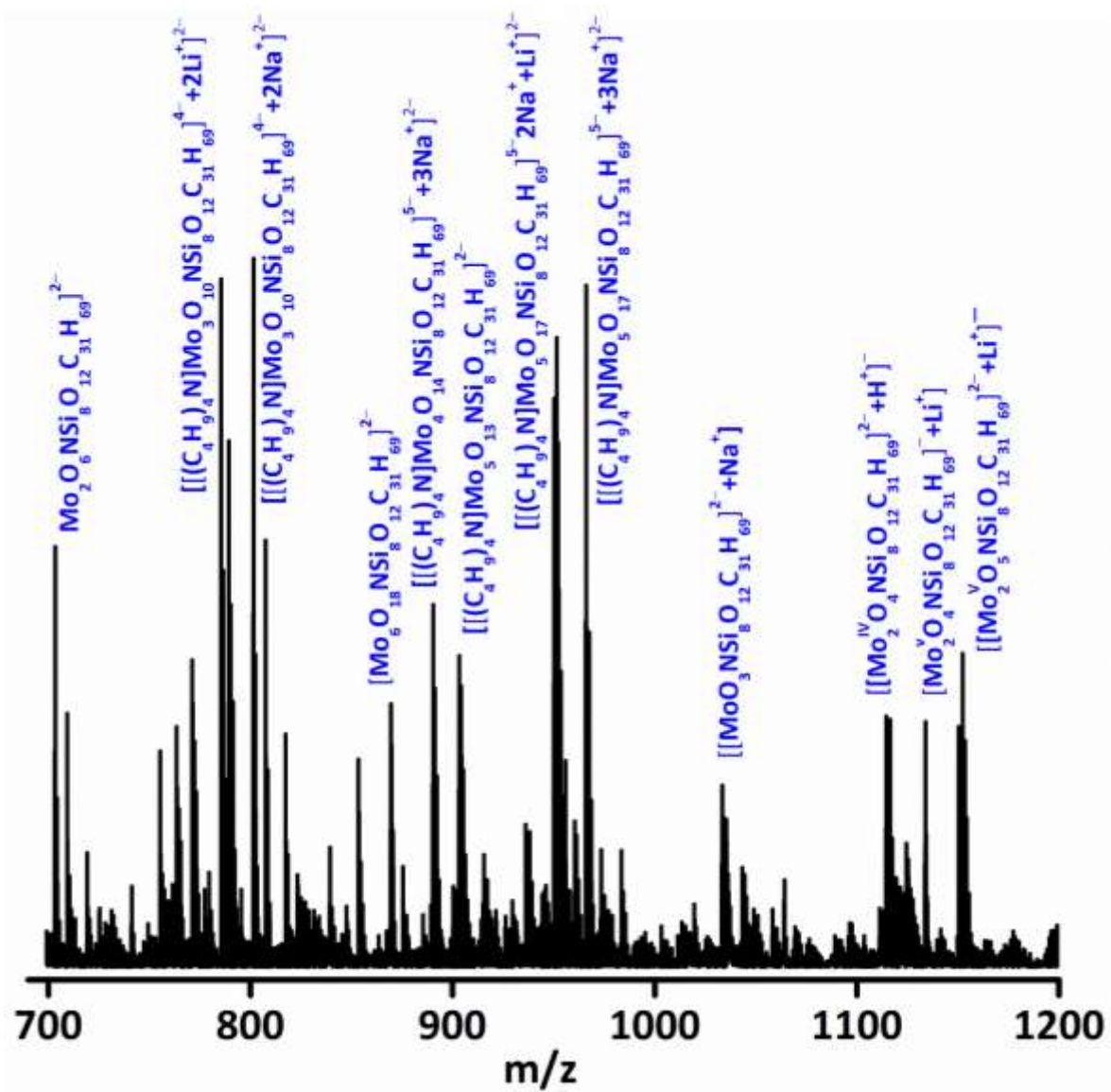


Fig. S8. Enlarged ESI-MS of POM- POSS (m/z between 700-1200) hybrid material.

