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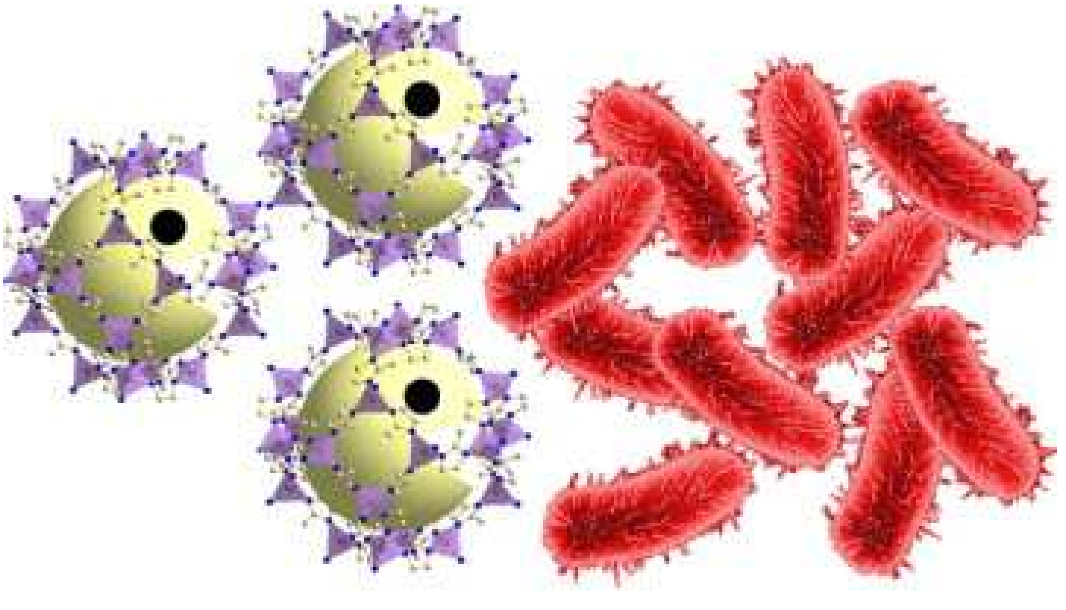

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Antimicrobial activity of cobalt imidazolate metal–organic frameworks

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Abstract
Two cobalt imidazolate metal–organic frameworks were evaluated as a bactericidal material against the growth of the Gram-negative bacteria *Pseudomonas putida* and *Escherichia coli*. Under the most unfavourable conditions, within the exponential growth phase and in the culture media for both microorganisms, the growth inhibition reached over 50% for concentrations of biocidal material in the 5–10 mg L^{-1} range. The release of metal gives excellent durability with the antibacterial effect persisting after 3 months. Both cobalt-based materials can be prepared with simple, cheap and easily accessible commercial ligands, leading to a more affordable possible future application as antimicrobial materials.

Keywords: Metal organic frameworks; Antibacterial; Escherichia coli; Cobalt

1. Introduction

Biocidal materials are required for a plethora of applications, which include the production of biomedical devices, the design of active food packaging and the preparation of antibiofouling membranes (Kenawy et al., 2007; Silvestre et al., 2011; Dasari et al., 2012).

Beyond the need to reduce food spoilage and to improve the durability of water treatment equipment, a driving force for the development of novel microbiocidals is the emergence and spread of multiresistant pathogen strains. Most of these works being performed on the control of biofouled surfaces as biofilm formation have been proved to protect pathogenic bacteria against antibiotic drugs, this being one of the main causes for the development of chronic infections (Landini et al., 2010). There is also a need to avoid the drawbacks of traditional chemical disinfectants such as the formation of harmful disinfection by-products and their reduced long term stability (Minear and Amy, 1996a,b).

