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Polyoxometalate-Ionic Liquids (POM-ILs) as Anticorrosion and Antibacterial Coatings for Natural Stones

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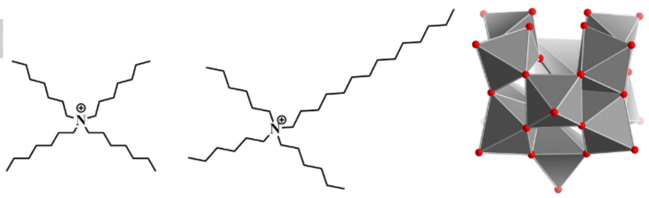
Abstract: Corrosion of stone by acid rain and deterioration from biofilms are global problems for industrial and residential buildings as well as cultural heritage such as statues or historic buildings. Here we show how typical building stones can be protected from corrosion ("weathering") and biofilm formation ("biodeterioration") by application of thin films of polyoxometalate-based ionic liquids (POM-ILs). Stone samples are coated with hydrophobic, acid resistant POM-ILs featuring biocidal properties. Exposure of the samples to simulated acid rain showed negligible corrosion compared to the significant deterioration of unprotected samples; while the biocidal properties of the POM-ILs suppress the formation of biofilms on coated stone slabs. A new class of modular molecular materials for protecting stones can now be developed for use in construction, environmental protection and cultural heritage preservation.

The corrosion of stones used in building construction is a major global issue, particularly when considering the loss of cultural heritage objects such as stone statues or ancient buildings. [1,2] Stone corrosion can be caused by thermal and mechanical stress (physical weathering) as well as chemical factors (chemical weathering). In this respect, acid corrosion is a major contributor and can be primarily attributed to "acid rain" based on industrial pollutants (SO_x, NO_x emissions).[3] In addition, aesthetic changes along with physical and chemical deterioration arising from microbial colonization also plague the conservation of stone materials.[4] Stone biodeterioration occurs predominantly by formation of biofilms, which discolour the stone surface and alter the stone porosity.[5] Exposure of stone artefacts to outdoor environments results in the need for continuous maintenance and the use of water repelling agents to as well as biocidal products to inhibit further biofilm growth. To overcome this challenge, protective coatings have been developed which either act as water repellents to prevent aqueous acid corrosion (*e.g.* alkoxysilanes, fluoropolymers, *etc.*) or as biocides to prevent biofilm formation on the stone surface.[6] Over recent years, metal oxide nanoparticles have received increased attention as antimicrobial agents,[6,7] as they feature higher environmental stability than organic antimicrobial agents and act against a broad range of microorganisms, reducing the development of antimicrobial resistance.[8]

Recently, ionic liquids (ILs, i.e. salts with a melting point < 100 °C)[9] have been proposed as anti-corrosive agents[10] due to their remarkable performance in corrosion protection by lubrication and coating formation.[11] ILs offer the advantage of a modular design where cation and anion can be independently tuned, thereby enabling the formation of multifunctional materials suitable for surface coatings.



$(n\text{-}C_7H_{15})_4N^+$ $(n\text{-}C_6H_{13})_3(C_{14}H_{29})N^+$ $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$

Figure 1: Illustration of the cations and anion used as components for POM-ILs **1** and **2.**

In the field of surface-active IL coatings, polyoxometalate-ionic liquids (POM-ILs) have recently received significant interest, owing to their outstanding chemical versatility and reactivity.[12] In POM-ILs, molecular metal oxide anions (polyoxometalates, POMs)[13] are combined with bulky organic cations (e.g. organic ammonium[14] or phosphonium[15] cations), often resulting in room-temperature ionic liquids.[12] The physical, rheological and chemical properties of POM-ILs can be tuned by chemical design, so that applications in thermo-regulated epoxidation catalysis,[16] large-scale petrochemical desulfurization,[17] light-driven water oxidation[18] and other technology areas have become possible.[12] Recently, it was shown that room-temperature POM-ILs such as $((n\text{-}C_7H_{15})_4N)_6[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)]$ are effective coatings, which prevent acid corrosion of metals.[19] Significantly improved performance was observed compared with commercial ILs (*e.g.* [hmim]Br) and with solid POM coatings (*e.g.* $((n\text{-}C_4H_9)_4N)_6[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)])$, highlighting the unique properties of POM-ILs. Further, immobilization of POM-ILs based on antimicrobial alkylammonium cations[20] and metal-binding POM anions on porous silica led to POM-SILPs (POM-supported ionic liquid

