Silver-Based Hybrid Materials from meta- or para-Phosphonobenzoic Acid: Influence of the Topology on Silver Release in Water

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S *Supporting Information*

ABSTRACT: Three novel silver-based metal−organic frameworks materials, which were synthesized from either 3-phosphono or 4-phosphonobenzoic acid and silver nitrate, are reported. The novel hybrids were synthesized under hydrothermal conditions; the pH of the reaction media was controlled by adding different quantities of urea thereby producing different topologies. Compound 1 ($Ag_3(4-PO_3-C_6H_4-COO)$), synthesized in the presence of urea, exhibits a compact 3D structure in which both phosphonic acid and carboxylic acid functional groups are linked to the silver-based inorganic network. Compound 2 ($Ag(4-PO_3H-C_6H_4-COOH)$), which was synthesized at lower pH (without urea), has a layered structure in which only the phosphonic acid functional groups from 4-phosphonobenzoic acid moieties are linked to the silver inorganic network; the carboxylic acid groups being engaged in hydrogen bonds. Finally, material 3 ($Ag(3-PO_3H-C_6H_4-COOH)$) was synthesized from 3-phosphonobenzoic acid and silver nitrate without urea. This material 3 features a layered structure exhibiting carboxylic acid functional groups linked via hydrogen bonds in the interlayer space. After the full characterization of these materials (single X-ray structure, IR, TGA), their ability to release silver salts in aqueous environment was measured. Silver release, determined in aqueous solution by cathodic stripping voltammetry, shows that the silver release capacity of these materials is dependent on the topology of the hybrids. The more compact structure 1 is extremely stable in water with only trace levels of silver ions being detected. On the other hand, compounds 2 and 3, in which only the phosphonic acid functional groups were bonded to the inorganic network, released larger quantities of silver ions into aqueous solution. These results which were compared with the silver release of the previously described compound 4 ($Ag_6(3-PO_3-C_6H_4-COO)_2$). The results clearly show that the release capacity of silver-based metal organic framework can be tuned by modifying their topology which, in the present study, is governed by the regio-isomer of the organic precursor and the synthetic conditions under which the hybrids are prepared.
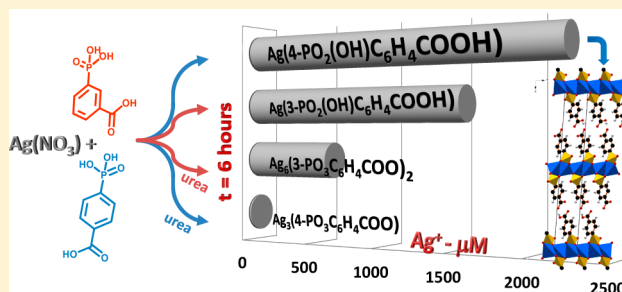
INTRODUCTION

Hybrid organic−inorganic materials have been extensively studied for their potential application in magnetism,[1] luminescence,[2,3] catalysis,[4] and gas storage.[5] Biomedical applications constitute another field of development which is currently the focus of much research. Different kinds of hybrid materials including sol−gel materials,[6] surface modified[7−9] inorganic nanoparticles or crystalline MOF materials (coordination polymers or metal−organic framework materials)[10] have been investigated as materials for drug delivery or diagnosis.[11,12] Regarding crystalline hybrids, early strategies was used to produce hybrid possessing the capability to release drug, were based on the intrinsic porosity of some materials that permitted their use as a reservoir of bioactive compounds including antithrombosis gas,[13−15] anti-inflammatory drugs,[16,17]

or anticancer drugs.[18] Later approaches were based on the use of an active drug that acts as a building block (template) for the construction of biodegradable hybrids. Accordingly, the drug, or pro-drug, (e.g., peptide,[19] nicotinic acid[20]) must possess a reactive functional group (e.g., carboxylate) that can interact with the inorganic network that is generated during the formation of the hybrid. In these two first strategies, the inorganic partner engaged in the structure of the hybrid must be as harmless as possible to avoid any toxicity. A further strategy consists of elaborate crystalline hybrids in which the inorganic part corresponds to the bioactive species. Following this strategy, the expected biological effects would arise from