Nanotechnology provides a tool for developing materials and products with antibacterial properties. Different antimicrobial nanomaterials have been described so far to produce biofilm resistant surfaces among which nanosilver proved to be particularly successful for a broad range of applications (Huh and Kwon, 2011). Several antimicrobial polymers have also been developed to this end (Kenawy et al., 2007; Fromm, 2008). A particularly interesting group of advanced functional materials are those created to deliver specific biocidals from a nanostructured matrix, a family which comprises from the well-known metal-exchanged zeolites to sophisticated nanocontainers (Bandow-Jun and Metzler-Nolte, 2009). Many of these metal-containing materials or nanoparticles can be used as macroscopic reservoirs (Choi et al., 2008; Kittler et al., 2010; Lalueza et al., 2011) or to functionalize antibacterial surfaces (Agarwal et al., 2010; Kusiak-Nejman et al., 2011; Alonso et al., 2012; Wang et al., 2012). Hybrid organic–inorganic and inorganic materials containing silver are the most known because of their strong antibacterial activity and high stability (Hindi et al., 2008; Kumar et al., 2008; Belser et al., 2009; Slenters et al., 2010). However, silver is expensive and unsuitable for use in a corrosive atmosphere. In contrast, cobalt is a relatively inexpensive element and effective as an antimicrobial agent. Indeed, cobalt is toxic for bacteria, although less toxic than silver (Alonso et al., 2012).

Metal–organic frameworks (MOF) constitute an important class of hybrid organic–inorganic crystalline porous materials (Yaghi et al., 2003; Kitagawa et al., 2004; Ferey, 2008). Since the introduction of the first porous MOF, more than 20 years ago, over 2000 three-dimensional MOF topologies have been described. The large surface areas and tunable pore sizes of MOF makes them well suited for a variety of applications including gas storage, molecular sieving, sensors, medical imaging, drug release or heterogeneous catalysis (Eddaoudi et al., 2002; Alaerts et al., 2007; Harbuzaru et al., 2008; Llewellyn et al., 2008; Taylor et al., 2008; Farrusseng et al., 2009a; Horcajada et al., 2010). MOF are attractive materials since their structures can be designed at the atomic scale by an appropriate choice of metal and organic ligand. Zeolitic imidazolate frameworks (ZIF), a sub-family of MOF, consist of transition metal ions (Zn^{2+}, Co^{2+}) and imidazolate linkers which form 3D

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tetrahedral frameworks frequently like zeolite topologies. Different to their MOF analogues with carboxylate ligands, several ZIF exhibit exceptional thermal, hydrothermal, and chemical stability (Park et al., 2006; Banerjee et al., 2008, 2009; Phan et al., 2009).

So far, only three cases of MOF with antibacterial activity have been reported. Berchel et al. (2011) presented a silver MOF material based on a 3-phosphonobenzoate ligand that can act as a ‘‘reservoir’’ of Ag^+. The cations are released into the solution and subsequently exert bactericidal properties upon *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. Another silver-based MOF was reported by Liu et al. (2010), who prepared a silver-based metal–organoboron framework that controls the release of silver ions. The material exhibited good antibacterial activity and durability against Gram-negative bacteria and Gram-positive human pathogens (Liu et al., 2010). Zhuang et al. (2012) described a cobalt-based metal–organic framework with tetrakis[(3,5-dicarboxyphenyl)-oxamethyl] methane acid as ligand as a disinfectant with elevated potency toward inactivation of *E. coli*. In all of these cases, the ligand used in the preparation of the MOF was not commercially available and must be synthesized in the laboratory after up to four reaction/separation steps.