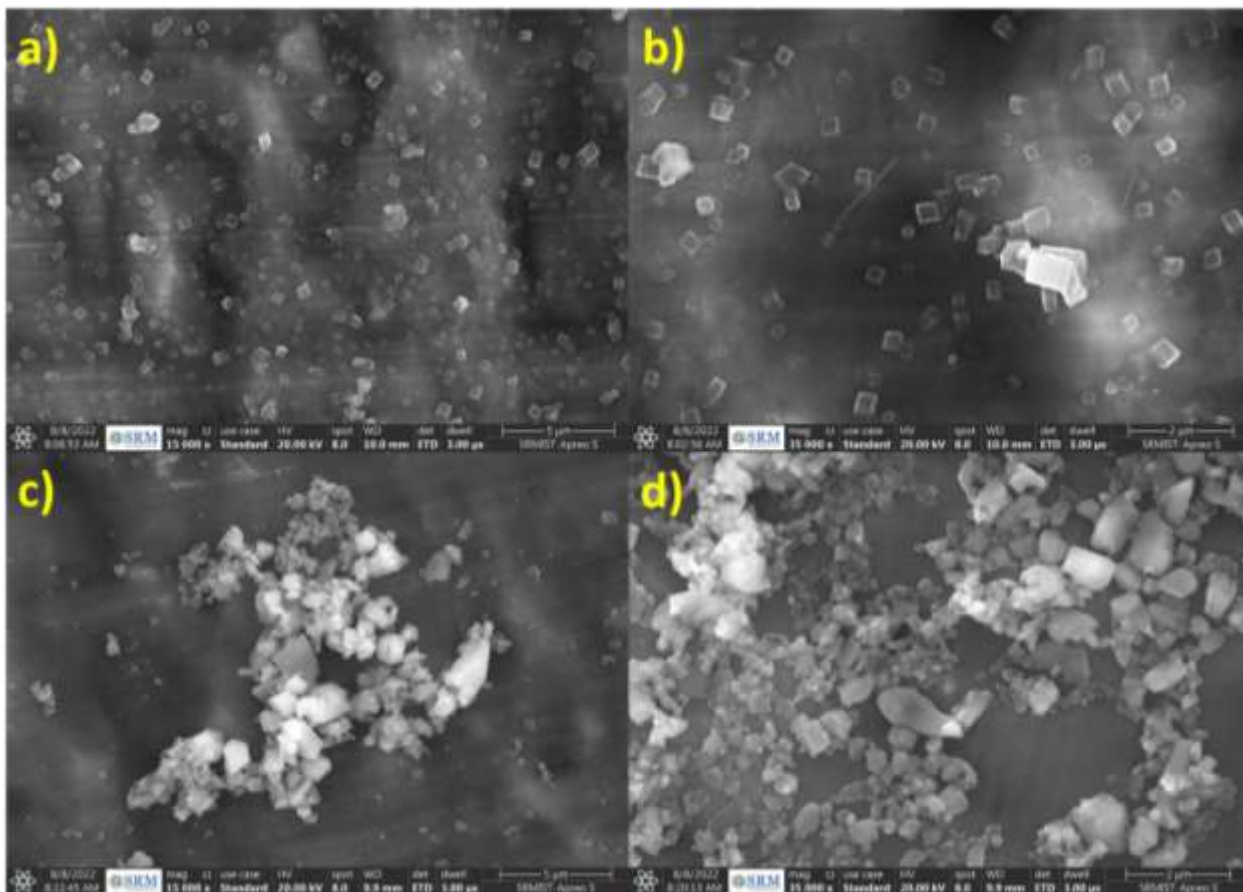


Fig. S9. HR-SEM micrographs of (a, b) POSS-NH₂ and (c, d) LPOM(Mo)

Table. S1. Atomic and weight percentage values of C, N, O, Si, and Mo in the POM-POSS hybrid