the release of the bioactive metallic salt into the surrounding media. It has indeed been established that some metallic salts and/or organometallic complexes may have biological effects including bactericidal[21−23] (e.g., Ag, Co, Cu) or anticancer actions[24,25] (e.g., Au, Ag, ...). The bactericidal action of silver salts, which is thought to arise from interaction with sulfur-containing proteins or binding to DNA,[26] was identified many years ago and recent developments have shown that organo-metallic silver-based compounds presented high bactericidal efficacies against Gram-negative bacterial strains.[27,28] Crystal-line coordination polymers were also studied for their bactericidal action. In this class of material most of the studies involved silver salts coordinated to aza-heterocyclic ligands (pyridyl,[29] pyrazolyl,[30] pyrazinyl[31]). Recently, we reported the first example of an efficient bactericidal silver-based hybrid in which phosphonic and carboxylate functional groups tether the organic part with the silver salt in a 3D arrangement.[32] This work was carried out in the context of using rigid phosphonic acid derivatives[33,34] as building blocks for the construction of crystalline hybrids under hydrothermal conditions to produce fluorescent,[35] thermally stable,[36] and noncentrosymmetic materials.[37,38] In a previous study reporting the behavior of silver-based hybrid material in aqueous media, we suggested that this type of material can act as a reservoir of silver ions and have exhibited interesting bactericidal properties.[31] The basis of proposed mode of action via disassembly is rationalized by the fact that in these materials hard bases (carboxylate, phosphonic acids), according to Pearson HSAB theory,[39,40] are associated with a soft acid (silver salt). Accordingly, the expected low stability of such materials leads to its degradation and the release of the bioactive silver ions when the material is placed in an aqueous environment. This scenario was indeed observed with $Ag_6(3\text{-}PO_3\text{-}C_6H_4\text{-}COO)_2$ (**4**),[41,32] which released less than 2% of the silver present in the starting materials and showed excellent bactericidal properties against clinically relevant Gram negative and Gram positive bacterial strains (including MRSA strains).[32] Other recent studies have also reported the bactericidal properties of cobalt,[42] silver,[43,44] and copper-based[45] metal−organic frameworks. In the recent study from Jones et al.,[44] it was shown that the quantities of silver salts released in solution were almost identical irrespective of the structure of the polymeric material tested. More recently, silver-based materials synthesized from glutathione,[46] aminophosphi-nethiooxide,[47] or aza-heteroaromatic compounds[30,48,49] were reported and their antimicrobial activities were commented upon. In all these studies, each silver-based material exhibited bactericidal action when placed in aqueous solution. It is assumed that the release of silver salts into the surrounding aqueous media, which was quantified in some of these studies, is the most likely explanation for the antibacterial action. The controlled release of bioactive silver species therefore constitutes a key indicator with respect to potential biomedical applications. In the present study, we hypothesized that the topology of silver-based hybrid may influence the release of silver ions into aqueous media. Herein, we report the synthesis of three new silver containing MOFs from two rigid difunctional organic precursors (3-phosphonobenzoic and 4-phosphonobenzoic acids). We have subsequently quantified the silver-release capacities of these hybrid materials in aqueous media by cathodic stripping voltammetry and demonstrate the relationship between topology and silver release in aqueous media as quantified by the amount of free silver ions present in water.

■ EXPERIMENTAL SECTION

General. 3-Phosphonobenzoic[32] and 4-phosphonobenzoic[35] acids (Figure 1) were synthesized according to the reported methods.
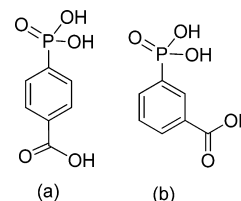

Figure 1. Chemical structure of the two organic precursors used in this study: 4-phosphonobenzoic acid (a) and 3-phosphonobenzoic acid (b).

Elemental analyses were recorded with an automatic apparatus CHNS-O Thermo-Quest NA 2500. The Infrared spectroscopy (IR) spectra were recorded on a PerkinElmer spectrometer working in the transmittance mode, in the 450−4000 cm^{-1} range, at 4 cm^{-1} optical resolution. Powdered samples were diluted by mixing with KBr (2 wt %). Thermogravimetric Analyses (TGA) were recorded with SETARAM TGA 92 apparatus. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed using a Zeiss supra 55 electron microscope. Silver concentration was determined by cathodic stripping voltammetry using Square wave mode and conducted with an μAutolabII instrument (Metrohm).

Hydrothermal Synthesis of the Materials. Compounds $Ag_3(4\text{-}PO_3\text{-}C_6H_4\text{-}COO)$ (**1**), $Ag(4\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$ (**2**), and $Ag(3\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$ (**3**) were obtained by hydrothermal synthesis according to the following reproducible method. Although the synthesis of compound **4** was already described elsewhere by Hix et al.,[41] we present here the conditions that achieved its synthesis in a shorter time and at a lower reaction temperature. For all syntheses, the pH of the synthesis media was measured after dispersion of the precursors in water (pH$_{initial}$) and directly at the end of the reaction (pH$_{final}$). These values are reported in Table 1.

Synthesis of $Ag_3(4\text{-}PO_3\text{-}C_6H_4\text{-}COO)$ (1). In a PTFE insert of 50 mL capacity, 3 equiv of silver nitrate salt (AgNO$_3$, 0.201 g, 1.2 mmol), 1 equiv of 4-phosphonobenzoic acid (4-PO(OH)$_2$-C$_6$H$_4$-COOH, 0.08 g, 0.4 mmol), and 1.5 equiv of urea (CO(NH$_2$)$_2$, 0.035g, 0.6 mmol) were dissolved in 15 mL of distilled water. This insert was placed in a Berghof pressure digestion vessel and heated from room temperature to 180 °C over 24 h, maintained for 96 h at 180 °C and cooled to room temperature over 12 h. The product was obtained as light brown needles, with suitable size for structure solution by single crystal diffraction. It was isolated by filtration, washed with water, rinsed with absolute ethanol, and dried in air.

