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Phosphate-Based Organic-Inorganic Hybrid Materials: Design, Construction and Technological Applications

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Abstract

The art of designing and synthesizing organic molecules has reached very high levels of sophistication, based on a *relatively simple set of rules* that guide both the invention and synthesis of new compounds. This set of rules is construed as the *rational synthetic method* of organic chemistry. As material chemists confronted to the task of building new solid structures with tailored chemical properties, we do inevitably need to develop some rational approach and to establish the corresponding set of rules allowing a realistic level of predictive knowledge in the construction of solid scaffolds. These conditions are reasonably accomplished by the use of layered salts of tetravalent transition metals, namely zirconium phosphate (ZrP). The placing of organic molecules between the layers of ZrP is quite straightforward, can easily be controlled and leads to enduring, solid materials where the confinement makes the organic molecules to show new properties at the supramolecular level. The chemistry of metal phosphates/phosphonates will be detailed in relation with the following topics: (i) molecular recognition, (ii) chemically driven porosity changes, (iii) chiral memory and supramolecular chirality, (iv) luminescence signalling, (v) photo-induced electron-transfer processes, (vi) hydrogen storage, (vii) confinement of drugs and (viii) metal uptake.

Keywords: hybrid-layered materials, zirconium phosphate, porous materials, intercalation reactions, topotactic exchange, hydrogen storage, luminescence signalling, supramolecular chirality, molecular confinement, metal uptake

1. Introduction

Phosphoric acid (PA) is an important industrial acid that is widely used to manufacture a myriad of different industrial products for an extensive range of applications. The exploitation of

PA has become global and its utilization to producing innovative chemical structures is a trend that is expanding worldwide as well. Along these lines, in this chapter, we focus on our past and ongoing research devoted to the rational design and construction of *porous frameworks* based on layered metal phosphates and their technological applications.

Phosphate-based-layered organic-inorganic materials, especially those built from octahedral corner-sharing zirconium and tetrahedral phosphate, have attracted much attention and aroused increasing interest from the viewpoint of developing novel functional porous materials for many fields of *modern technology*, such as luminescence materials [1], chiral molecular selectors [2, 3], hydrogen adsorbents [4–6], drug-delivery systems [7] and materials for waste water treatment [8–10].

2. Layered metal (IV) phosphate

The area of chemistry that explores the porous materials has received a great impulse in the past 40 years. In addition to the classic porous materials (e.g. activated charcoal, silica, alumina and zeolites), synthetic materials have been developed with analogous structures to those observed in Nature. An important landmark in this field has been the preparation of synthetic zeolites, which have a significant role as they could be used as catalysts, adsorbents and ion exchangers.

An important effort has been dedicated to the development of other porous materials with analogous three-dimensional (3D) structures. To this effect, the chemistry of metallic phosphates [11] with laminar structure has received a great impulse, because they are very versatile materials whose handling complies with what we have termed rational synthetic method, that is, the development of a set of relatively simple rules that confers sufficient predictive knowledge to the building of crystalline materials. The synthetic rationale elaborated by us through a number of years [12] is modular because it comprises the design and synthesis of appropriate organic molecules in one hand, and on the other their stepwise introduction into the inorganic framework. Common characteristics of this synthetic approach to solid materials based on layered metallic phosphates are as follows: (i) their reactions proceed at low temperatures; (ii) they can be functionalized with either organic or inorganic molecules, by ionic or covalent bonds, which confers them with very specific properties and a broad field of application; (iii) their functionalization is accomplished by means of *topotactic* reactions, which do not affect the fundamental structure of the material, so that it is possible to predict the arrangement of the final products; (iv) when the introduced organic moieties have two reacting ends, it is possible for them to bind consecutive lamellae of these materials and three-dimensional, pillared structures can be thus easily created.

Basically, layered structures formed by zirconium phosphate (ZrP) are produced by octahedra-tetrahedra combinations in two main different formats, named α - and γ -phases, where zirconium coordination varies from one to another (**Figure 1**). In both α - and γ -structures, zirconium coordinates octahedrally to six oxygens of six surrounding phosphates. However, in α -phase, all phosphates (HPO_4) are equivalent and they all use three oxygens to bond to zirconium, whereas in the γ -phase phosphates are of two types: PO_4 that uses its four oxygens to

