Supporting information

Multifunctional Polyoxomolybdate Ionic Liquid Coatings for Mitigating Microbiologically Influenced Corrosion

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Contents

1. Instrumentation

Elemental analysis: Elemental analysis (CHN) was performed on the Thermo Flash 1112 equipment

FT-IR Spectroscopy:FT-IR spectra were recorded on an anFT-IR Spectrometer (©PerkinElmer, USA) equipped with an ATR mode and controlled by The Spectrum 10™softwarein the 4000–350 cm^{-1} region and a resolution of 2 cm^{-1}

Impedance spectroscopy: EIS measurements were performed with a VSP Biologic potentiostat with a sinusoidal signal of 50mV over a frequency range from 200kHz to 10mHz in a three- electrode configuration where the reference electrode (RE) is a Pt-Ag wire, counter electrode (CE) a Pt-Ag mesh and Working Electrode (WE) is the brass coupon with an active area of 1.13 cm^2 .

SEM: SEM images and energy dispersive X-ray spectroscopy (EDX) spectra were acquired using a field emission SEM Inspect F50 with an EDX system INCA PentaFETx3 (FEI Company, Eindhoven, The Netherlands) or a Zeiss DSM 962 SEM equipped with a EDAX system with Genesis software.

TGA: A Universal V4.5A TA Instrument equipment was used for the measurements of weight against temperature. The quantification of organic material loss was performed by heating the samples in air, increasing the temperature at a rate of 10 °C min^{-1} until a final temperature of 800 °C. The quantification was done between 100 °C and 400 °C using TA Instruments Universal Analysis 2000 software for the analysis and plotting.

NMR: ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance 400 spectrometer. Data were registered in $CDCl_3$ and chemical shifts were given in ppm relative to the solvent residual peak, which was used as an internal reference. Coupling constants are given in hertz (Hz). Spectra were processed with MestReNova.

2. Antimicrobial Assays

Microorganisms: *Escherichia* coli DH5-alpha as Gram-negative (G-) bacteria and *Bacillus subtilis* 1904-E as Gram-positive (G+) bacteria were used in the assays. Luria-Bertani (LB) liquid medium (Miller's formulation) and Nutrient Broth (NB) liquid medium were freshly prepared and sterilized by autoclave. Trypticase Soy Agar plates were purchased from Thermo Scientific™.

Bacterial growth: Bacterial growth was recorded by measuring the optical density (OD) of the samples at 600 nm over a 24-hour period using a microplate reader (BioTek ELx800). Results were compared with the OD variation of a control culture containing only bacteria. All controls and antibacterial assays were replicated in sextuplet to verify the reproducibility of the results and to calculate the mean values and standard deviations.

General Remarks: All chemicals were of reagent grade and purchased from SIGMA ALDRICH, ABCR CHEMICALS or ACROS ORGANICS. The chemicals were used without further purification and the reactions were carried out under ambient atmosphere, unless stated otherwise

3: Characterization of polyoxomolybdate-ionic liquids (POM-ILs)