$Ag_3(4\text{-}PO_3\text{-}C_6H_4\text{-}COO)$ (1) ($Ag_3PO_5C_7H_4$, 522.68 g/mol). Yield: 0.16 g (76%). Elemental Analysis: Calcd. C 16.09, H 0.77; Found C 15.88, H 1.00. IR (cm^{-1}, 2 wt % in KBr): 3399.68, 1649.60, 1586.19, 1536.96, 1390.75, 1148.63, 1113.03, 1071.05, 968.25, 842.96, 788.84, 730.67, 669.1, 600.71, 547.77, 531.21, 479.43, 458.63.

Synthesis of $Ag(4\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$ (2), and $Ag(3\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$ (3). In a PTFE insert of 50 mL capacity, 3 equiv of silver nitrate salt (AgNO$_3$, 0.201 g, 1.2 mmol), and 1 equiv of 3- or 4-phosphonobenzoic acid (3-PO(OH)$_2$-C$_6$H$_4$-COOH or 4-PO(OH)$_2$-C$_6$H$_4$-COOH, 0.08 g, 0.4 mmol) were dissolved in 15 mL of distilled water. This insert was placed in a Berghof pressure digestion vessel and heated according the following thermal cycle: heating from room temperature to 140 °C over 12 h for **3** and 24 h for **2**, heated for 48 h at 140 °C, and cooled to room temperature over 12 h for **3** and 24 h for **2**. Final products obtained as colorless needles with suitable size for structure solution by single crystal diffraction, were isolated by filtration, washed with water, rinsed with absolute ethanol, and dried in air.

$Ag(4\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$ (2) ($AgPO_5C_7H_6$, 308.96 g/mol). Yield: 0.055 g (44%). Elemental Analysis: Calcd C 27.21, H 1.96; Found C 27.01, H 2.31. IR (cm^{-1}, 2 wt % in KB): 3378.6, 2974.14, 1690,

Table 1. Details of the Data Collection for the Samples 1−3

precursor (number of equivalents)		urea (equiv)	$pH_{initial}$	pH_{final}	compound	compound number
AgNO₃ (3)	4-PO(OH)₂-C₆H₄-COOH (1)	1.5	1.05	3.41	Ag₃(4-PO₃-C₆H₄−COO)	**1**
AgNO₃ (3)	4-PO(OH)₂-C₆H₄-COOH (1)	0	1.49	1.42	Ag(4-PO₃H−C₆H₄−COOH)	**2**
AgNO₃ (3)	3-PO(OH)₂-C₆H₄-COOH (1)	0	1.44	1.26	Ag(3-PO₃H−C₆H₄−COOH)	**3**
AgNO₃ (3)	3-PO(OH)₂-C₆H₄-COOH (1)	1.5	1.59	5.31	Ag₆(3-PO₃−C₆H₄−COO)₂	**4.**

Table 2. Synthetic Condition Used to Produce the Silver-Based MOFs 1−3

	1	2	3
chemical formula	Ag₃(4-PO₃-C₆H₄-COO)	Ag(4-PO₃H-C₆H₄-COOH)	Ag(3-PO₃H-C₆H₄-COOH)
cell parameters at 293 K			
a (Å)	6.9399(4)	4.5995(8)	4.7615(2)
b (Å)	5.7694(2)	5.6145(16)	5.8234(3)
c (Å)	22.9600(17)	33.008(8)	15.8905(8)
β (deg)	92.558(6)	93.91(1)	89.3664(17)
ρ_{calcd} (g/cm³)	3.78	2.39	2.43
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
diffractometer	KappaCCD Nonius	KappaCCD Nonius with Apex2	KappaCCD Nonius with Apex2
wavelength (Å)	0.71069	0.71069	0.71069
scan strategy	Ω/Φ	Ω/Φ	Ω/Φ
scan angle (deg)/Δx (mm)	0.8/34	0.8/40	0.5/40
$(\sin \theta/\lambda)$max	0.80	0.92	0.66
reflns index limit	$0 \leq h \leq 11; 0 \leq k \leq 9; -36 \leq l \leq 36$	$-8 \leq h \leq 8; 0 \leq k \leq 10; 0 \leq l \leq 60$	$-6 \leq h \leq 6; -7 \leq k \leq 7; 0 \leq l \leq 18$
measured reflns	16 166	88 350	14 388
unique reflns	4433	5424	1357
unique reflns with $I \geq 3\sigma(I)$	2243	3288	1277
abs correction	numerical/SADABS	numerical/SADABS	numerical/SADABS
internal R value after correction (obs/all)	0.0431	0.0585	0.0156
refinement program	JANA2006[51]	Olex2[52]	Olex2[52]
number of refinement params	141	127	128
weighting method	sigma	sigma	sigma
ρ_{min}/ρ_{max} (e/Å³)	2.25/−2.3	2.08/−2.00	0.71/−0.53
F(000)	968	600	296
reliability factors (R/R_w)	0.0403/0.0416	0.0489/0.0923	0.0189/0.0374
goodness of fit	1.63	1.78	1.40

1631.29, 1557.66, 1495.65, 1395.13, 1368.66, 1337.05, 1303.93, 1283.10, 1148.69, 1119.94, 1034.61, 966.18, 868.30, 779.55, 762.80, 722.48, 704.89, 632.69, 586.27, 548.91, 522.13, 480.84.