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phases) capable of removing organic, inorganic and biological contaminants from water by simple filtration.[21]

Here, we explored the development of water-repellent, acid-stable POM-ILs featuring biocidal activity as multifunctional corrosion protection coatings for natural carbonate stones typically used in construction. Our study shows that the combination of long-chain quaternary alkylammonium cations with acid-stable polyoxotungstate anions can be used to access room-temperature POM-ILs which combine facile application and high surface adhesion on porous and non-porous stone surfaces with high water repellency, acid stability and biocidal activity. Significantly increased corrosion-resistance is achieved under harsh chemical conditions and when exposed to typical biofilm-forming microbes, so that novel POM-IL based acid- and bio-corrosion protection now is possible.

Table 1. Composition and properties of the POM-ILs **1** and **2**.

POM-IL	POM-IL formula	Contact angle (°)[b]
1[a]	$((n\text{-}C_7H_{15})_4N)_8[\alpha\text{-}SiW_{11}O_{39}]$	53.9
2[a]	$((n\text{-}C_6H_{13})_3(C_{14}H_{29})N)_8[\alpha\text{-}SiW_{11}O_{39}]$	41.1

[a] Room-temperature ionic liquids; [b] measured by sessile drop method, see SI.

Table 2. Three types of natural building stones used as test samples.

ID	Stone type	Chemical composition (wt%)					Porosity (%)
		$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	MgO	
BB[22]	Belgian Blue stone	98.2	-	-	0.4	-	*ca.* 0.3
RO[23]	Romery stone	81.1	17.0	0.2	1.0	0.5	*ca.* 5
DO[24]	Dom stone	96.3	1.1	0,5	1.4	0.4	*ca.* 30

We used an established cation metathesis route[19–21] to combine the acid-stable polytungstate anion $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$[25] with two antimicrobial quarternary alkylammonium cations,[26] tetraheptylammonium (= $(n\text{-}C_7H_{15})_4N^+$) and trihexyl tetradecyl ammonium (= $(n\text{-}C_6H_{13})_3(C_{14}H_{29})N^+$), to give the respective POM-ILs **1** and **2**, see Table 1. The composition and purity of both compounds was verified by elemental analyses and FT-IR spectroscopy, see SI. Note that both compounds are room temperature ILs, they are insoluble in water but show high solubility in a wide range of polar and unipolar organic solvents. In addition, the hydrophilicity/hydrophobicity of the POM-ILs was assessed by the sessile drop method, giving values of 53.9° for **1** and 41.1° for **2** (also see SI). To assess the POM-IL performance as acid corrosion protection coatings, three typical limestone samples used in the Northern part of France and in Belgium were selected. The stone samples varied in chemical composition and porosity (see Table 2).

First, we examined the acid corrosion protection properties of the POM-ILs **1** and **2**. To this end, cubic samples of the stones (dimensions: 1.0 x 1.0 x 1.0 cm^3, geometric surface area: 6 cm^2) were brush-coated with a concentrated acetone solution of the respective POM-IL ([POM-IL] = 200 mg/mL), giving a POM-IL loading of ~ 17 mg/cm^2 or 100 mg per sample (see SI for details). Initial coating studies showed that brush coating resulted in homogeneous surface coverage whereas other methods (dip-coating, spray-coating) displayed less homogeneous POM-IL distribution.