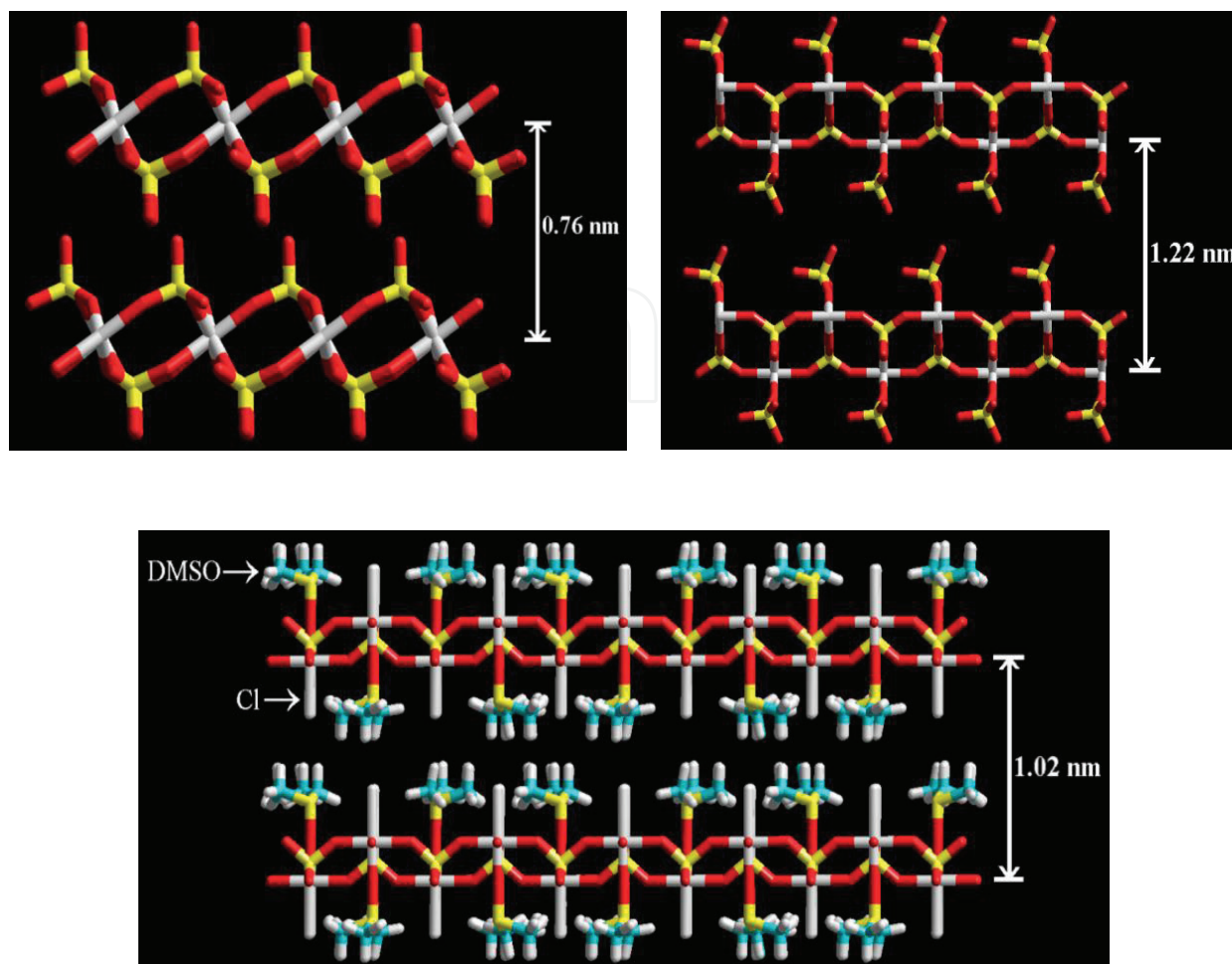


Figure 1. Tube models (Zr, grey; P, yellow; O, red; H, white) of two consecutive layers of α -ZrP (top left), γ -ZrP (top right) and λ -ZrP (bottom). The experimental interlayer distances are shown (Color figure online).

coordinate to zirconium and H_2PO_4 that puts into play only two oxygens to do that. Thus, the molecular formulae for α - and γ -ZrP are $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$, respectively [13–15].

A third type of ZrP (hereafter referred as λ -ZrP) structurally related to γ -ZrP can be obtained by coordinating the four oxygen atoms of the PO_4 group to four different zirconium atoms and completing the zirconium octahedral structure with one negatively charged monodentate ligand (usually chloride or fluoride ion) and another neutral monodentate ligand (dimethylsulphoxide) [13–15]. The structure of λ -ZrP [$\text{ZrPO}_4\text{Cl}(\text{dmsO})$] is shown in **Figure 1**.

3. Reactions

3.1. Intercalation

The intercalation properties of zirconium phosphate have been extensively investigated due to their interesting fundamental aspects and possible applications as well, including ion

exchange, high-temperature stable organic-inorganic composites, ion conduction, catalysis, and so on [16–18].

It is well known that the intercalation chemistry of α - and γ -ZrP is dominated by the presence in the interlayer region of Brønsted acid OH groups [19]. They are powerful phases for the entrapping and exchanging of organic cations such as primary alkylamines and aminophenyl- and pyridinium-substituted porphyrins among many other examples [8, 9, 19].

We have recently prepared λ -ZrP with Brønsted acid properties, λ -ZrPO₄[OOC-(CH₂)₄-COOH] (CH₃)₂SO (**Figure 2**), by means of topotactic anion exchange of the chloride ligand in λ -zirconium phosphate [λ -ZrPO₄Cl(CH₃)₂SO] with adipic acid (AA). The so-synthesized λ -(AA)ZrP solid phase has a higher acidic character and a larger gallery height in comparison to the pristine λ -ZrP (1.47 and 1.02 nm, respectively). Therefore, this material is expected to be a suitable host for intercalation of relatively large basic guests [20].