Hence, we have sought to use MOF produced with a simple, relatively cheap, and commercially accessible linker. We report here the antimicrobial activity of two cobalt-based MOF (ZIF-67 and Co-SIM-1) and one silver coordination polymer (AgTAZ). Among the enormous number of silver coordination compounds known for their antimicrobial properties, we here focused on this particular one based on the low price and easy availability of its organic ligand. AgTAZ was prepared with a polyazaheteroaromatic compounds, 1,2,4-triazole, a well-known intermediate compound of industrial relevance (Haasnoot, 2000), which is also widely used as ligand (Zhang et al., 2005). ZIF-67 ($Co(Hmim)_2$) is isostructural to ZIF-8 (Huang et al., 2006), and is formed by bridging 2-methy-limidazolate (Hmim) anions and cobalt cations resulting in a sodalite topology (Banerjee et al., 2008; Qian et al., 2012). Co-SIM-1 (cobalt-based Substituted Imidazolate Material) is a novel analogue of its zinc-based parent SIM-1 (Farrusseng et al., 2009b; Aguado et al., 2010, 2011). It belongs to the class of ZIF or ZMOF materials and it is isostructural to ZIF-8 and ZIF-67.

2. Experimental

2.1. Synthesis and characterization of materials

ZIF-67, Co-SIM-1 and AgTAZ were synthesized by solvothermal procedure reported elsewhere (Huang et al., 2006; Banerjee et al., 2008; Farrusseng et al., 2009b). It follows a brief description of each synthesis (see Supplementary Information).

2.2. Biological testing

The microorganisms used in this study were *Saccharomyces cerevisiae* CECT 1170, P*seudomonas putida* CECT 4584 and *E. coli* CECT 4102, kept at -80 ºC in glycerol (50% v/v) until use. The reactivation of microorganisms was performed by cultivation in 50 mL Erlenmeyer’s and tracked by measuring optical density (OD) at 600 nm. Inoculums were prepared by incubation at 30 ºC, 150 rpm until OD = 2 were reached. *S. cerevisiae* was grown in universal medium for yeast (pH = 6.8 ± 0.2) while for bacteria, a Luria Bertani medium (pH = 7–7.2) was used. The culture medium used for the yeast *S. cerevisiae* contained 10 g L^{-1} glucose, 5 g L^{-1} mycopeptone, 3 g L^{-1} yeast extract and 3 g L^{-1} malt extract. The culture medium used for the bacteria *P. putida* and *E. coli* contained 10 g L^{-1} peptone, 5 g L^{-1} sodium chloride, 3 g L^{-1} meat extract and 0.25 g L^{-1} $MnSO_4 7H_2O$. Stock solutions of the three MOF were prepared in 50 mL culture medium with a concentration of 40 mg L^{-1} dispersed by sonication using a Sonics VibraCell ultrasound disperser (BioBlock Scientific, France) operating at 500 W (90% amplitude).

The biocidal materials were subjected to an antibacterial experiment using the diffusion method described by Fiebelkorn et al. (2003). Agar plate diffusion assay is the standardized method recommended by the National Committee for Clinical Laboratory Standards, based on the method described by Bauer et al. (1966). Petri dishes were prepared with culture media as indicated before. The cellular concentration in inoculums was adjusted to OD = 1 using the corresponding culture media. 500 μL of each microbial suspension were transferred to plates for inoculation and allowed to dry at room temperature before the addition of antimicrobials. All materials were used in powder form by placing a small amount of them (~1 mg) directly onto the inoculated agar plate. Zone diameters in the disk diffusion assay were measured to the nearest whole mm at the point where there was a prominent reduction of growth after 24 h. Control plates were incubated at the same time without antimicrobial agents to check correct microbial growth.

Sterile plates without inoculation were also incubated to detect possible sample contamination. Minimum inhibition concentration was measured as follows. Microorganisms were exposed to MOF in 96-well disposable microplates. Aliquots of the inoculums described above were transferred to obtain initial OD = 0.1 for *P. putida* and OD = 0.4 for *E. coli* and *S. cerevisiae*. These initial cellular densities were selected to maintain all microorganisms in the exponential growing phase during the entire time of exposition, which was 20 h. The reason for this choosing was to provide the most severe conditions to check the biocidal functionality of MOF. Temperature and agitation were the same used in the inoculum preparation step. Three different concentrations of each material were assayed by triplicate (5, 10 and 20 mg L^{-1}). Optimal density was

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measured using a Rayto microplate reader RT-2100C initially and at the end of experiment. The microorganism growth was evaluated by the increment of the OD and compared with the controls without antibacterial material.