3.1 TGA

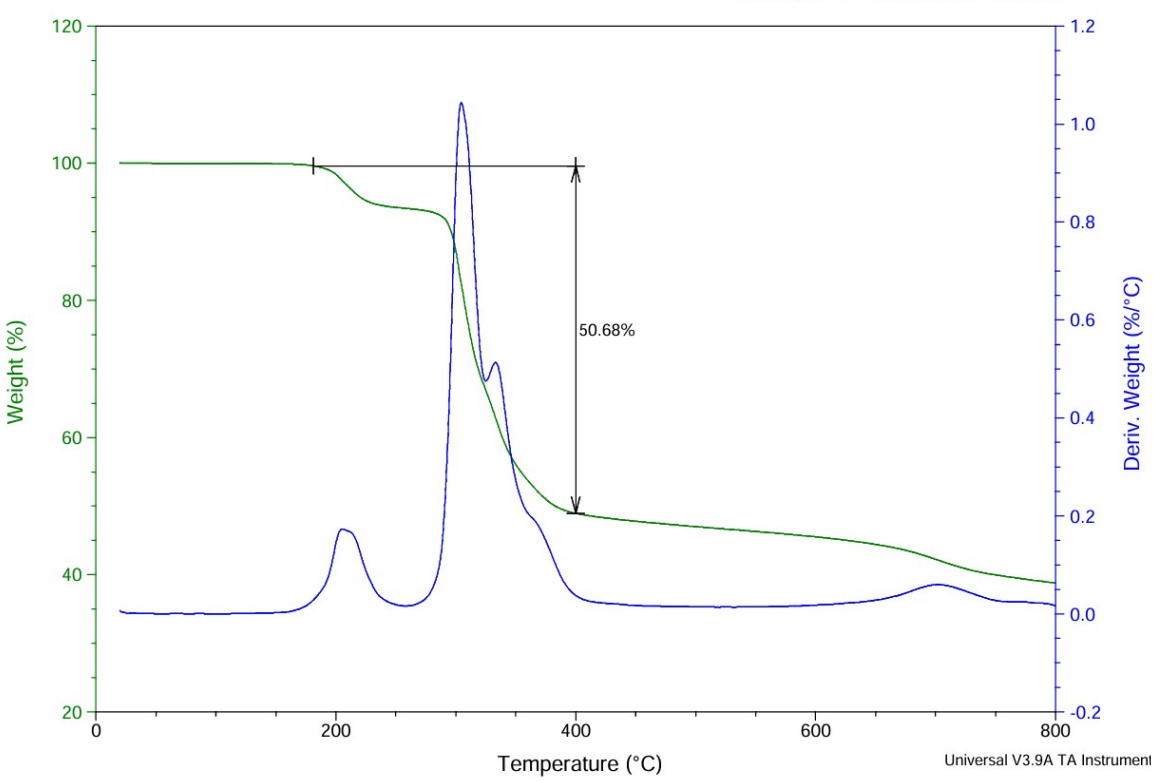

Figure S1. TGA of $\mathbf{Mo_6}$ Exp. weight loss (Calc.) %: 50.68 (48 %).

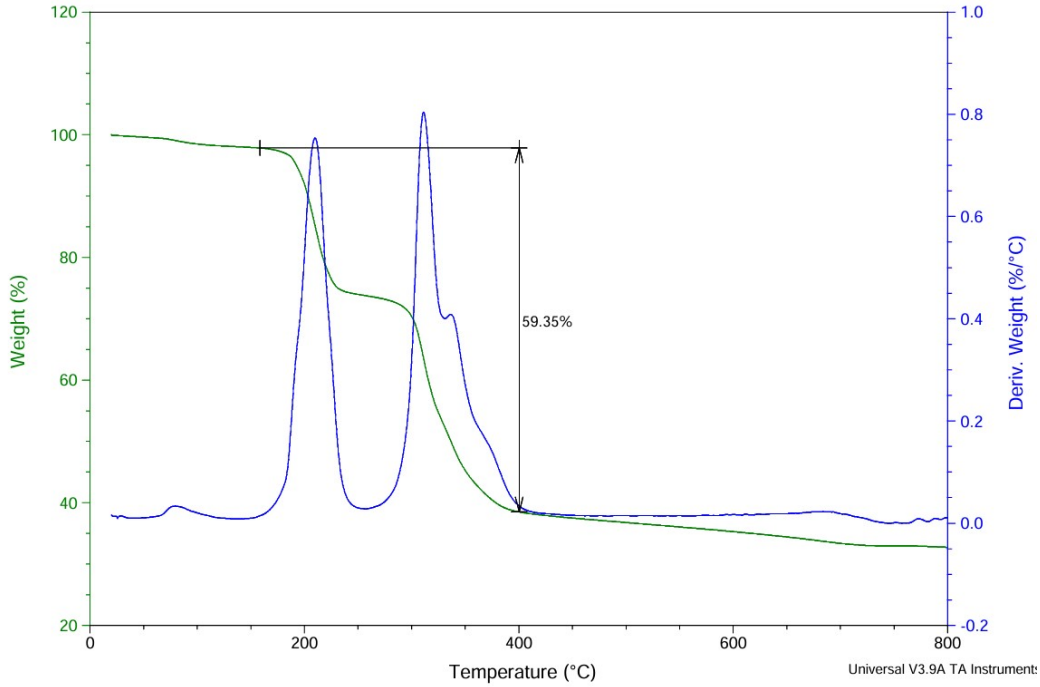

Figure S2. TGA of **Mo_8** Exp. weight loss (Calc.) %: 59.35 (58 %).