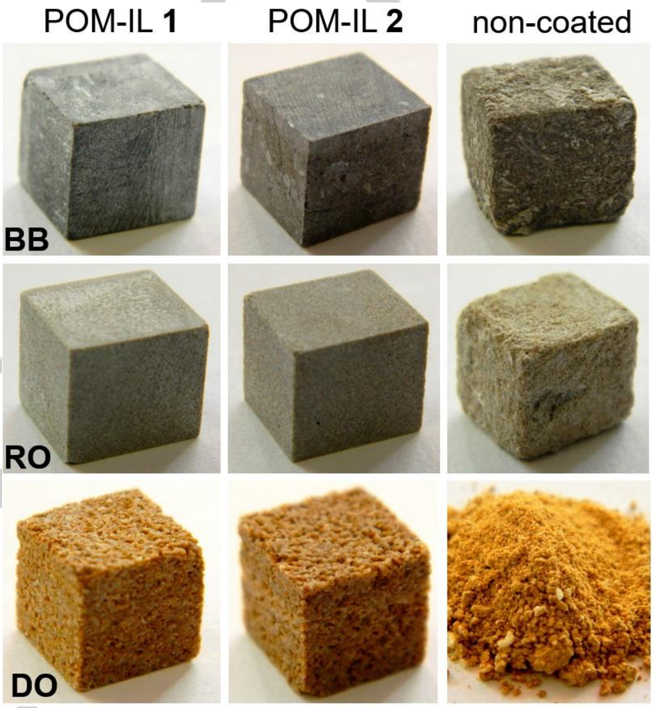

Figure 2. Acid vapour corrosion protection of POM-IL-coated stone samples, studied by exposing the samples to acetic acid vapour for 72 h; for weight losses see Table 3. RO: Romery stone; BB: Belgian Bluestone; DO: Dom stone.

Stone corrosion by acid vapor was then explored by exposing the samples (as well as uncoated references) to acetic acid vapor inside a closed glass vial for 72 h. Acetic acid was selected as a model corrosive agent with environmental relevance.[27] After exposure, the stones were rinsed with water and acetone (to remove the POM-IL), oven-dried (120 °C, 1 h) and the weight loss of each sample was determined. Visual inspection of the stones (Fig. 2) shows that the coated samples retain the original shape, smooth surface and sharp edges of the original sample. In contrast, the uncoated references are significantly corroded, leading to notable surface damage and visible "weathering". Strikingly, the highly porous, acid-sensitive Dom stone showed complete structural disintegration after acid vapor exposure when washed with water (also see SI video). In contrast, the Dom samples coated with **1** or **2** both show only minor corrosion and structural integrity of the stone samples is retained (Fig 2). When analyzing the weight losses observed for the acid vapor tests (Table 3), both POM-ILs show significant

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corrosion protection compared to non-coated samples. When comparing both POM-ILs, **1** shows slightly higher corrosion protection (i.e. lower weight losses) compared with **2**, highlighting that chemical tuning of the POM-IL performance by cation modification is possible. Notably, comparative experiments using 50 % POM-IL loading (i.e. ~50 mg POM-IL coating per sample) showed only small increases in the amount of corrosion observed. This emphasizes that tuning of film thickness and coating procedure can be used to achieve high acid corrosion resistance even at low POM-IL loading (Table 3).

Table 3. Acid corrosion protection data for POM-ILs **1** and **2**.

Stone type	**Coating**[a]	**Acid Vapour Test Weight loss** [wt-%]		**Acid Rain Test Weight loss** [wt-%]
		POM-IL loading ~50 mg/sample	POM-IL loading ~100 mg/sample	
BB	-	10.1 ± 0.2	10.1±0.2	28.0 ± 0.4
BB	POM-IL **1**	0.1 ± 0.1	0.0 ± 0.0	7.0 ± 0.5
BB	POM-IL **2**	0.6 ± 0.1	0.4 ± 0.1	10.6 ± 0.4
RO	-	6.2 ± 0.2	6.2 ± 0.2	32.1 ± 0.6
RO	POM-IL **1**	0.1 ± 0.1	0.1 ± 0.1	5.9 ± 0.4
RO	POM-IL **2**	0.4 ± 0.1	0.3 ± 0.1	7.6 ± 0.4
DO	-	Complete breakdown	Complete breakdown	84.4 ± 0.4
DO	POM-IL **1**	1.4±0.06	0.4±0.04	13.5± 0 .4
DO	POM-IL **2**	8.7 ± 0.3	3.4 ± 0.1	18.5 ± 0.4

[a] for details on coating procedure, see SI.