2.3. Metal ion release test

To investigate the metal ion release from the samples, the three MOF were immersed in distilled water, in culture media or in media in the presence of microorganisms up to a concentration of 20 mg L^{-1}. The concentration of ion metals in the immersion liquid was measured by ICP-AES on an Iris Advantage 1000 Inductively Coupled Plasma Emission Spectrometer after removing the solids by filtration.

3. Results

3.1. Material characterization

ZIF-67, Co-SIM-1 and AgTAZ were characterized by XRD to assess their crystallinity. As shown in Fig. 1, the diffractograms of the three synthesized materials agreed with the corresponding simulated patterns. SEM micrographs of crystals are shown in Fig. 2.

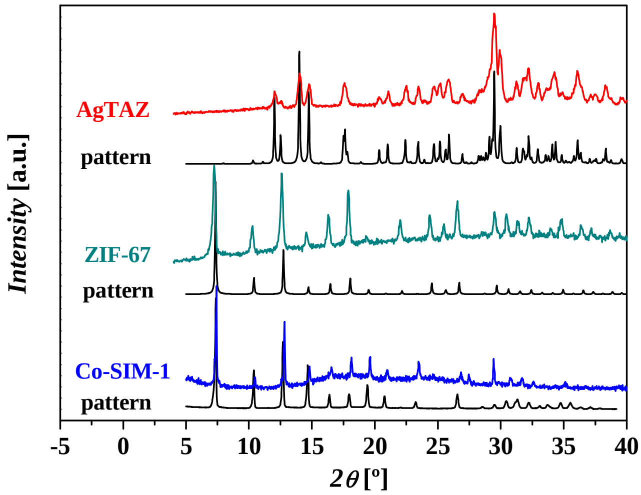

Figure 1. XRD patterns of AgTAZ, ZIF-67 and Co-SIM-1.

The antibacterial activity of the three MOF was evaluated using the disk diffusion method described before. All MOFs based on cobalt ions show a significant antibacterial activity, with an inhibition diameter of around 15 mm (Fig. 3). Surprisingly, AgTAZ appears to be the weakest to inhibit the growth of the bacterial

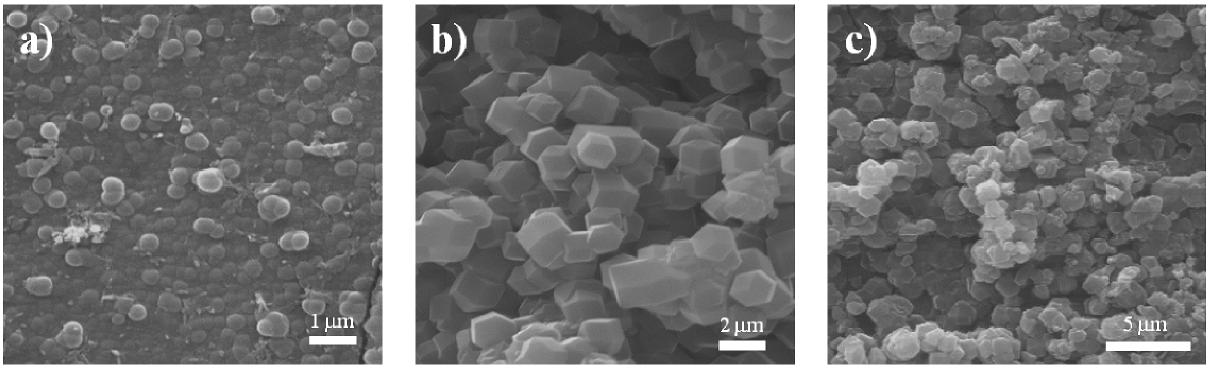

Figure 2. SEM micrographs of crystals of (a) AgTAZ, (b) ZIF-67 and (c) Co-SIM-1.