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Element	Line Type	k Factor	k Factor type	Absorption Correction	Wt%	Wt% Sigma	Atomic %
C	K series	2.769		1.00	36.95	0.65	61.51
N	K series	3.515		1.00	0.49	0.37	0.70
O	K series	2.020		1.00	18.17	0.41	22.71
Si	K series	1.000		1.00	11.58	0.27	8.24
Mo	K series	4.561		1.00	32.81	0.73	6.84
Total:					100.00		100.00

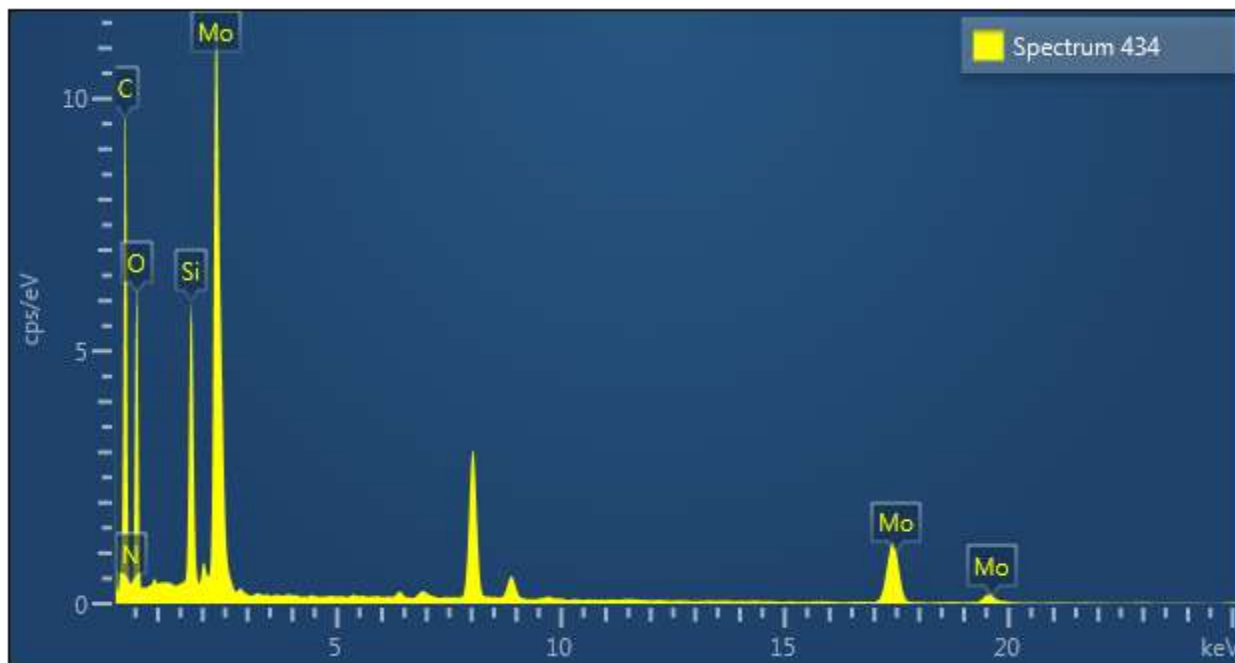


Fig. S10. HR-TEM-EDAX spectrum of POM-POSS hybrid material.