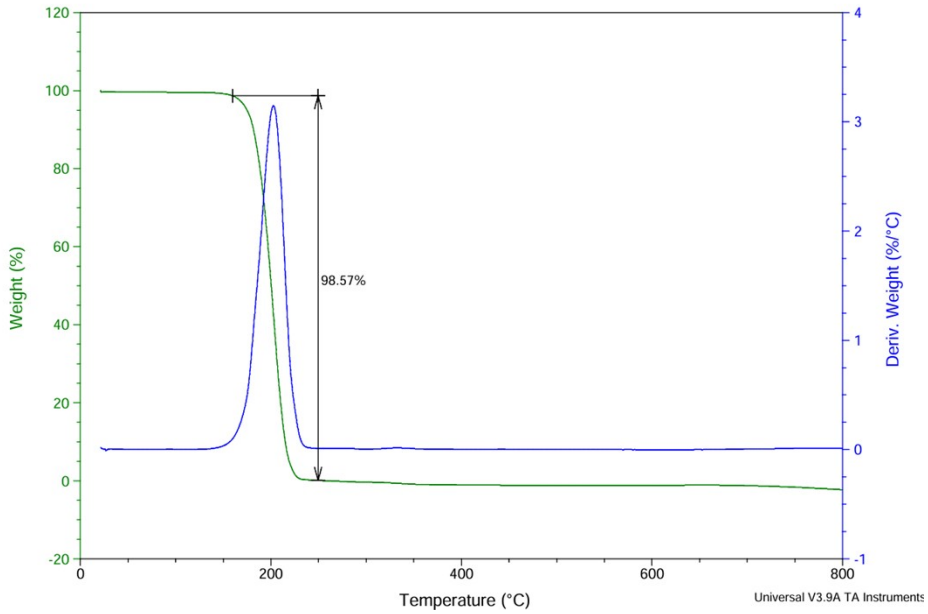

Figure S3.TGA of THEPA.

3.2 NMR

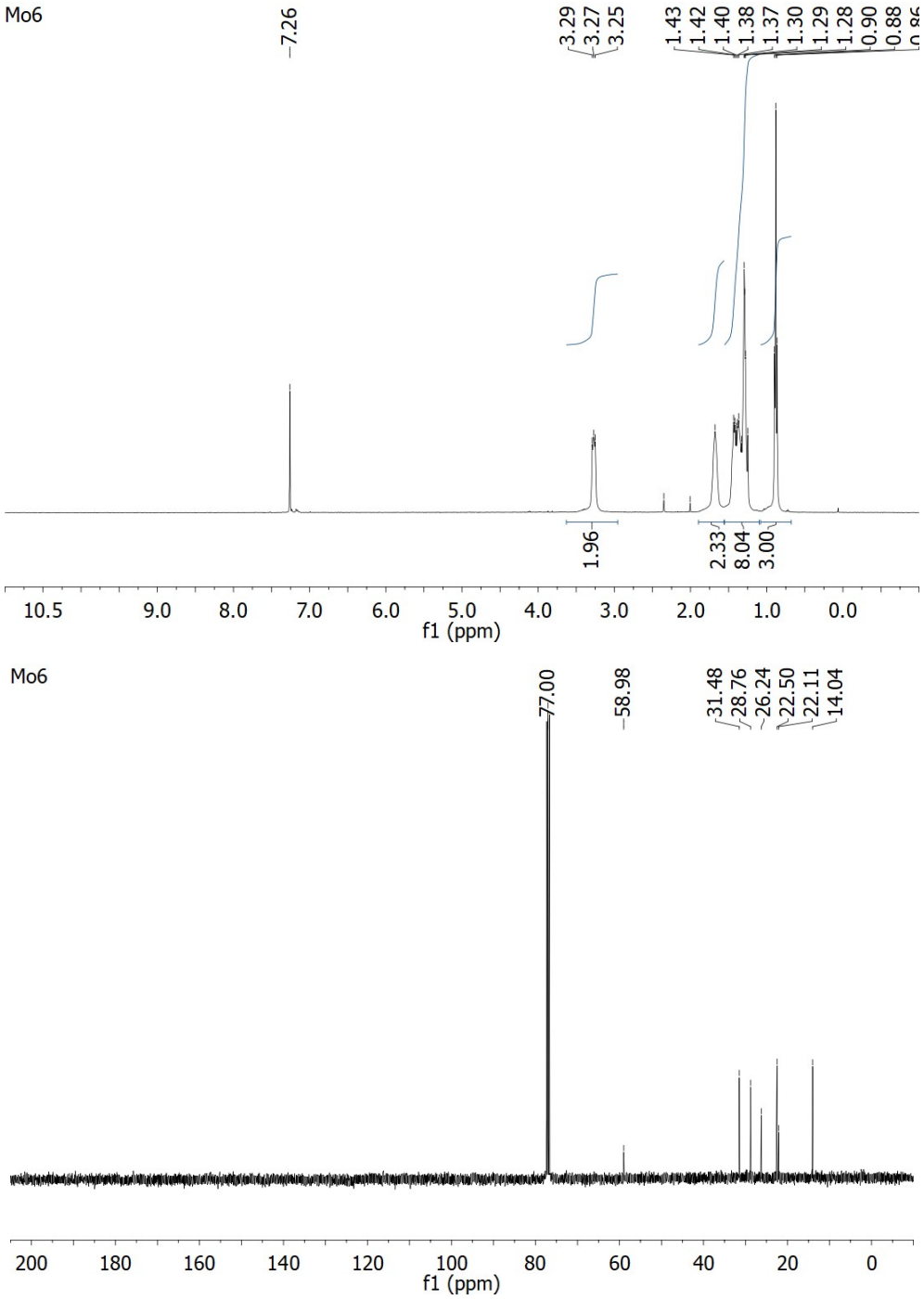

Figure S4. ^{1}H and ^{13}C NMR analysis of **Mo_6** in $CDCl_3$.