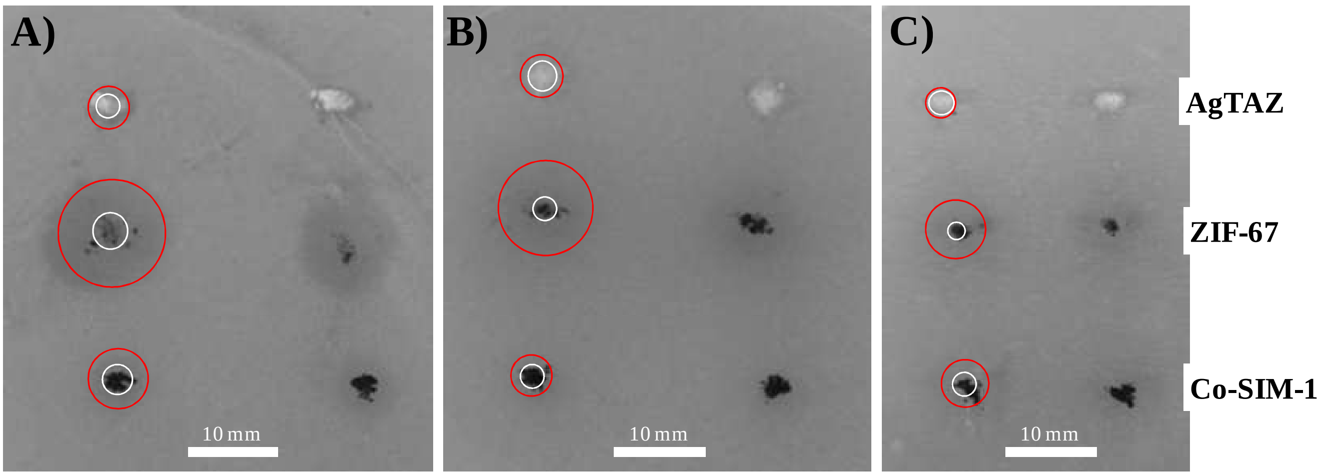

Figure 3. Agar plate diffusion experiment to estimate antibacterial activity on (A) *S. cerevisiae*, (B) *P. putida* and (C) *E. coli* with AgTAZ, ZIF-67 and Co-SIM-1. The white circles indicate deposited material, the red circles indicate inhibition areas. Incubation conditions, 303 K, 24 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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strains (inhibition diameter of 2 mm). This initial experiment shows that both ZIF-67 and Co-SIM-1 are able to diffuse in this medium and to inhibit the growth of all microorganisms used.

3.2. Antibacterial activity

We also performed tests to determine the biocidal effect of the tested materials in suspension as well as the release of free metals to the solution. The results of these experiments, performed with microorganisms growing in their exponential phase, are shown in Fig. 4. No inhibition for the yeast growth was observed higher than 10% with any of the materials tested. This could be explained by a lower cation release in presence of the yeast (Fig. 5). In the case of *P. putida*, there is almost no difference in antibacterial behaviour from the three materials tested, with an inhibition of about 70% for all the concentration range investigated. However, we observed large differences in the effect on *E. coli* growth. The initial concentration leading to growth inhibition increased from less than 5 to 5 and 10 mg L^{-1} for ZIF-67, Co-SIM-1 and AgTAZ, respectively. These results are consistent with the cation release in water shown in Fig. 6. After 24 h, the concentration of metals in solution reached about 0.4, 1.8 and 3.2 mg L^{-1} for AgTAZ, Co-SIM-1 and ZIF-67, respectively. This initial amount is probably due to the release of surface cations which occurs first. Then, the concentrations increased linearly within 108 h, for example, for AgTAZ at a release rate of about 0.2 mg L^{-1} (2 lg per day), corresponding at 1% of the overall cation content of the samples (0.4 mg). These values of cation release and antibacterial activity are comparable to previous reports (Liu et al., 2010; Berchel et al., 2011; Zhuang et al., 2012). However, it is noteworthy that in these cases the ligand into the MOF material was synthesized in the laboratory, after several preparation steps. In contrast, the three materials presented in this work are synthesized with easily accessible commercial ligands.