Ag(3-PO₃H-C₆H₄-COOH) (3) (AgPO₅C₇H₆, 308.96 g/mol). Yield: 0.046 g (37%). Elemental Analysis: Calcd C 27.21, H 1.96; Found C 27.39, H 2.08. IR (cm⁻¹, 2 wt % in KB): 3079.51, 2759.50, 2402.19, 1674.88, 1597.48, 1581.64, 1406.04, 1295.26, 1266.42, 1112.82, 1078.34, 1051.23, 929.42, 906.52, 846.27, 828.34, 748.61, 722.64, 684.65, 656.47, 568.48, 547.51, 533.23, 460.18.

Hydrothermal Synthesis of Ag₆(3-PO₃-C₆H₄-COO)₂ (4) by Microwave Heating. In a TFM insert of 100 mL capacity, 3 equiv of silver nitrate salt (AgNO₃, 0.201g, 1.2 mmol), 1 equiv of 3-phosphonobeinzoic acid (3-PO(OH)₂-C₆H₄-COOH, 0.08 g, 0.4 mmol) and 1.5 equiv of urea (CO(NH₂)₂, 0.035g, 0.6 mmol) were dissolved in 15 mL of distilled water. This insert was placed in a CEM MARS 5 microwave oven and heated from room temperature to 140 °C over 1 h, heated for 3 h at 140 °C and allowed to air cool to room temperature. The final product, obtained as light brown plates, with suitable size for structure solution by single crystal diffraction, was isolated by filtration, washed with water rinsed with absolute ethanol and dried in air.

Ag₆(3-PO₃-C₆H₄-COO)₂ (4) (Ag₃PO₅C₇H₄, 522.68 g/mol). Elemental Analysis: Calcd C 16.09, H 0.77; Found C 16.04, H 1.01.

Structural Description of Ag₃(4-PO₃-C₆H₄-COO) (1), Ag(4-PO₃H-C₆H₄-COOH) (2), and Ag(3-PO₃H-C₆H₄-COOH) (3). Single crystals of high crystalline quality and suitable size were selected using stereomicroscope. Details of the data collection for the samples **1**, **2** and **3** are reported in Table 2. The Apex2 or EvalCCD[50] software

suites were used to extract reflections from the collected frames and the intensities were corrected for absorption using the empirical method implemented in SADABS.[51] Structural models considering the ad hoc space group were built up with SUPERFLIP[52] using the charge flipping method. The model was then introduced into the refinement programs; all the atomic positions were refined and anisotropic displacement parameters (ADP) were considered for all the atoms (except for H atoms). The positions of the H atoms were determined geometrically and restricted in bonds to their O or C nearest neighbor. It can be noted that the main residues in the electron density map are located in the vicinity of the Ag atoms. Atomic parameters for the samples **1**−**3** are summarized in Supporting Information Tables SI-1, SI-3 and SI-5. The refinements of the structures were achieved with Jana2006[53] and OLEX2[54] software.

Thermal Gravimetric Analysis (TGA). In an alumina crucible, an accurate mass around 15 mg of crystalline sample were weighed and heated under air flow from 25 to 1000 °C at 3 °C/min, left at 1000 °C during 1 h and then allowed to cool to room temperature. The mass losses were recorded with a SETARAM TGA 92 apparatus (Figure 2).

Quantification of Silver Release in Water. Twelve milligrams of a selected sample (compounds **1**−**4**) was suspended in 1 mL of distilled water. The sample is then maintained in the dark at room temperature. At different time points (t = 2, 24, and 48 h), 100 μL of the solution was taken up and immediately mixed with a calculated volume of potassium iodide water solution (C = 2.096 mM). This volume was examined as follows: the number of silver atoms presents in 12 mg of a
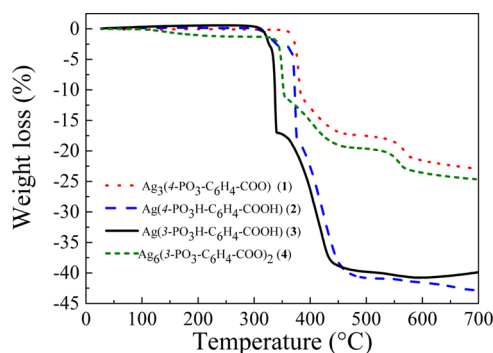
Figure 2. TGA analysis of materials **1−4**.