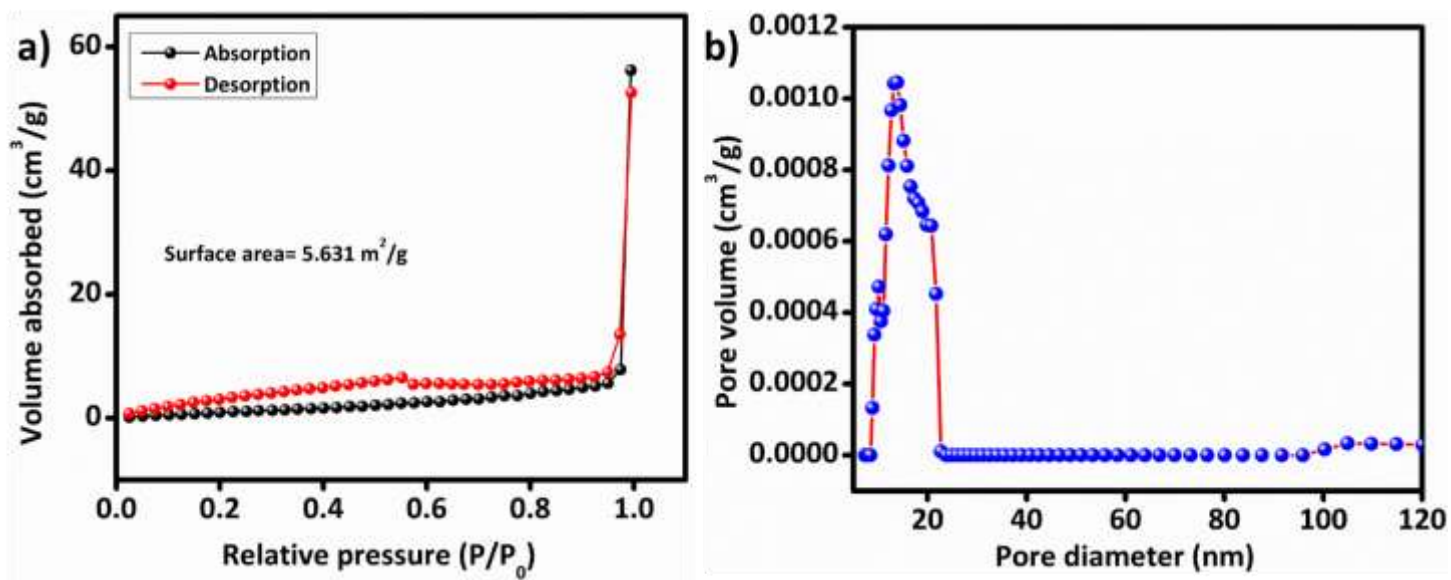


Fig. S11. Surface area and pore volume plots for the POM-POSS hybrid material.