With respect to the intercalation of primary alkylamines into layered ZrP, it has many potential uses and technological applications. Moreover, it constitutes a very powerful synthetic tool to facilitate the insertion of large organic and inorganic radicals inside the interlayer gallery of layered solid materials [21–31]. In this regard, it should be mentioned that the intercalation chemistry of λ -ZrP has not as yet been as well investigated as that of α - and γ -ZrP [21–29].

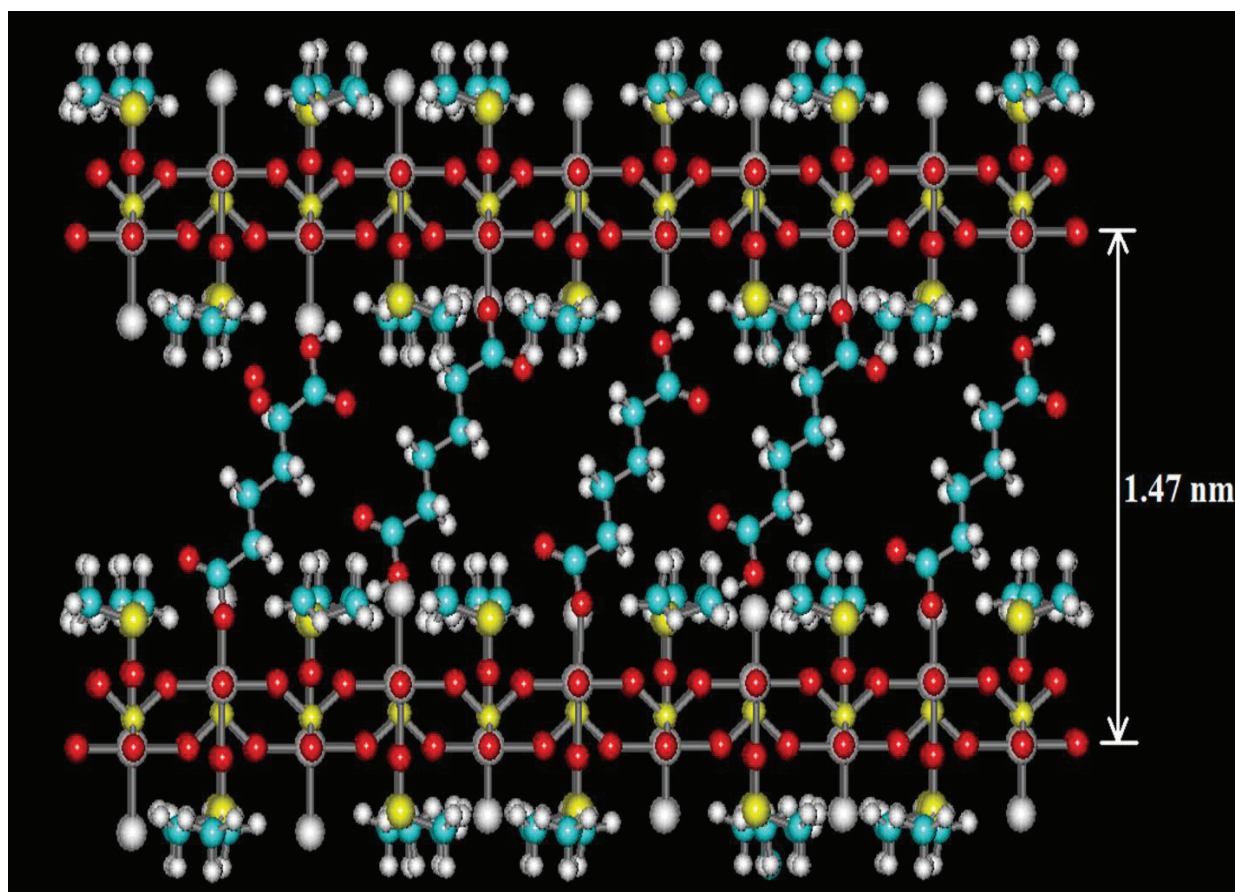


Figure 2. Possible arrangement of AA molecules in λ -(AA)ZrP complying with the observed interlayer distance.

Recently, primary alkylamines, namely methyl-, ethyl-, butyl- and hexylamine, has been successfully intercalated into λ -ZrP in our laboratory. In this way, λ -type materials with increasing interlayer separation are easily obtained [32].

The experimental data are only compatible with the formation of a double layer of alkylamines in a zig-zag conformation as shown in **Figure 3**. This behaviour is common to all ZrP phases, the relationship between interlayer distance and amine chain length being linear indicating that the longitudinal axis of the alkyl group should be inclined relative to the average plane of the inorganic layers [32].

The increase of basal spacing suffered by ZrP upon alkylamine intercalation makes it possible for the water molecules to penetrate the interlayer region to solvate the polar groups. The suspension of the resulting amine-intercalated materials in water may be further manipulated to carry out topotactic exchange reactions and insert large organic and inorganic species of different functionality (polar-non-polar, rigid-flexible, chiral-achiral, acid-base, etc.) inside the interlayer galleries of ZrP. Accordingly, new tailored organic-inorganic materials for many scientific applications can be obtained [33, 34].