Next, we examined the integrity of the POM-IL coatings by exposing the coated stones to simulated acid rain. To this end, the samples were sprayed continuously with aqueous acetic acid (20 wt-%) for a period of 3 h at a flow rate of ~60 mL min^{-1}, see SI. After the acid rain treatment, the samples were recovered, rinsed with water and acetone, oven-dried (120 ºC for 1 h) and the weight loss was determined, see Table 3. The acid rain tests show corrosion protection effects similar to the vapor chamber study, while the corrosion observed is overall higher due to the harsh mechanical and chemical treatment: both POM-ILs result in significantly reduced acid corrosion. As described above, we note slightly higher corrosion protection (i.e. lower weight loss) for POM-IL **1** compared with POM-IL **2**. The acid rain simulator study further highlights the POM-IL coating durability, enabling the coating to retain its structural integrity even under harsh spraying conditions.

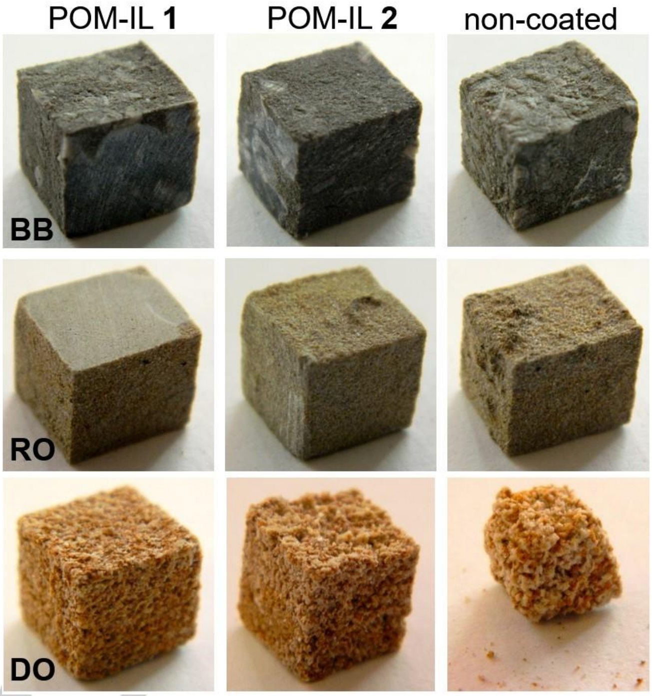

Figure 3. Acid rain corrosion protection of POM-IL coated stone samples. Conditions: simulated acid rain: aqueous acetic acid (20 wt-%), flow rate 60 mL/min per sample, exposure time: 3 h, for weight losses see Table 3. RO: Romery stone; BB: Belgian Bluestone; DO: Dom stone.

Biofilms on stones are typically formed by groups of microorganisms bound in an extracellular biopolymer matrix,[28] and both Gram-negative and -positive bacteria are common in biofilms [29] In particular, spore-forming bacteria of the *Bacillus* and *Bacillus*–related genera have been frequently identified on monumental stones, which is perhaps unsurprising since they are commonly found in soil, and their spore-forming ability enables them to withstand extreme environments.[30]. The biodegradation activity of this genera is caused by the production of organic acids and surfactants[31] and, moreover, examples of white fuzzy biofilm layers in deteriorated caves and catacombs indicate that they may actively participate in the precipitation of mineral phases[32]

To assess the bactericidal activity of POM-ILs **1** and **2**, we used a combination of *in vitro* cell proliferation assays and colorimetric cell viability assays to quantify bacterial growth over an incubation period of 24 h. As bacterial models, we used Gram-positive *Bacillus subtilis* (*B. subtilis*) and Gram-negative *Escherichia coli* (*E. coli*). Both POM-IL **1** and **2** showed potent bactericidal activity against sporulating *B. subtilis* at concentrations of 0.5 µg/mL and 5 µg/mL, respectively (Figs. S5 & S6). The bactericidal concentration of POM-IL **1** and **2** against more resistant *E. coli* was 50 µg/mL and 500 µg/mL, respectively. In summary, POM-IL **1** was the most potent variant *in vitro* and *B. subtilis* was more susceptible to the POM-ILs (see SI for further details).