RESULTS AND DISCUSSION

Phosphono-benzoic derivatives (Figure 1) constitute a unique class of rigid organic compounds, which can be employed as precursors for hybrid materials. Their rigidity provides some explanation for the fact that they give rise to thermally stable materials[35] and in few cases non centro-symmetric materials.[37,38] These organic precursors, which can be synthesized at a multigram scale in 3 steps from commercially available bromo-benzoic acid, must be also be classified as heterodifunctional compounds in which both functional groups (phosphonic acid, carboxylic acid) can independently be used to connect the organic moiety to an inorganic network. More interestingly, it has been previously shown that during the synthesis of hybrids under hydrothermal conditions, chemoselectivity can be controlled by the pH of the reaction media. Indeed, at low pH, materials in which only the phosphonic acid functional groups were bonded to the inorganic network were produced while, at higher pH, the two functional groups were linked to the inorganic network thus producing 3D structures. These findings are also consistent with the work of Zhang et al. that reported the effects of the pH on crystal size of some MOF materials.[55] With the aim of following our previous study reporting the ability of compound **4**, $(Ag_6(4\text{-}PO_3\text{-}C_6H_4\text{-}COO)_2)$, to release silver ions and to act as an efficient bactericidal material,[32] we investigated whether the chemoselectivity principle, previously observed with copper-based materials, could be also applied to silver-based hybrids. Accordingly, we expected to produce silver-based hybrids with different topologies, which might then exhibit different silver release properties when placed in aqueous media. Such modulation of the silver release might open new perspectives for the use of such type of hybrid materials as bactericidal agents. In this study, two organic precursors (3-phosphono-benzoic and 4-phosphonobenzoic) were used as organic precursors of hybrids (Figure 1). For the synthesis of the hybrid materials **1−3**, hydrothermal synthesis were used (140
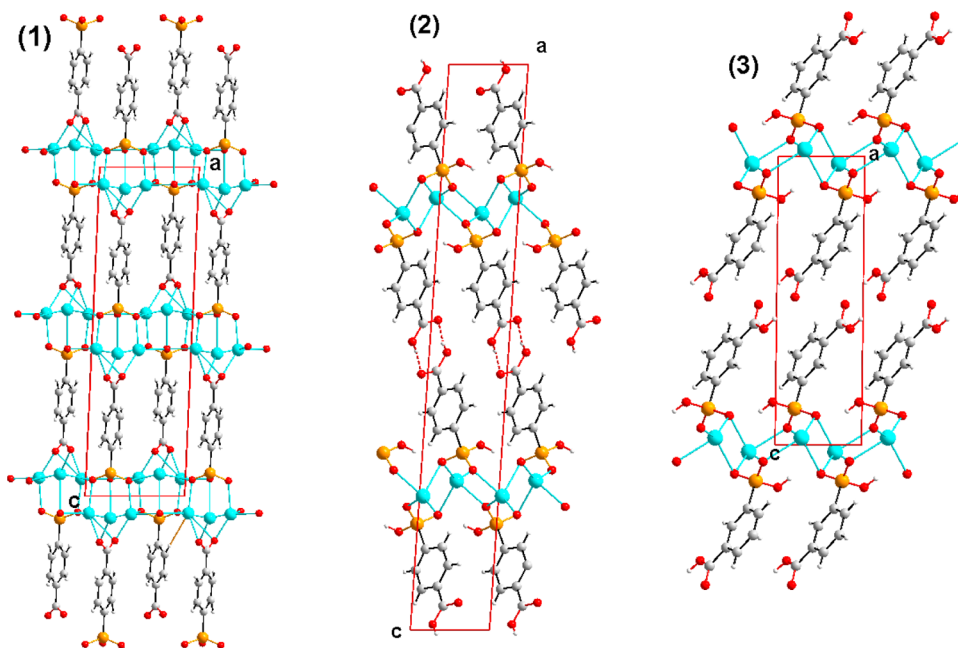
selected materials (**1−4**) was calculated; the amount of KI added corresponded to 4% of the number of silver atom previously calculated (this quantity of KI correspond to an excess when compared to the silver release in solution). The suspension was maintained in the dark until the quantification of the remaining iodide ions in solution by cathodic stripping voltammetry.

This solution was diluted by a factor of 200 in water. Depending on the concentration of iodide in the sample a volume between 50 and 100 μL of the diluted solution was added to 20 mL of the electrolytic solution and the excess of iodide was determined by cathodic stripping voltammetry. After degassing with nitrogen for 10 min, iodide was deposited onto the surface of a hanging mercury at -0.1 V for 30s. The stirring was then stopped and after a rest period of 10 s the scan was initiated in the negative direction. Accordingly, the deposited mercurous iodide was reduced by the cathodic potential scan. Under our experimental conditions, 0.5 M NaCl, 0.01 M HEPES, and triton 0.001% used as electrolytic solution, a current peak is observed at about −0.325 V with respect to to the Ag/AgCl/3 M KCl reference electrode. A platinum wire is used as the auxiliary electrode. The following experimental parameters were used: square wave modulation, pulse height 50 mV, step 1 mV, frequency 50 Hz. At the beginning of each accumulation/stripping cycle 5 mercury drops were discarded. Iodide was quantified by the standard addition method. Indirectly the concentrations of silver in solution were calculated.