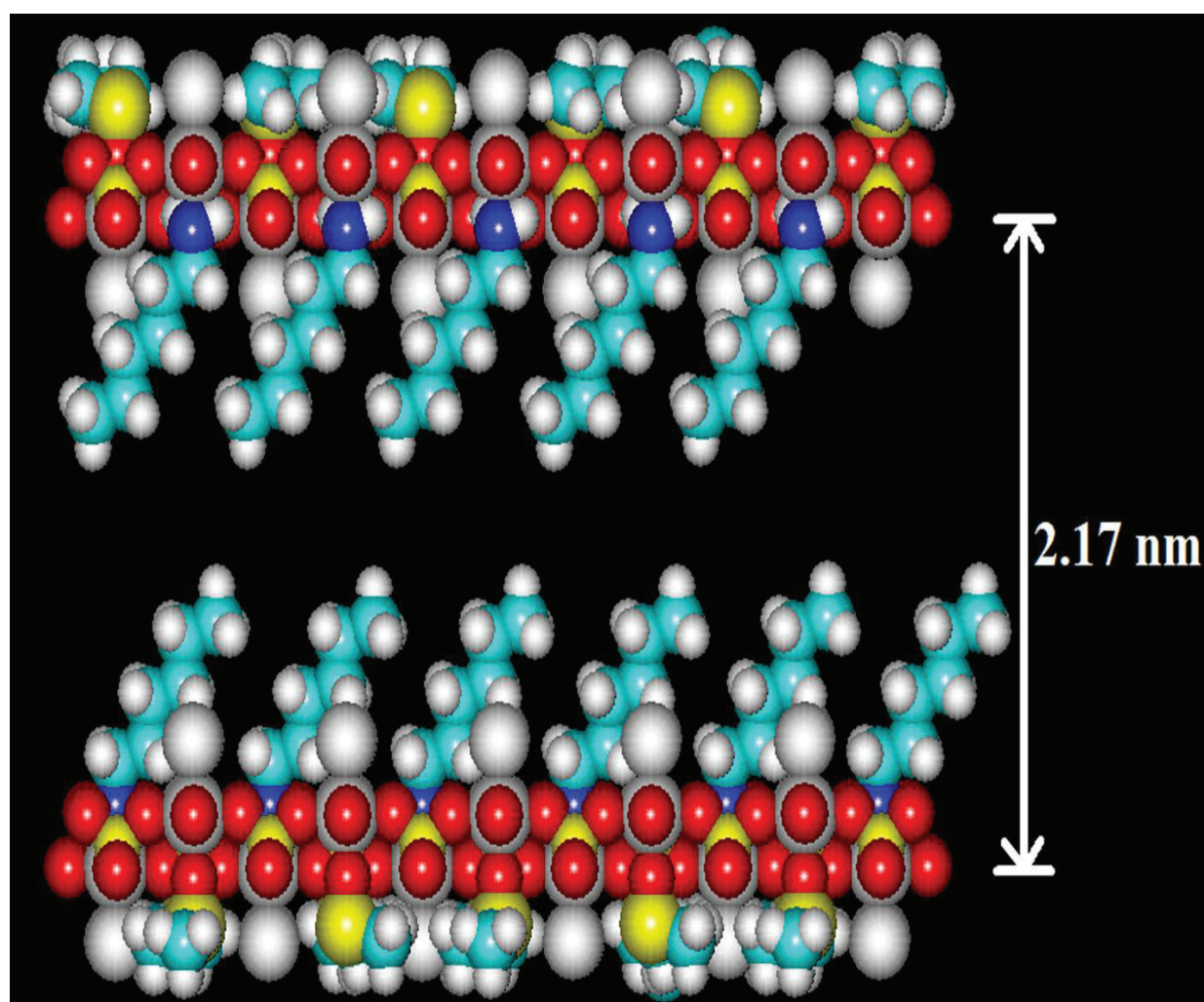


Figure 3. Possible arrangement of hexylamine inside λ -ZrP complying with the observed interlayer distances.

3.2. Topotactic exchange

The most interesting reaction of γ -ZrP is that in which the acidic surface phosphates are replaced by other phosphorous functions such as phosphonates (**Figure 4**) [26, 27]. For this reaction to take place at a reasonable rate, the layers of γ -ZrP have to be separated first in a process named exfoliation [22], either by intercalation of an alkylamine of sufficient chain length or by solvation of the inorganic layers in a 1:1 mixture of water-acetone at 80°C. The exchange reaction takes place in a topotactic manner, that is, it occurs without affecting the integrity and rigidity of the inorganic layers.

Mixed organic derivatives of γ -ZrP such as γ -ZrP/phosphonate, γ -ZrP/phosphite and γ -ZrP/phosphinate compounds are possible. Thus, γ -ZrP derivatives can be represented by the formula $\text{ZrPO}_4 \cdot \text{O}_2\text{PRR}' \cdot n\text{S}$, where R and R' can be H, OH or an organic group and S is the intercalated solvent.

When the topotactic phosphate/phosphonate exchange reactions occur at the same time on the facing surfaces of two adjacent layers by a molecule with two phosphonate groups, pillared γ -ZrP is formed (**Figure 4**).