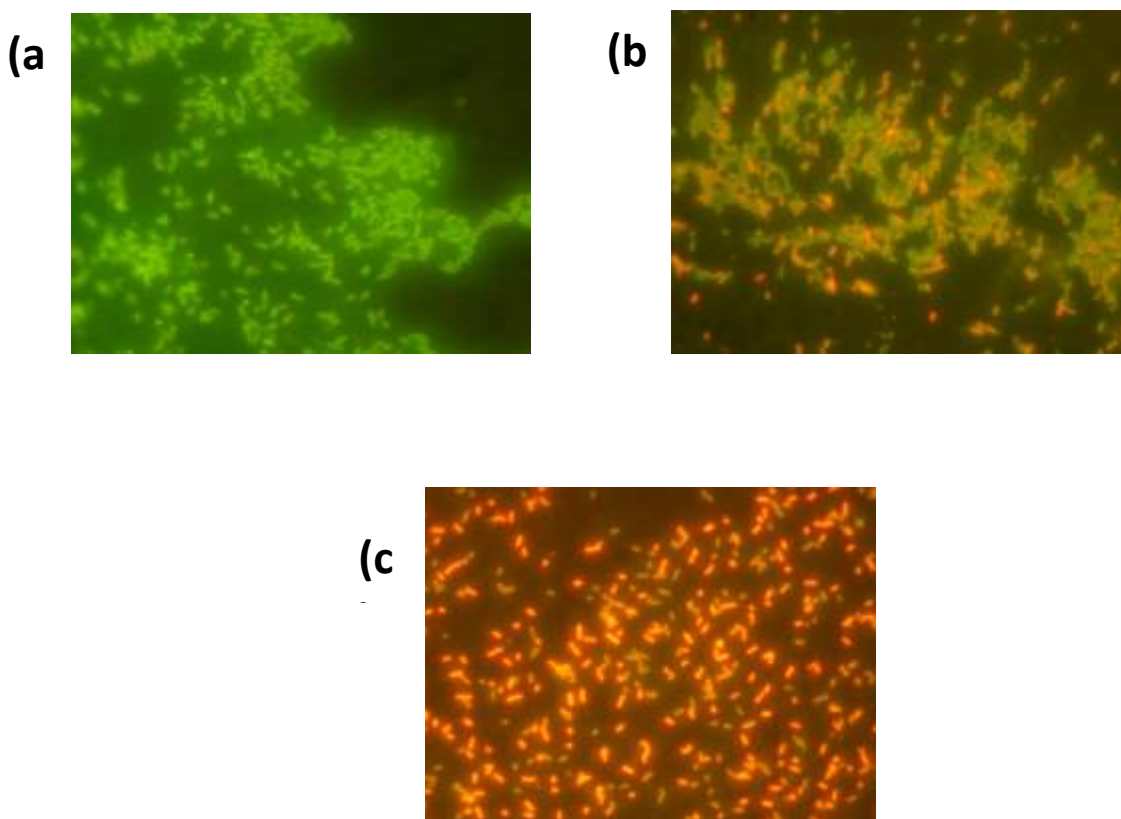


Fig. S12. Epi-fluorescence micrographs of POM-POSS hybrid material inhibited bacterial growth in a time-dependent manner using dual staining of FITC and PI at ambient conditions, (a) after 5 mins at dark conditions, (b) sunlight exposure to tested photoreactor medium (POM-POSS hybrid and *E.coli* cells) at 30 mins and (c) over the 60 mins of sunlight exposure.

Table. S2. Comparison of photocatalytic H₂ production with POM-based catalysts

S.No	POM-based catalyst	Co-catalyst	Irradiance source	Sacrificial donor	Amount of H ₂ production (μmol g ⁻¹ h ⁻¹)	Ref
1	Co/Zn-POM	–	300 W Xenon Lamp	TEOA	2000	1
2	AgBr/PMo ₁₂ /GO	–	300 W Xenon lamp (λ > 400 nm).	TEOA	256.0	2
3	AgBr/PW ₁₂ /GO	–	300 W Xenon lamp (λ > 400 nm).	TEOA	223.2	2
4	AgBr/SiW ₁₂ /GO	–	300 W Xenon lamp (λ > 400 nm).	TEOA	212.0	2
5	AgBr/P ₂ W ₁₈ /GO	–	300 W Xenon lamp (λ > 400 nm).	TEOA	207.2	2
6	AgBr/P ₂ Mo ₁₈ /GO	–	300 W Xenon lamp (λ > 400 nm).	TEOA	177.2	2
7	Cu-Ni-P ₂ W ₁₈ O ₆₂ ⁶⁻	–	300 W Xenon Lamp (200-400nm)	MeOH	833.0	3
8	TiO ₂ -SiNH ₂ -W ₁₁ Pt ₂	Pt	sunlight of 400 W xenon lamp	MeOH	4500	4
9	[Cu ^{II} ₅ (2-ptz) ₆ (H ₂ O) ₄ (GeW ₁₂ O ₄₀)]·4H ₂ O	–	Xe lamp irradiation (without a light filter)	MeOH	3813	5
10	[Cu ^I ₂ (ppz) ₄][H ₂ GeW ₁₂ O ₄₀]·8H ₂ O	–	Xe lamp irradiation (without a light filter)	MeOH	500.0	5
11	CS ₁₄ K ₄ [(Si ₄ W ₃₆ Nb ₁₂ O ₁₅₆)Cu(H ₂ O) ₂]·47H ₂ O	–	500 W Xe lamp	MeOH	35.50	6
12	CS ₁₀ K ₈ [(Si ₄ W ₃₆ Nb ₁₂ O ₁₅₆)Zn(H ₂ O) ₂]·28H ₂ O	–	500 W Xe lamp	MeOH	41.90	6
13	CS ₁₆ [(H ₂ Si ₄ W ₃₆ Nb ₁₂ O ₁₅₆)Cd(H ₂ O) ₂]·75H ₂ O	–	500 W Xe lamp	MeOH	61.30	6
14	CS ₅ K ₂ [(Si ₂ W ₁₈ Ta ₆ O ₇₈)Cr(H ₂ O) ₄]·8H ₂ O	–	300 W Hg lamp	MeOH	1001	7
15	CS ₃ K ₄ H ₂ [(Si ₂ W ₁₈ Ta ₆ O ₇₈)FeCl ₂ (H ₂ O) ₂]·15H ₂ O	–	300 W Hg lamp	MeOH	747.8	7
16	[SiTa ₃ W ₉ O ₄₀] ⁷⁻	–	300 W Hg lamp	MeOH	26.10	7
17	CS _{12.5} K _{4.5} H[Ta ₁₂ Si ₄ W ₃₇ O ₁₅₈]·25H ₂ O	Pt	500 W Xe lamp	MeOH	297.5	8
18	CS ₁₉ K ₂ [(Nb ₄ O ₆ (SiW ₉ Nb ₃ O ₄₀) ₄]Cl·27H ₂ O	–	150 W Hg lamp	MeOH	1151.84	9
19	Na ₂₇ [Fe ₁₁ (H ₂ O) ₁₄ (OH) ₂ (W ₃ O ₁₀) ₂ (α-SbW ₉ O ₃₃) ₆]·103H ₂ O	–	250 W high-pressure Hg lamp	-	820.0	10
20	POM-POSS hybrid	–	250 W Xe lamp	TEOA	2461	This work