Figure 3. Projection along *b* of the structures of **1−3**. Blue, orange, red, gray, and white spheres correspond to Ag, P, O, C, and H atoms, respectively.
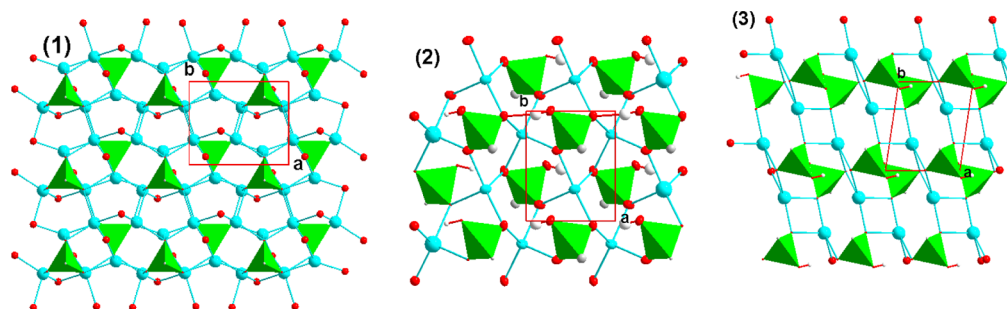
Figure 4. Projection along *c* of inorganic slab of **1**−**3**. Blue, red, and white spheres correspond to Ag, O, and H atoms, respectively, PO$_3$C groups are drawn using green tetrahedra.

°C, 12 or 24 h) in presence or absence of urea as summarized in Table 1.

Thermal Analysis. Thermogravimetric analyses (TGA) were recorded to confirm the absence of water molecules in the structure of each compound and to determine their thermal stability. The analyses were recorded in air flow from 25 to 1000 °C (Figure 2). As expected, no mass lost was observed for these compounds from room temperature to 360 °C thus confirming the data obtained by X-ray diffraction that concluded that no water molecules were present in the structures. These analyses also showed the thermal stability of this series of compounds up to 300 °C. Above 360 °C several weight losses were observed which can be attributed to the degradation of the organic network. The weight losses recorded at 600 °C for **2** and **3** which are respectively of 41.6% and 40.76%, are in good agreement with weight loss expected to the formation of the silver phosphate AgPO$_3$. Concerning **1** and **4**, the weight loss of 21% recorded respectively at 579 and 550 °C is in good agreement with the expected value corresponding to the formation of silver phosphate Ag$_3$PO$_4$. After further heating the final product of this thermal decomposition obtained as pellet was identified by X-ray diffraction as silver metal for (**3**) (Ag, cubic, *Fm$\overline{3}$m*, *a* ≈ 4.087 Å) (Supporting Information Figure SI-7).

Ag$_3$(4-PO$_3$-C$_6$H$_4$-COO) (**1**), Ag(4-PO$_3$H-C$_6$H$_4$-COOH) (**2**), and Ag(3-PO$_3$H-C$_6$H$_4$-COOH) (**3**) were obtained as single crystals. Their structures were solved by single crystal X-ray diffraction. They exhibit a lamellar structure consisting of regular intergrowth of inorganic and organic layers.[33,56] The main difference between these three materials is related to the structure of the organic layers; the organic slabs exhibit a thickness corresponding either to one phosphonobenzoate group or to the stacking of two phosphonobenzoic groups. Following this observation, compounds **1**−**3** can be described as a function of the architecture of the organic part: single or double slab.

The structure of Ag$_3$(4-PO$_3$-C$_6$H$_4$-COO) (**1**) is characterized by an organic slab with a thickness ∼10 Å corresponding to a single 4-phosphonobenzoate group. Its main characteristics are reported in Table 1. In Figures 3 and 4 the projections of the structure along *b* and *c* directions are shown. The organic slab is constructed from 4-phosphonobenzoic groups; both phosphonate and carboxylate functions are involved in the bonding scheme with the Ag atoms; the result is that the 4-phosphobenzoic groups bridge two successive inorganic layers. The three oxygen atoms of the phosphonate end are bonded to three Ag atoms while those of the carboxylate groups are bonded to two Ag atoms. It can be noted that within an organic slab all the 4-phosphonobenzoate groups exhibit head to tail

organization. Owing to this specific organization, the inorganic slabs stack in the *c* direction each having a double layer configuration resulting from the stacking of two adjacent single layers as shown in Figure 5. The oxygen environments of Ag1
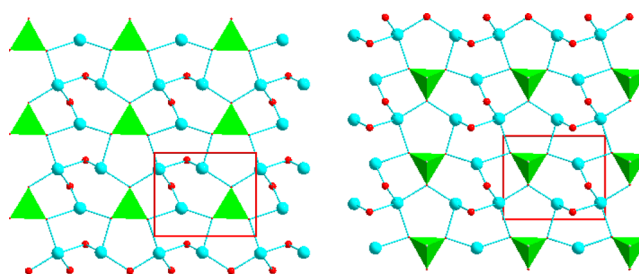