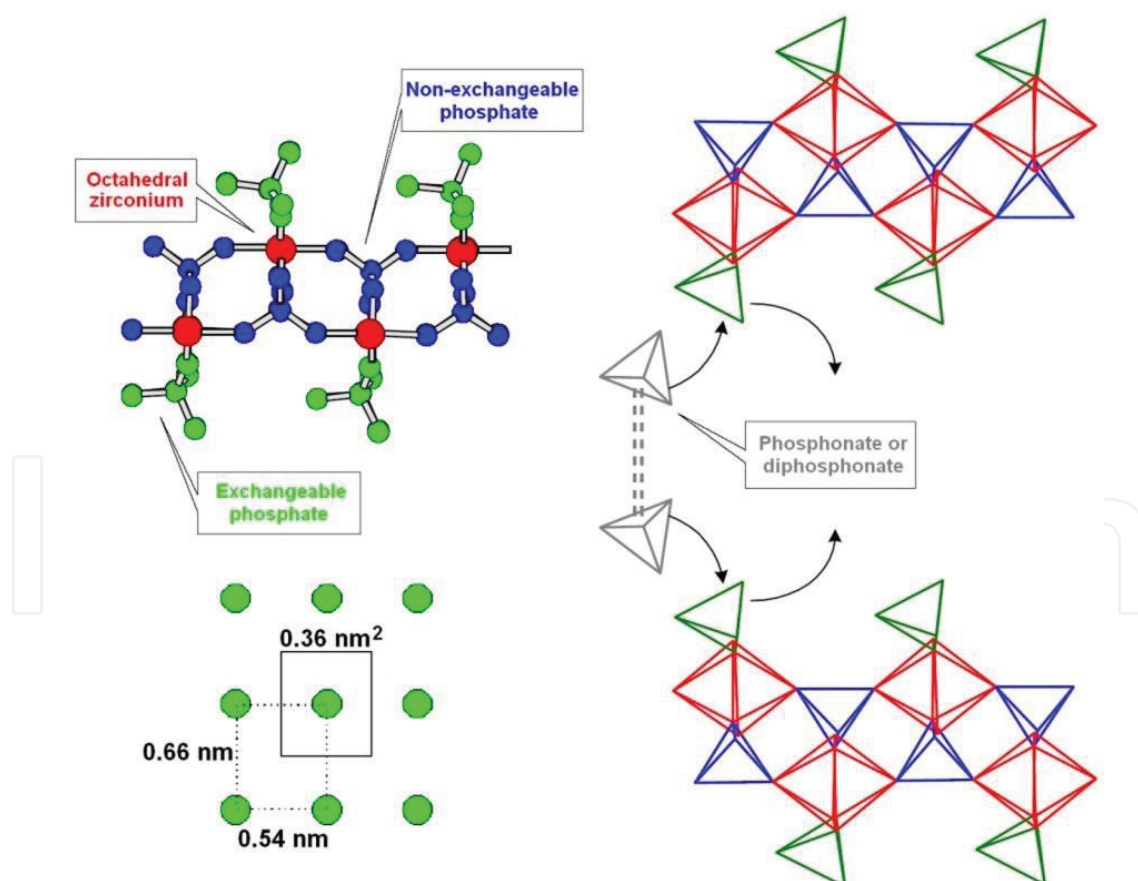


Figure 4. From top-left counterclockwise: (i) schematic structure of a portion of a layer of γ -ZrP; (ii) dimensions of the grid formed by superficial phosphates on a layer; (iii) representation of the topotactic exchange of γ -ZrP by a phosphonate or diphosphonate.

Regarding the pillared derivatives of α -ZrP, they are obtained by allowing zirconium fluoro-complexes to decompose in the presence of diphosphonic acids [26, 27].

If the pillars have a suitable height and are sufficiently spaced, microporous materials are thus obtained. Pillars could be either rigid or non-rigid, the latter being the most versatile as the porosity of the materials can be controlled by simple chemical means [35–38]. The outstanding features of these materials come from their ability to combine the properties of both the organic pendant groups with those of the inorganic host [39]. Such an approach can result in the design and development of hybrid organic-inorganic materials with tailor-made properties. These materials can function as molecular sieves of controlled pore size [39], shape-selective catalysts [40, 41], molecular sorbents [42, 43] and stationary phases for chiral molecular recognition [2, 44].

Concerning the relatively unexplored λ -ZrP phase, it is worth mentioning that the chloride and dimethyl sulphoxide ligands of λ -ZrP (*cf.* **Figure 1**) can be topotactically exchanged by other monovalent anionic ligands (alkoxides, carboxylates, etc.) and neutral monodentate ligands (sulphoxides, amines, etc.), respectively [45]. If dialkoxides or dicarboxylate ligands are used, λ -layered-pillared organic-inorganic derivatives are obtained.