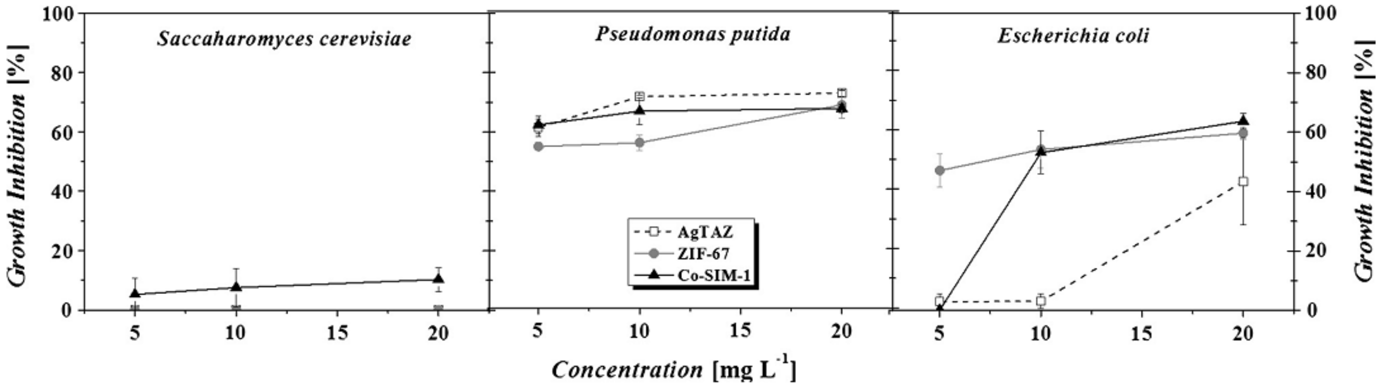

Figure 4. Microorganism inhibition of AgTAZ, ZIF-67 and Co-SIM-1 against *S. cerevisiae*, *P. putida* and *E. coli*. Incubation conditions, 303 K, 20 h.

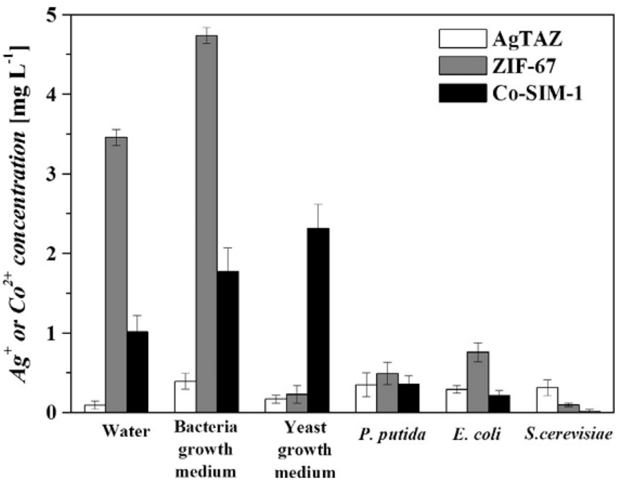

Figure 5. Evolution of cation release from different materials at 20 h from an initial concentration of 20 mg L^{-1}.

Since some triazolate (Chohan et al., 2002) and imidazolate (Bansal et al., 2010) derivatives are well known for their antimicrobial actions, we separately evaluated the ligands used for the synthesis of the MOF, and we found that they do not exhibit any antibacterial activity.