Next, we assessed the performance of both POM-ILs in preventing biofilm formation *in situ* on BB, RO and DO stones. *E.coli* was chosen as a model organism, as it represents a more

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resistant bacterium and is also more effective at generating a biofilm in laboratory conditions. The surface biocidal activity of the POM-ILs on stone surfaces was quantified using a modified Japanese Industrial Standard (JIS).[33] JIS Z 2801 standard analysis showed that POM-IL **1** was more effective at reducing cell viability than the POM-IL **2**, reaching up to 100 % of bacterial reduction in the BB stone (Table 4). In addition, a TBX agar method was established as a convenient means of detecting and quantifying the growth of *E. coli* on the stone samples. TBX agar contains X-β-D-glucuronide, a chromogenic compound hydrolyzed by the β-glucuronidase (an *E. coli* enzyme) making the bacterial colonies turn green-blue on a conventional agar plate. The treated and untreated stones were compared and counting of the green-blue *E. coli* colonies illustrated how POM-IL **1** prevented colonization of the BB and RO stones samples (Fig. S7). Note that no colony forming was observed in DO stone, even after longer growth period, since bacteria embed themselves within the highly accessible pores. Moreover, water is quickly absorbed by porous stone and quickly evaporated too, resulting in less available nutrients for bacterial growth, which means that the short-term bacterial proliferation in this study could therefore be due to a number of factors.

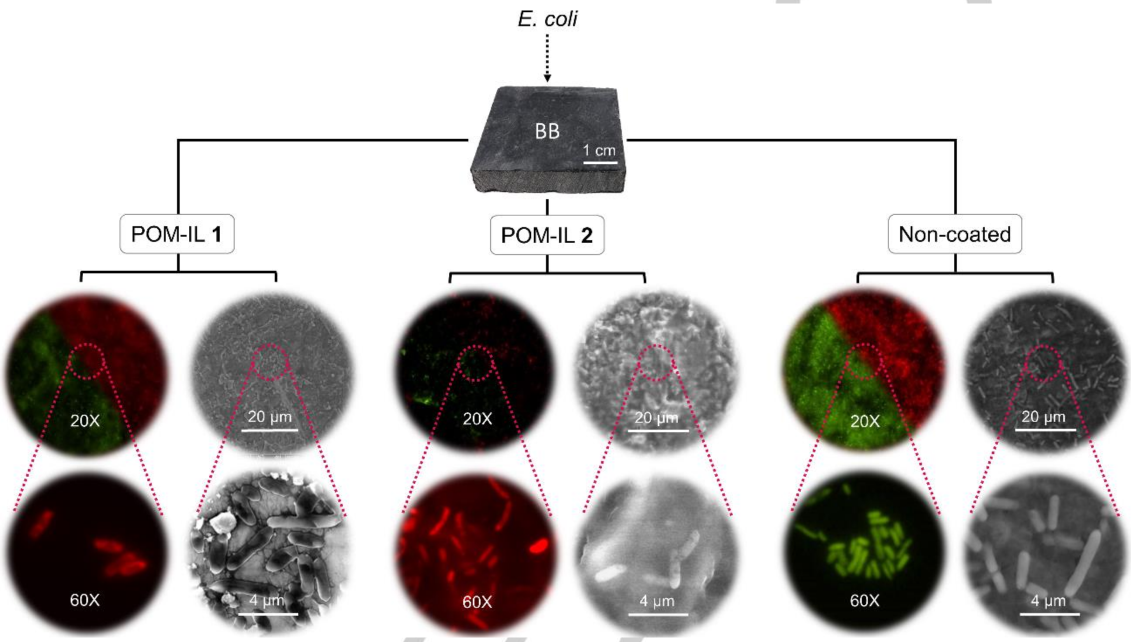

Figure 4. Environmental scanning transmission electron microscopy (ESTEM) and fluorescence microscopy analyses summarizing the bactericidal effects of POM-IL **1** and **2** on BB stone for *E.coli* biofilm prevention. Green cells = live (viable) bacteria; Red cells = dead (non-viable) bacteria. See SI for additional ESTEM and fluorescence microscopy images for both *E. coli* and *B. subtilis*.

Table 4. Surface antimicrobial activity data for POM-ILs **1** and **2**.

Stone type	Coating[a]	Bacterial reduction (%)
BB	POM-IL **1**	100
BB	POM-IL **2**	11.4
RO	POM-IL **1**	36.4
RO	POM-IL **2**	24.1
DO	POM-IL **1**	55.9
DO	POM-IL **2**	33.9

[a] Each stone sample was coated with a 10 mg/mL solution of the respective POM-IL, for details see SI.