We have recently prepared several new porously dynamic layered-pillared materials (**Figure 5**) with a general formula of λ -ZrPO₄(OH)_{1-x}(OOC(CH₂)_nCOO)_{x/2}(dmsO)_n ($n = 6, 8$ and 10) by post-synthesis modification of the inorganic layers of λ -zirconium phosphate (λ -ZrP), where the superficial chloride monovalent anionic ligands of λ -layer are partially exchanged with the divalent anionic ligands of a series of long-chain aliphatic dicarboxylic acids, namely octanedioic, decanedioic and dodecanedioic acids.

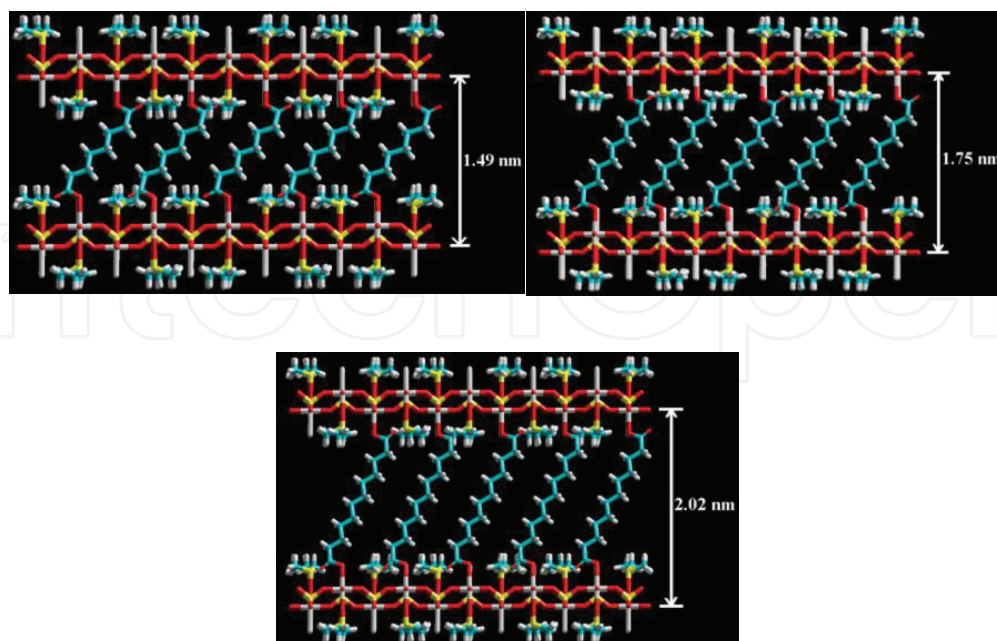


Figure 5. Possible arrangement of octanedioic acid (*top left*), decanedioic acid (*top right*) and dodecanedioic acid (*bottom*) inside λ -ZrP.

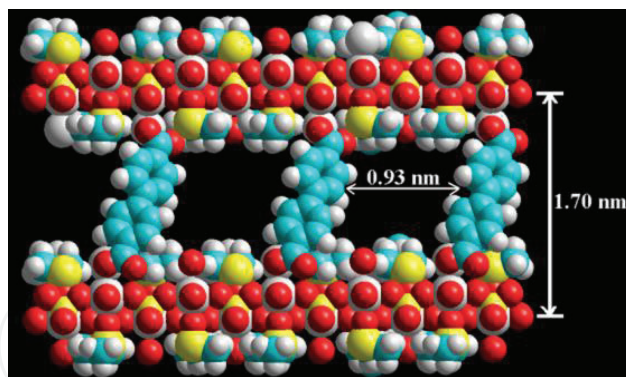


Figure 6. Possible arrangement of bpdc inside λ -ZrP (40% pillaring).

More recently, a new λ -type-layered-pillared rigid microporous framework based on λ -ZrP and 1,4-biphenyldicarboxylate (bpdc) (**Figure 6**) has been prepared in our laboratory [46].

4. Design, processing and applications of ZrP-based porous materials

Over the past decades, the chemistry of ZrP structures has been studied intensively [12]. In particular, compounds with organic radicals covalently attached to the inorganic layers of ZrP. These organic-inorganic frameworks are prepared by two main synthetic approaches: (i) thermal decomposition of zirconium fluoro-complex in the presence of phosphonic acids (α -type derivatives) [19, 24, 26, 27, 35], and (ii) post-synthetic modification of the inorganic surface of γ - or λ -ZrP by means of topotactic ligand exchange reactions with phosphonic acids [5, 19, 24, 26, 27, 47] or carboxylic acids [32, 33, 45], respectively.

It is important to stress out that the post-modification of the inorganic surface of γ - or λ -ZrP is carried out without the destruction of the former framework structure (**Figure 4**). Therefore, protocols and strategies of rational synthetic design can be easily applied which turn ZrP into a *chemical-engineering tool* to build organic-inorganic frameworks in the solid state. This rationale provides the opportunity to effectively adjust the relative position of the organic radicals inside the solid matrix and thus adjust the latter's molecular geometry as a whole. As a result, the *by and large properties* of the final material are tuned with high precision [12]. At this point, the reader should not be misled by the conceptual, apparent simplicity of the topotactic exchange reactions. In particular, the mechanism of the replacement of the surface phosphates in γ -ZrP must imply a phenomenal process, even though it looks schematically simple. Unfortunately, there are no studies in the literature concerning the thermodynamic parameters of this process, probably because the colloidal milieu, in which the reaction is performed, makes the measurements difficult.