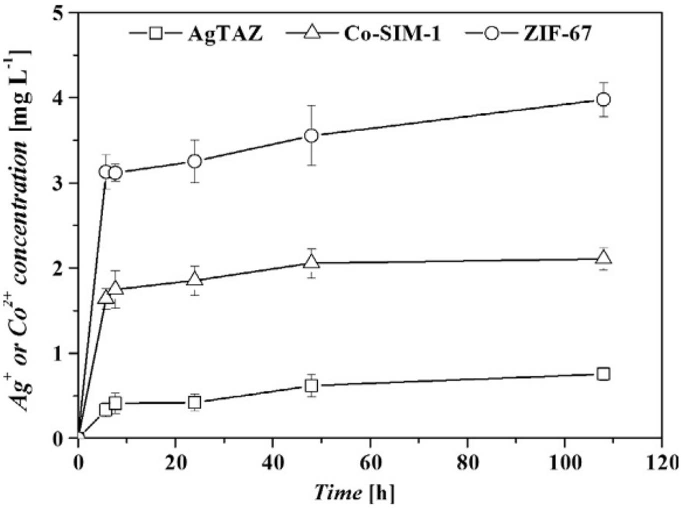

Figure 6. Evolution of cation release from different materials in distilled water with time (initial concentration of 20 mg L^{-1}).

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To establish whether the materials are suitable as long-term biocidal agents, we took optical images of the zone of inhibition after 3 months of incubation. The results indicated that the anti-bacterial activity remains almost unaffected.

5. Conclusions

In summary, our work demonstrates that it is possible to use cobalt-based metal organic frameworks as antibacterial materials. The materials exhibit remarkable antibacterial activity and durability, due to the control of the release of cobalt ions in biocidal solutions. Another benefit of ZIF-67 and Co-SIM-1 is their preparation with simple, relatively cheap, and easily accessible commercial ligands, leading to a more affordable possible future application as antimicrobial materials. Such liberation of bactericidal species from these hybrid materials opens up novel visions for biological applications of MOFs. Current experiments are focus on the incorporation of these MOFs within the polymer matrix of a fiber.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.05.029.

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Supplemantary Information

Antimicrobial activity of cobalt imidazolate metal–organic frameworks

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1.- Synthesis of materials

ZIF-67, Co-SIM-1 and AgTAZ were synthesized by solvothermal procedure reported elsewhere (Huang et al., 2006; Banerjee et al., 2008; Farrusseng et al., 2009b). It follows a brief description of each synthesis.

In a typical synthesis of ZIF-67 a solid mixture of 0.073 g (0.25 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ and 0.062 g (0.75 mmol) of 2-methylimidazole was dissolved in 5 mL of N,N-dimethylformamide (DMF). Afterwards, the solution was poured into a vial and heated in an oven at 373 K for 72 h. After the synthesis, the resulting powder was washed 3 times with DMF then with ethanol. The samples were dried at 373 K overnight. Elem. anal. calcd. for $[C_8H_{10}N_4Co]$: C, 39.8%; H, 10.0%; N, 23.2%; Co, 27.1%, found C, 39.8%; H, 10.1%; N, 23.1%; Co, 27.1%.

In a typical synthesis of Co-SIM-1, a solid mixture of 0.199 g (0.68 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ and 0.301 g (2.7 mmol) of 4-methyl-5-imidazolecarboxaldehyde is dissolved in 5 mL of DMF. The solution was then poured into a vial and heated in an oven at 358 K for 72 h. After the synthesis, the resulting powder was washed 3 times with DMF then with ethanol. The samples were dried at 373 K overnight. Elem. anal. calcd. for $[C_{10}H_{10}N_4O_2Co]$: C, 42.3%; H, 3.5%; N, 19.8%; Co, 23.1%, found C, 42.3%; H, 3.6%; N, 19.7%; Co, 23.0%.

For the synthesis of AgTAZ, A mixture of $AgNO_3$ (1.70 g, 10 mmol), aqueous ammonia (25%, 20 mL), and 1,2,4-triazole (0.69 g, 10 mmol) was sealed in a 45 mL Teflon-lined reactor and heated in an oven at 373 K for 60 h. After the synthesis, the resulting powder was washed 3 times with ethanol. The samples were dried at 373 K overnight. Elem. anal. calcd. for $[C_2H_2AgN_3]$: C, 13.6%; H, 1.1%; N, 23.9%, Ag, 61.3%, found: C, 13.6%; H, 1.2%; N, 23.8%; Ag, 60.4%.