Figure 5. Projection along *c* of the single layers at *z* ≈ 0.06 and −0.06 for the structure of **1**.

and Ag2 define a distorted tetrahedron with the silver located at the center of one face of the polyhedron. Ag3 is surrounded by three nearest neighbor O atoms and is thus located at the center of a triangular plane. The Ag−O distances range from 2.2 to 2.6 Å. Two Ag1O$_4$ (or Ag2O$_4$) tetrahedra share one edge and form an Ag$_2$O$_6$ unit. This unit shares edges with four PO$_3$C tetrahedra, one Ag$_2$O$_6$ and three Ag$_3$O$_3$ units. The main interatomic distances are summarized in Supporting Information Table SI-2.

The second layered architecture is characterized by an organic slab with a thickness of ∼16 Å corresponding to the stacking of two phosphonobenzoic groups; Ag(4-PO$_3$H-C$_6$H$_4$-COOH) (**2**) and Ag(3-PO$_3$H-C$_6$H$_4$-COOH) (**3**) compounds both crystallize with this type of layer structure. The main characteristics of these two materials are reported in the Supporting Information Table SI-2 and SI-5. Contrary to in the situation for material **1**, only the phosphonic acid groups are involved in the bonding with the Ag atoms. As a consequence, the organic slab of **2** and **3** is constructed from dimers formed by two phosphonobenzoic groups connected together via hydrogen bonds involving the free carboxylic acid functions. As revealed by the crystallographic study, two oxygen atoms of the phosphonate group take part to the chemical bond with Ag; one of the acid functions is not deprotonated. In Ag(4-PO$_3$H-C$_6$H$_4$-COOH) (**2**), the silver(I) atoms are surrounded by four oxygen atoms and the Ag−O distances range from 2.30 to 2.46 Å; the resulting coordination is thus a distorted tetrahedron. Each edge of this AgO$_4$ tetrahedron is connected to one HPO$_3$C and to one AgO$_4$ polyhedron.

For Ag(3-PO$_3$H-C$_6$H$_4$-COOH) (**3**) the inorganic sub network is comprised of Ag$^+$ cations which have a highly

distorted tetrahedral coordination geometry. As for the previous compound, the silver cations are surrounded by the four oxygen atoms from phosphonate groups. The distance between the Ag$^+$ cations and the coordinating oxygen atoms range from 2.28 to 2.56 Å and are slight greater than the distances observed for **2**. The observed distorted polyhedra are connected together via one edge to form $[AgO_2]_\infty$ parallel chains running along the $a + b$ direction. These chains are separated by PO$_3$C groups; the structure of one chain is similar to the structure of the tetranuclear unit {Ag$_4$O$_6$} described by Zheng et al.[57] in the silver(I) pyrophosphonates Ag$_2$(ptp) and Ag$_2$(ppp) with [ptp^{2-} = pyro-3-thienylphosphonate, ppp^{2-} = pyrophenylphosphonate. In one chain of compound (**3**), the planes passing through two successive motifs (made of the atoms (Ag$_1$ and O$_3$) and (Ag$_1$ and O$_2$)) are at an angle of 62.677° with respect to one another. Finally, to confirm that the crystal structures obtained by single crystal X-ray diffraction were representative of the whole sample, powder X-ray diffraction were recorded from powder of ground crystals. As shown in Supporting Information Figures SI-1−SI-3 good fits were obtained between powder diffraction and simulation of powder diffraction form single crystal X-ray data.

Pictures recorded by scanning electron microscopy (SEM) confirmed the homogeneity of the samples **1−3**. These three samples exhibited platelet shape as shown in the Supporting Information (SI 4−6).