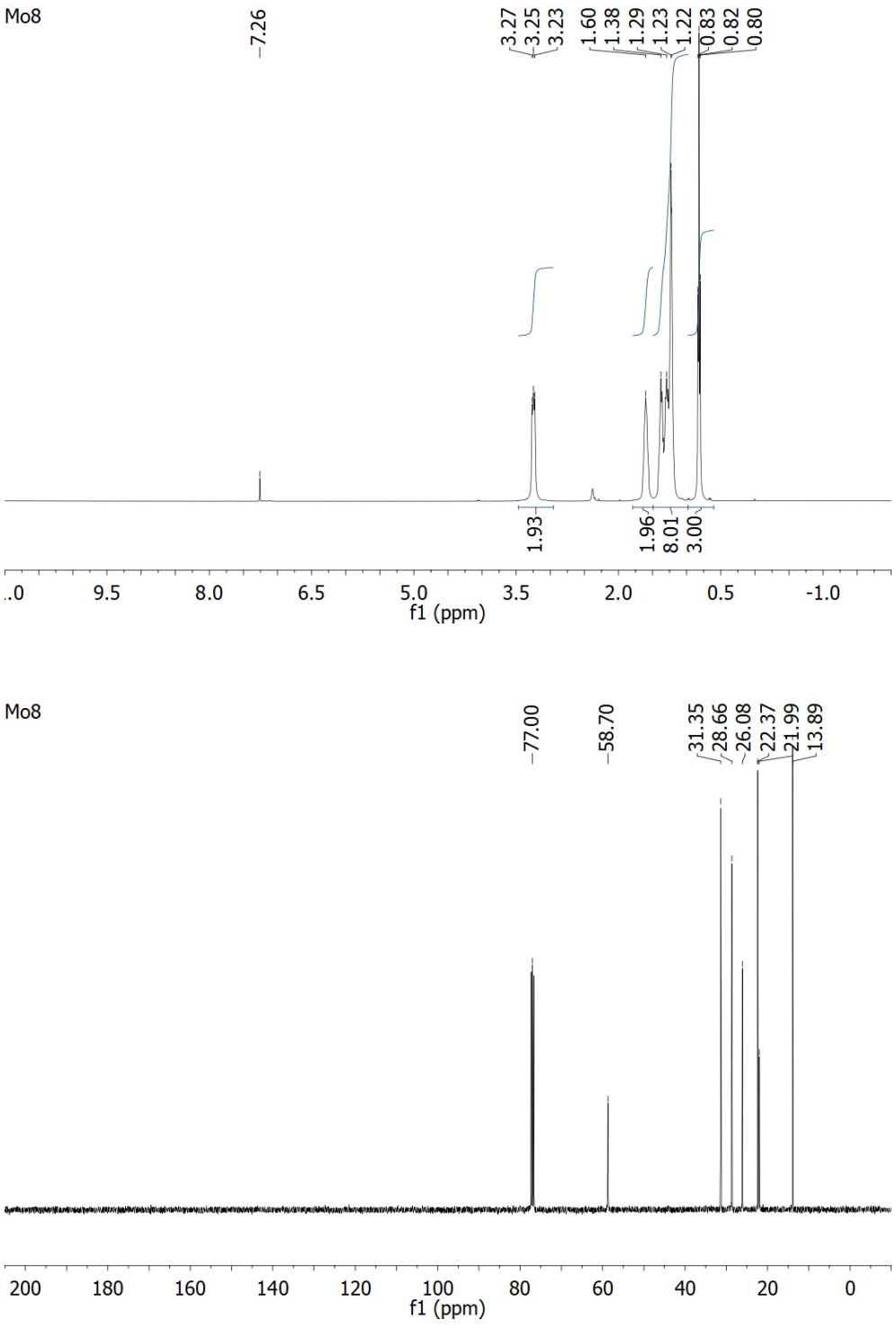

Figure S5. ^{1}H and ^{13}CNMR analysis of **Mo_8** in $CDCl_3$.

3.3 Elemental analysis

Table S1. Elemental analysis of POM-ILs exp.(calc.) %.