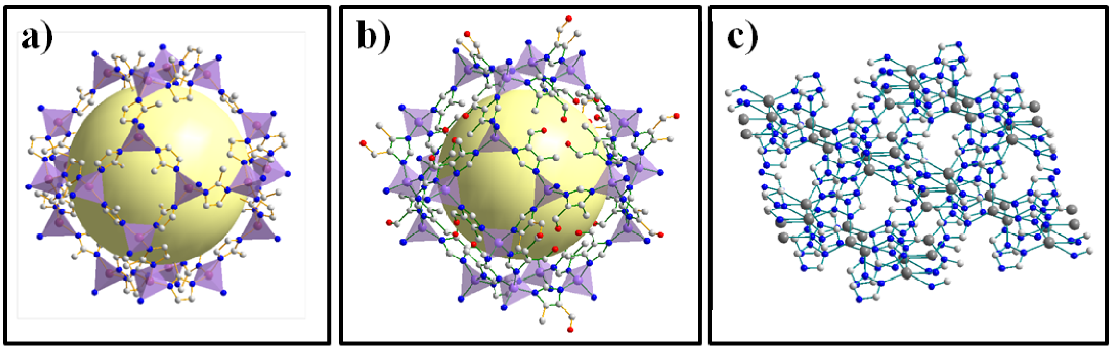

Figure S1.- Crystal structures of a) ZIF-67, b) Co-SIM-1 and c) AgTAZ.

2.- Characterization of materials

XRD measurements were recorded in the 10–90º 2θ range (scan speed = 20 s, step = 0.04°) by powder XRD using a Shimadzu 600 Series Diffractometer employing CuKα radiation (λ = 1.5418 Å). The morphology of the as-synthesized materials was examined by scanning electron microscopy (SEM) using a DSM-950 (Zeiss) microscope.

3.- Biological testing

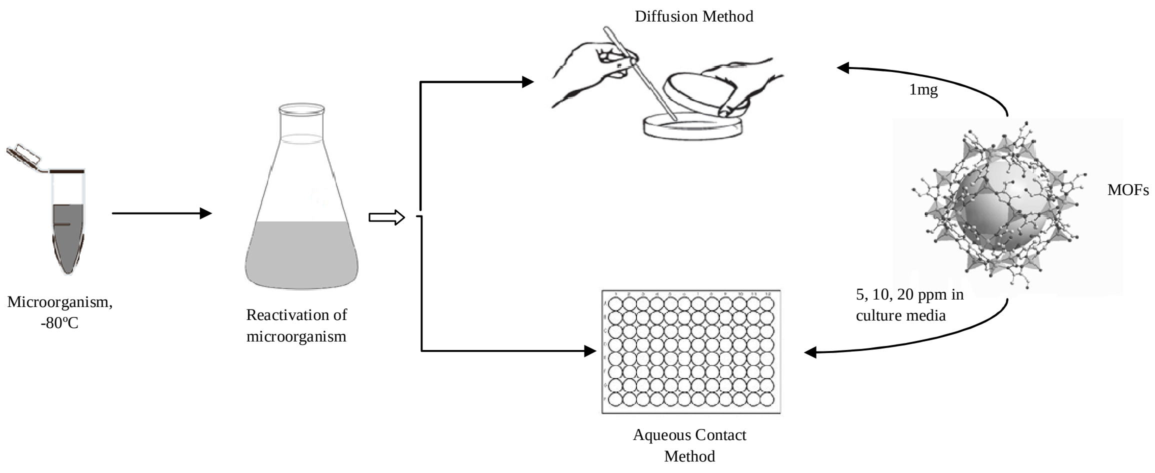

Figure S2.- Biological testing scheme.