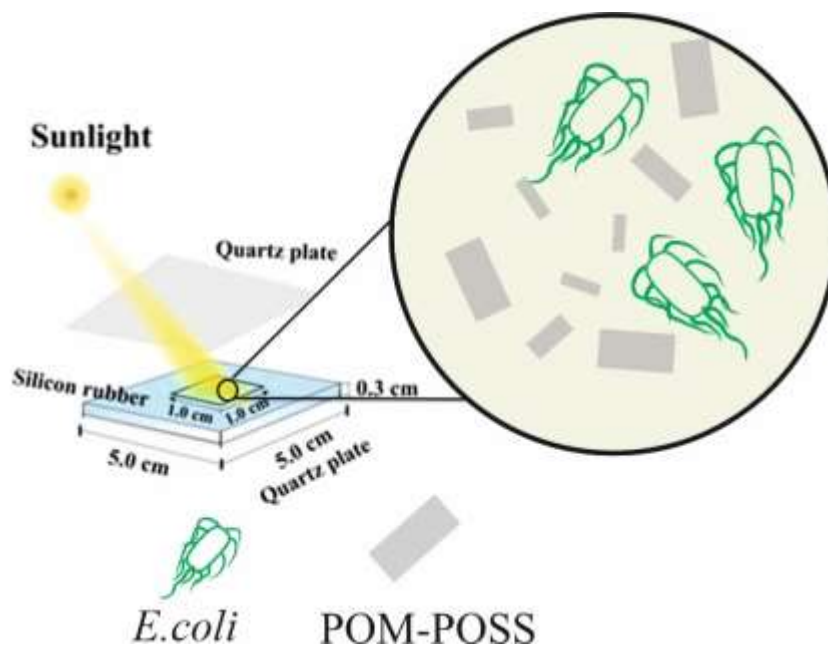


Fig. S13. Schematic diagram of the photo-activated antibacterial experiment setup.

Sample preparation details for Epi-fluorescence microscope

Fluorescein isothiocyanate (FITC) and propidium iodide (PI) double staining were used to identify live and dead cells in bacterial populations. Propidium iodide (PI) enters only damaged cells, binds to DNA and emits red colour, whereas FITC stays outside the undamaged cell wall and produces green luminescence. Approximately 0.5 μ l of double staining (FITC-PI; 1:1%) was added to solution suspensions (POM-POSS and *E. coli* strains exposed to sunlight) at various time intervals and incubated for 15 min. The excess dye was rinsed with sterile distilled water and examined under an Epi-fluorescence microscope (E200 Coolpix -Nikon, Tokyo, Japan).

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