Code	Formula	MW (g/mol)	%C	%H	%N
Mo_6	$[(CH_3(CH_2)_6)_4N]_2[Mo_6O_{19}]$	1701.12	41.91 (39.54)	6.94 (7.11)	1.73 (1.65)
Mo_8	$[(CH_3(CH_2)_6)_4N]_4[Mo_8O_{26}]$	2826.48	51.63 (47.59)	8.53 (8.56)	2.07 (1.98)

4: Antimicrobial activity of POM-ILs

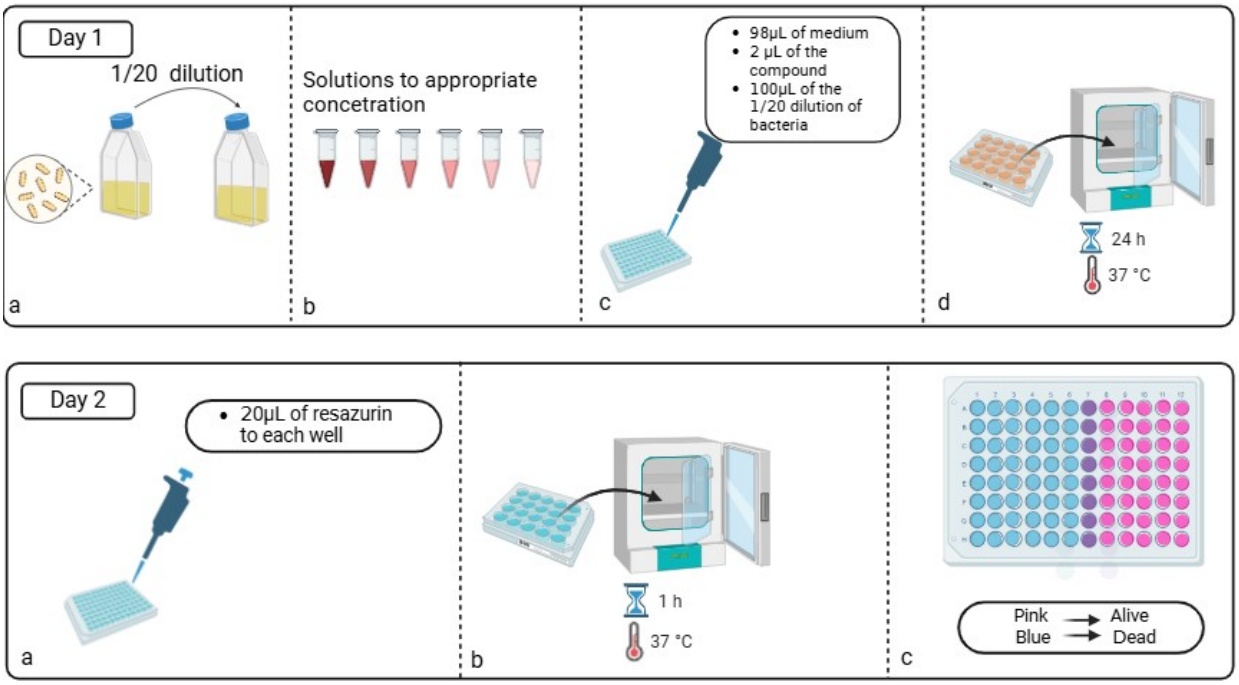

Figure S6. Schematic diagram of microbial viability assessment and Minimum Bactericidal Concentration (MBC) determination using colorimetric Resazurin cell viability assay.

4.1 Minimum Bactericidal Concentration (MBC)

Table S2. Corresponding Minimum Bactericidal Concentrations (MBCs) of $THEPA^+$ and POM-ILs against *E. coli*, *B. subtilis* and *S. epidermidis.*

	Minimum Bactericidal Concentration (MBC) (µg/mL)		
	E. coli	*B. subtilis*	*S. epidermidis*
$THEPA^+$	*3*	0.3	0.3
Mo_6	3.5	0.6	0.4
Mo_8	4	0.4	0.4

Resazurin cell viability assay

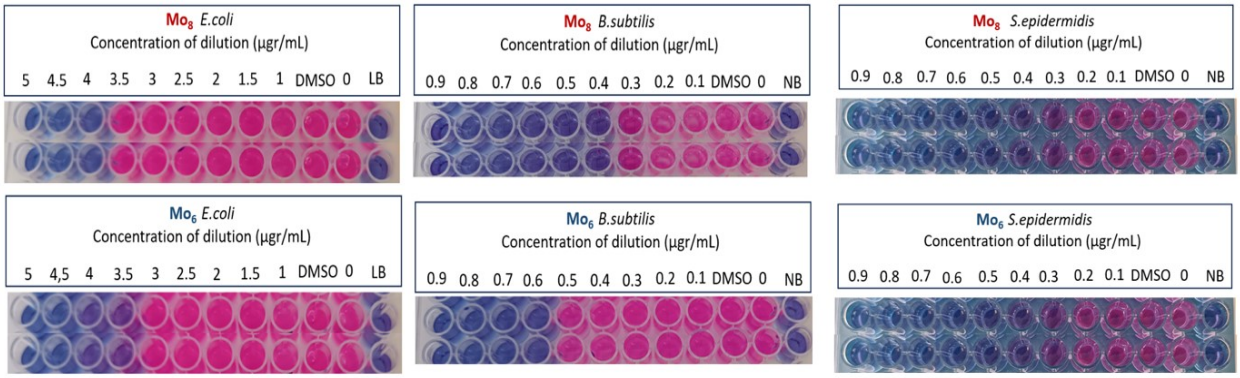

Figure S7. Results obtained after resazurin cell viability assay of **Mo_6** and **Mo_8** with *E. coli* (left), *B. subtilis* (middle) and *S. epidermidis* (right), where blue = non-viable and pink = viable/live bacteria.