Considering versatility, the lambda structure is special. As we mentioned earlier, a layer of phosphates sustains the zirconium metals whose apical bonds are bonded to negative and neutral basic species, both pointing to the interlayer space (bottom of **Figure 1**). In the starting lambda structure, each zirconium is typically bonded to chloride anion and neutral

dimethylsulphoxide molecule [48, 49] which, in principle, can be replaced by any organic chemical structure, that is, carboxylates and amines, in a topotactic manner [32–34, 45]. Recently, we have prepared several new soft and rigid phosphate-based λ -type organic-inorganic two-dimensional (2D) and 3D frameworks with *variable porosity* [10, 20, 32, 34].

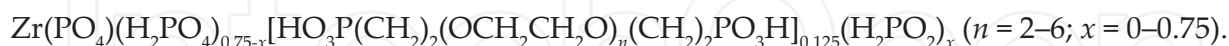
In summary, the chemical properties of the ensuing composites can be tailored by carefully selecting the physical and chemical functionalities of the organic building blocks that will be modified by their confinement between the inorganic layers. We envisage that the only limitation of this entire approach is the imagination and needs of the researcher.

4.1. Variable porosity

The realization that the layers of ZrP phases containing organic derivatives can be considered as a multiple-storey labyrinth immediately hits the idea of molecular recognition. In principle, if one was able to control the level of incorporation of organic molecules within the layers, the resulting material would be porous enough to allow guest molecules to travel between the lamellae and differentially interact with them. One way of achieving this goal is to include crown ethers.

Our seminal paper on the topotactic exchange with various crown ethers [50] of different sizes, containing one or two phosphonate groups, allowed for a higher control of the number of incorporated species, giving rise to highly porous materials. Yet, despite all the interesting structural findings, the true importance of the work is the achievement for the first time ever of multiple, sequential topotactic exchange reactions, namely the further replacement with methylphosphonate of the remaining phosphates from the initial, partial phosphate/crown-ether phosphonate exchange reaction.

Another way of approaching the building of crown-ether-like supramolecular structures is the use of diphosphonates derived from linear polyethylene glycol chains, in order to create pillared materials with polyethylenoxa chains (**Figure 7**). By simply varying the chain length, the access to a set of different labyrinths with sticky columns of different height and different porosity is made accessible. Further replacement of the remaining phosphates by hypophosphite (H_2PO_2) led to different sets of materials, named as *polar/polar* (polar columns and polar surface phosphates) and *polar/non-polar* (polar columns and non-polar surface hypophosphites) of the following general formula:



The unexpected behaviour occurred when these materials were treated in aqueous dispersion with the small base methylamine. Surprisingly enough, the *polar/polar* material steadily augmented its interlayer distance (*ca.* 1 nm) with the increasing amount of the small intercalating amine (pH = 2–9). Yet, its *polar/non-polar* counterpart suffered an abrupt increase of interlayer distance (*ca.* 1.4 nm) in a much narrower pH range (pH = 4–5). The starting interlayer distance at low pH was way shorter (1.3–1.7 nm) than that expected considering the length of the polyethylenoxa chains. Therefore, in the absence of methylamine, the chains had to arrange in a parallel fashion to the inorganic layers leading to a compact material. Nonetheless, at high pH the distance heavily increased reaching a value only compatible with extended, perpendicular polyethylenoxa columns. Yet, methylamine is so tiny that the substantial distance increment could not be solely attributed to the size of the intercalated amine. The plausible explanation could be that, owing to the intercalation with the basic methylamine molecules, hydrogen bonds between pillars (polyethylenoxide chains)