These antibacterial assays illustrate the potent biocidal and biofilm prevention properties of the POM-ILs. To further analyze biofilm growth on stone surfaces, and to obtain in-depth information about the effect of the POM-ILs on the bacterial cells we used a combination of environmental scanning transmission electron microscopy (ESTEM) and fluorescence microscopy. Non-porous BB was chosen as a model stone surface due to its non-porous surface, which enables facile detection of biofilm formation, see Figure 4. BB samples treated with POM-IL **1** & **2** were inoculated with *E. coli* and *B. subtilis* and stained with a LIVE/DEAD® BacLight™ Bacterial Viability Kit to determine the viability of the bacteria and assess the biofilm formation after incubation. The samples incubated with the POM-ILs display lower bacterial density than the untreated stones, highlighting the antiproliferative effect of both POM-ILs (Figs. S8 & S9). However, a more detailed confocal microscopy analysis of biofilm formation on glass cover slips showed higher biofilm reduction with POM-IL **1** compared to POM-IL **2** (Fig. S10), which is in line with the results obtained from the antimicrobial surface analysis (JIS Z 2801 standard, Table 4). ESTEM can provide information on bacteria morphology, health and visual indicators of the extent of biofilm formation. This technique demonstrated how the POM-ILs clearly

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lead to distinct responses from the bacterium cells on the stone surface (Figs. 4, S11). In general, both bacterial strains incubated with POM-ILs showed evidence of stress and damage including general loss of cell shape, cell membrane damage and leakage of cytoplasmic material. *B. subtilis* showed signs of sporulation, an indicator of cell stress. Both POM-ILs substantially reduced the number of bacterial cells on the stone surfaces, and higher bactericidal efficiency was observed for POM-IL **1** (Table 4, Fig. S11). Importantly, images of *E.coli* on BB with POM-IL **2** appeared to show the presence of high molecular weight extracellular polymeric substances (EPSs) secreted by the *E.coli* biofilm (Fig. S11), which is in line with the more dense biofilm observed by confocal microscopy (Fig. S10). Finally, a modified optical density analysis of coated stones confirmed that POM-IL **1** was the more bactericidal compound against both *E. coli* and *B. subtilis* across all three types of stone (Table 4 and Fig. S12).

In summary, we report a multifunctional polyoxometalate ionic liquid (POM-IL) based transparent coating for natural building stones, which can easily be applied by brush coating onto various corrosion-sensitive surfaces. Here, we show that the POM-IL coating protects the stone surfaces from acid corrosion and biofilm formation by forming an acid-stable, biocidal surface layer. The surface coating is mechanically stable and is not removed even under harsh mechanical and chemical treatment (e.g. under accelerated acid rain simulation). Tuning of the rheological, physical and chemical properties of the POM-ILs is possible and our results demonstrate that modification of the cation affects the anti-corrosive properties as well as the biocidal activity. Future studies will explore the longer-term performance of POM-ILs when applied under *“real life”* conditions to prevent biodeterioration in outdoor buildings or cultural heritage objects and will pay particular attention to their antifungal activity.

Experimental Section

Full synthetic, analytical and anti-corrosion /antibacterial data are given in the SI.

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Keywords: Polyoxometalate • Ionic Liquid • Corrosion • Self-Assembly • Metal Oxide

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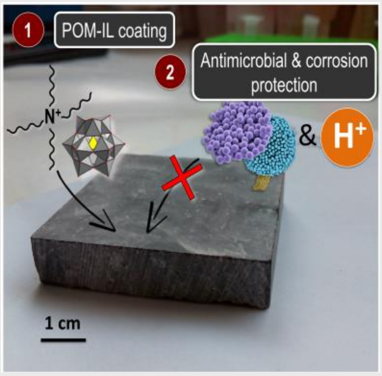
Entry for the Table of Contents

COMMUNICATION

Polyoxometalate ionic liquids (POM-ILs) are used as multifunctional brush-on protective coatings for natural building stones. The POM-ILs protect sensitive stones from acid corrosion and microbial biodeterioration and prevent the growth of biofilms on the stone samples. Tuning of the physical, chemical and rheological properties opens new opportunities for deploying POM-ILs on construction stones or outdoor cultural heritage such as statues or ancient buildings.



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