4.2 Metal surface antimicrobial activity

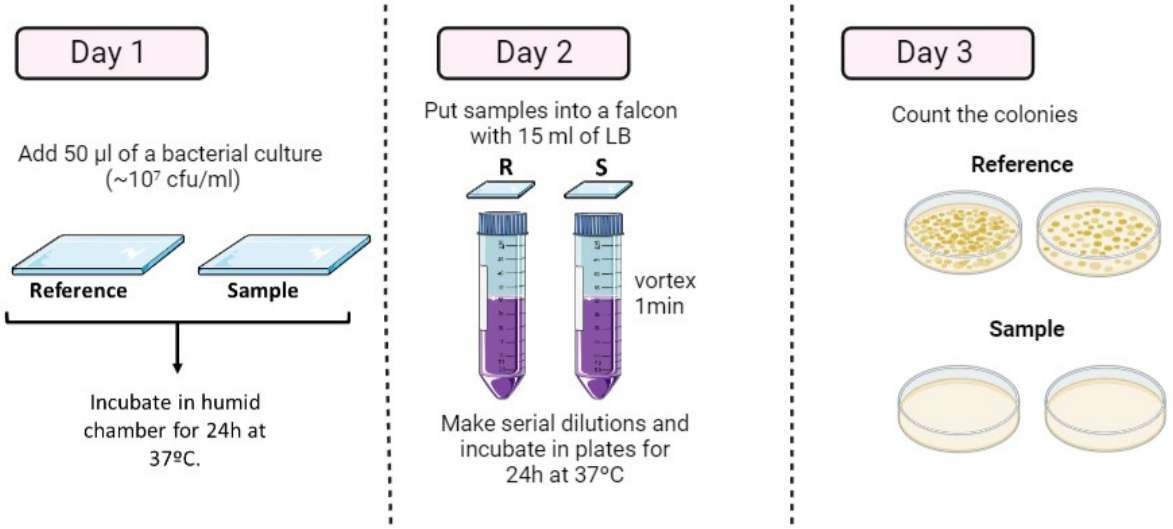

Figure S8. Schematic diagram of the JIS Z 2801 protocol (Reference number: JIS Z 2801: 2000 (E); ICS 07.100.10; 11.100) for determining surface antibiofilm activity.

Table S3. Bacterial reduction of *E. coli* on metal surfaces coated with **Mo_6** (40 mg/mL) and **Mo_8** (40 mg/mL).

	Steel	**Brass**	**Iron**	**Aluminium**
Mo_6	20%	100%	100%	100%
Mo_8	100%	100%	100%	100%

5. Corrosion

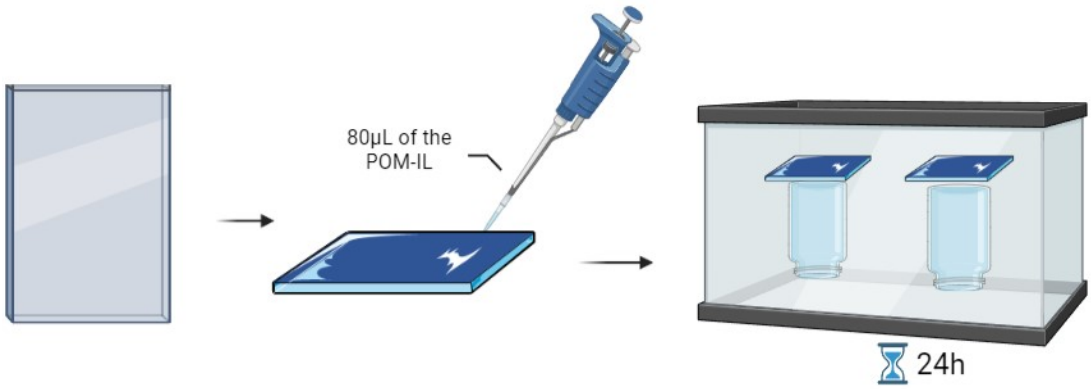

Figure S9. Schematic digraph of the experimental process of corrosion resistance of brass coupons coated with POM-IL exposed to10% aqueous acetic acid vapour.