With four silver-based metal organic materials, including the three new materials **1−3**, their capacity to release silver ions when placed in water was studied. In view of the crystal structure of these materials, we might expect to observe different behaviors in terms of silver release. We have previously reported that compound **4** releases silver ions; this silver release accounted for the bactericidal property of this material against six different bacterial strains.[31] The new materials **1−3** were tested as potential reservoirs of silver ions using the same experimental procedure. Among the different methods frequently used to determine low concentration of silver in water solution, cathodic stripping voltammetry is a very sensitive and highly reliable method.[58] The silver-based hybrid materials **1−3** were suspended in water solution (see Experimental Section) and aliquots were taken up at different times and mixed with an aqueous potassium iodide solution of known concentration. Then, the silver concentrations were indirectly determined by cathodic stripping voltammetry. The results, including the value when compound **4**, used here for comparative purpose, are summarized in Figure 6. First, it was observed that the quantities of silver released into aqueous solution were very different and depended on the structure of the hybrid. Indeed, the more condensed material **1**, in which the carboxylic and the phosphonic acid (para relative position on the benzene ring) were both engaged in bonds with the inorganic network, exhibited only traces of silver ions in water solution after an immersion period of 2 days. In comparison, compound **4**, which was previously studied, exhibited a higher release despite the fact that in this material the two functional groups (carboxylic and phosphonic acid in a meta relative position on the benzene ring) are also connected to the inorganic network. As shown in Figure 3, the structure of compound **1** seems to be denser than that of compound **3** or **4**.[32] This observation is confirmed by the calculated densities (Table 1) which are 3.78, 2.43, and 3.63 g/cm^3 for **1**, **3**, and **4**, respectively. With respect to the silver ion release capacity, the more open structure of compound **4**, is the likely reason for its
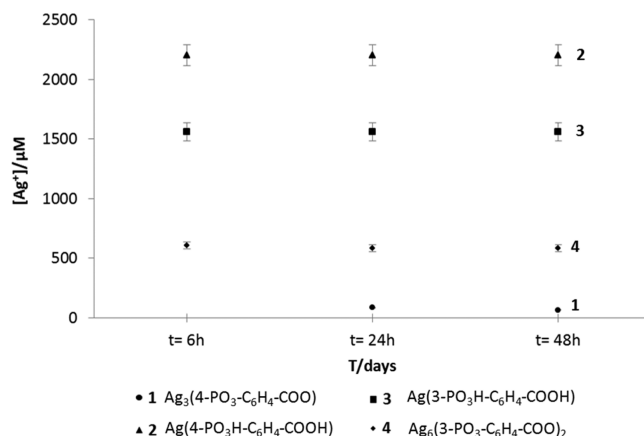

Figure 6. Concentration (μM) of Ag$^+$ in solution as a function of time when 12 mg of a selected material (**1−4**) was placed in 1 mL of water (t = 6 h corresponds to the first analysis). (Error bars for the quantification of silver release from material **1** are not visible.)

higher capacity to release silver ions when compared to compound **1**. For the materials **2** and **3**, in which only the phosphonic acid functional group is linked to the inorganic network, the quantity of silver released was profoundly increased when compared to **1** and **4**. This result could be explained by the presence of free carboxylic acid functional groups within the structure that could favor the initial hydration of the materials leading to an enhancement in their solubility. Moreover, it is likely that the stability of these hybrids toward dissolution in polar solvents is dependent on the number of functional groups that are connected with the inorganic network. In other words, this can be view as a stabilization by a cooperative effect. Another point to note concerns the kinetics of release. It can be observed that the silver concentration in water (Figure 6) reached a plateau after 2h for compounds **2−4**. This observation could be explained by an equilibrium that involves the silver ion in solution and the silver ion immobilized at the surface of the hybrid materials. We have previously shown that this equilibrium can be shifted toward the dissolution of the hybrid in water by successive replacement of the supernatant water solution by fresh water solution.[32] Altogether, these results suggest that the hybrid materials can act as reservoirs of silver ions. The release process likely occurs at the interface of the solid and water solution until equilibrium is reached. Finally, the amount of silver release in solution depends on the structure of the hybrid, thus demonstrating that the topology of the hybrid material can be used to design materials possessing a tunable capability of releasing silver ions in its aqueous environment.

■ CONCLUSION

Three new silver-based metal−organic frameworks were synthesized and structurally characterized. These hybrid materials were synthesized from either 3-phosphonobenzoic and 4-phosphonobenzoic acids and silver nitrate under hydrothermal conditions. For these silver-based MOFs, as we previously reported for other copper and zinc-based metal organic frameworks, the pH of the reaction media is a key factor which explains the chemoselectivity observed during the formation of the hybrid. At low pH only the more acidic phosphonic acid is bonded to the inorganic network as in compounds **2** and **3**. On the other hand, the addition of urea in the pressure vessel, increased the pH thus producing a hybrid in

which both functional groups were connected via iono-covalent bonds to the inorganic network as illustrated with compound **1**. These results also demonstrate the interest of using heterodifunctional organic precursors since hybrids with different topologies can be produced by simply altering the pH of the reaction media. The silver ion release capability was then tested by placing these materials in water solution. The silver ion concentration in supernatant solution was determined by cathodic stripping voltammetry. It was shown that materials (**1**) ($Ag_3(4\text{-}PO_3\text{-}C_6H_4\text{-}COO)$), which exhibited the more compact structure released only traces of silver ions in solution while materials (**2**) (Ag ($4\text{-}PO_3H\text{-}C_6H_4\text{-}COOH$) and (**3**) ($Ag(3\text{-}PO_3H\text{-}C_6H_4\text{-}COOH)$)), characterized by the presence of free carboxylic acid functional groups in their structure, released more easily silver salts in water. These results, concomitantly with the silver release capacity of material **4** previously reported, clearly show that the silver release is dictated by the topology of the hybrid. Accordingly, the silver release capacity in a surrounding aqueous solution can be tune by designing hybrids with an adapted structure as exemplified in this study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data positional parameters and hydrogen bonds length and angle for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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