5.1 EDX Analysis

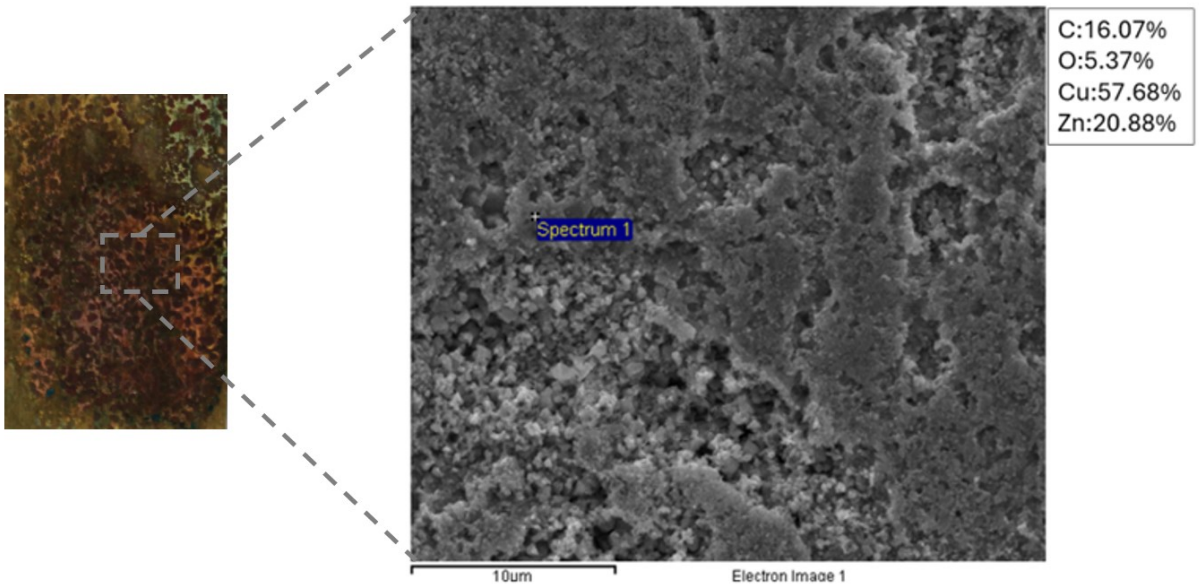

Figure S10. EDX analysis for uncoated brass coupons after being exposed 1 day to 10% aqueous acetic acid vapour.

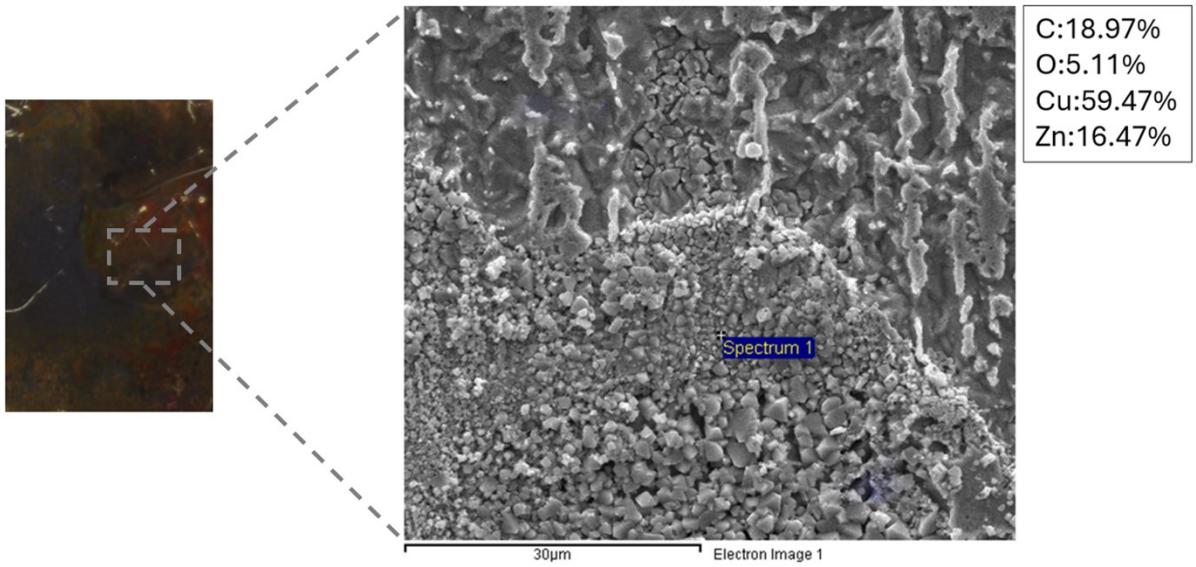

Figure S11. EDX analysis for uncoated brass coupons after being exposed 4 days to 10% aqueous acetic acid vapour.

5.2 Impedance measurements

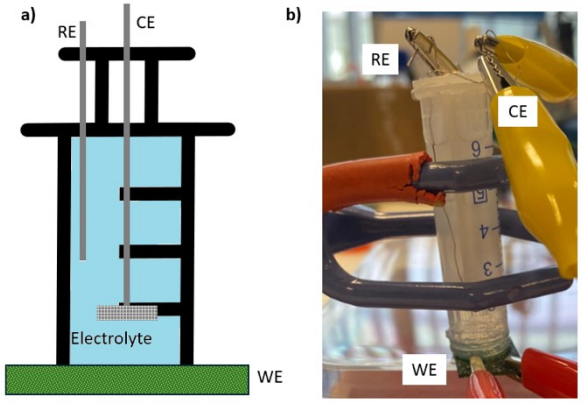

Figure S12. a) Scheme of three-electrode configuration and b) Photograph of the experimental set-up used for EIS characterisation.

6. Preventing Microbially Influenced Corrosion

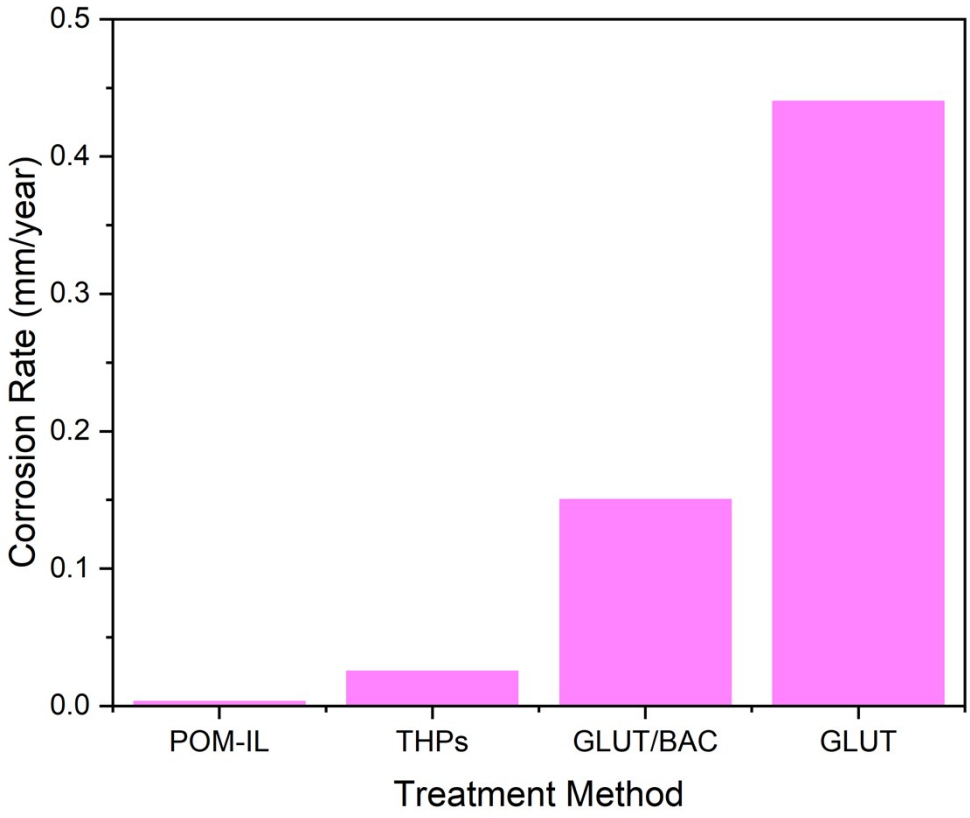

Figure S13: Comparison of corrosion rates (mm/year) for different biocidal treatments against *Desulfovibrio ferrophilus IS5*.The tested treatments include polyoxometalate-ionic liquid (POM-IL), tetrakis(hydroxymethyl)phosphonium sulfate (THPS), a combination of glutaraldehyde (GLUT) and benzalkonium chloride (BAC), and glutaraldehyde (GLUT) alone. Data adapted from Sharma et al. (2018).

Figure S 14: Cut-open syringe for sediment sampling: sterilized syringes were cut open to ensure gathering of larger quantities of sediment

Table S4.Calculated Sulfide Concentrations for Environmental sediment representing each condition: biotic and abiotic samples, as well as coated and uncoated brass coupons

	Sample	Sulfide concentration [Mm]
Biotic	Uncoated	0.106
	coated with Mo_8	0.087
Abiotic	Uncoated	0.131
	coated with Mo_8	0.102

Table S5. Weight loss estimation for environmental sediment representing each condition: biotic and abiotic samples, as well as coated and uncoated brass coupons

	Sample	Initial weight [g]	Final weight [g]	Corrosion Rate (CR) [mm/y]
Biotic	Uncoated	2.0995	2.0978	2.68×10^{-3}
	coated with Mo_8	2.1002	2.0992	1.58×10^{-3}
Abiotic	Uncoated	2.0983	2.0961	3.47×10^{-3}
	coated with Mo_8	2.1005	2.0995	1.58×10^{-3}