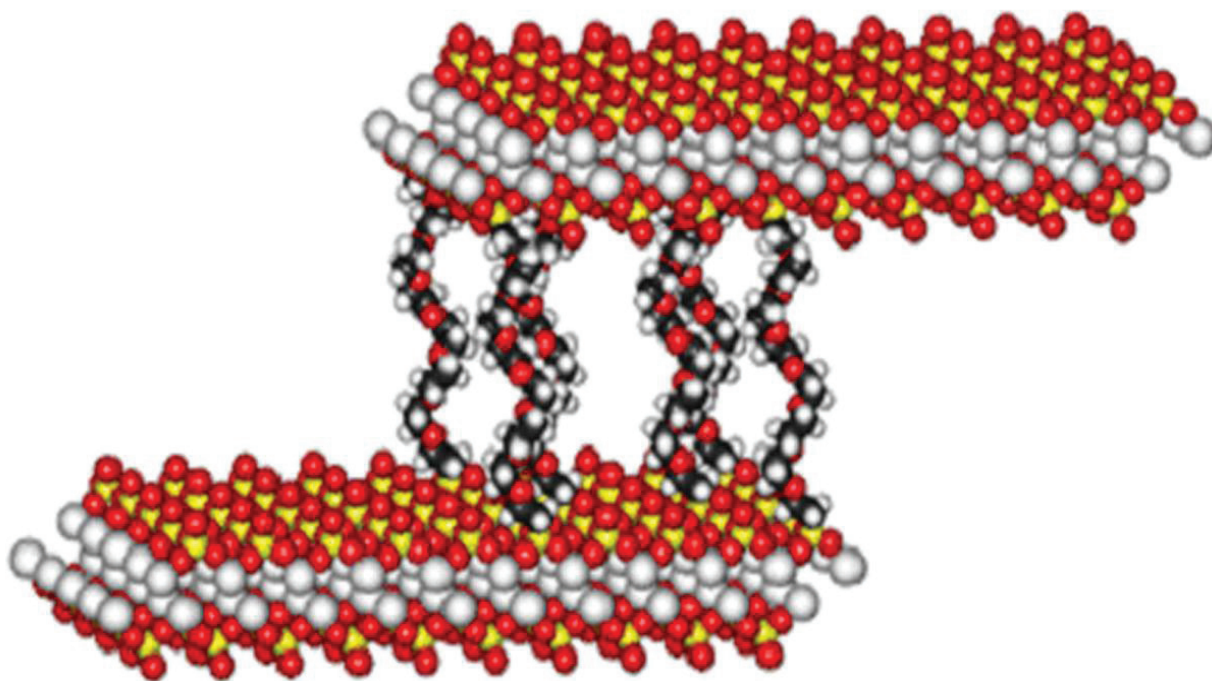


Figure 7. Idealized molecular model of γ -ZrP exchanged with pentaethylene glycol diphosphonate as a representative example.

and $\text{O}_2\text{P}(\text{OH})_2$ acidic groups of the layers are broken. Therefore, the number of water molecules in the interlayer region is increased and the polyethylenoxide chains are forced to align perpendicular to the layers. This odd supramolecular behaviour in the solid state, where the porosity of a layered material is abruptly increased in response to a simple acid-base reaction in the solid-liquid interface, has never been observed before [44].

4.2. Dissymmetry and luminescence signalling

Molecular modelling of the *polar/polar* and *polar/non-polar* materials (see previous section) in the extended arrangement, that is, when the amine was present, suggested that in order to fit the largest achieved interlayer distances, the polyethylenoxa columns had to be helicoidally arranged. Polyethylene glycols are actually known to attain that conformation in aqueous solution. Yet, what makes a notable difference in the previously discussed materials is that the polyethylenoxa columns are covalently attached by both ends to the inorganic layers, thus conferring to the whole scaffold a supramolecular dimension. In principle, should the appropriate conditions be established, the random P/M helicity of the chains could be driven towards homochirality. Notably, this homochirality has been revealed by optical rotation measurements. To achieve that, we performed the following simple experiment.

Dispersions of small amounts in water/acetone of either native γ -ZrP or exchanged at 25% with hexaethylene glycol diphosphonate ($n = 6$; cf. molecular formula in previous section) displayed no sizeable optical rotation as expected. However, the material pillared with hexaethylene glycol diphosphonate intercalated with (+)-phenethylamine rendered a relatively large value of optical rotation. Surprisingly, when the enantiomerically pure amine was smoothly

replaced with achiral hexylamine, the optical rotation kept amazingly showing through. Nuclear magnetic resonance (NMR) experiments proved that the (+)-phenethylamine was no longer in the material. Hence, the only possibility left to explain the remaining optical activity must be laid upon the polyethylenoxa columns that had to acquire a certain bias in their initially random P/M helicity. This bias had to be induced by the concurrence of the chiral (+)-phenethylamine and maintained when the latter was replaced by the achiral hexylamine. These facts were interpreted as an expression of supramolecular chiral memory [3]; no similar cases can be found in the literature.

The unexpected findings went a step further. What would happen if the chiral influence was intrinsic to the polyethylenoxa chains? To answer this question, enantiomerically pure diphosphonates were prepared [2] and topotactically exchanged into γ -ZrP at the 25% level. The intrinsically chiral polyethylenoxa columns were forced to acquire different conformations by the intercalation of amines of increasing length. The longer the amine, the more elongated the organic pillar. As anticipated, the basal spacing progressively increased with the length of the amine. On the contrary, it was outstandingly found that the optical rotation presented a maximum value when hexylamines were intercalated. Molecular modelling of the different intercalates, performed by maintaining the interlayer distance fixed at the corresponding experimental value and allowing the organic chain to freely reach the most stable conformation, showed that the maximum expression of helicity was precisely achieved at the spacing attained with butyl- or hexylamine. No other reasonable explanation could be found to account for the observed variation of the optical rotation versus interlayer distance.

In summary, the unexpected chirality behaviour of the accounted materials clearly pointed to the important fact that chiral properties can be created and amplified at the supramolecular level in the solid state and finely tuned by mild reactions in the solid-liquid interface [51–53].

Important research is being directed to the design of molecular systems able to display the strong luminescence of lanthanide metals [53]. To accomplish it with efficiency, two stringent conditions have to be met: (i) a suitable organic chromophore should absorb light and efficiently transfer energy to the metal (*antenna effect*), (ii) the coordination sphere of the metal should be free of water molecules because the OH oscillators easily quench metal emission. The first condition has been achieved either by simple acid-base intercalation or by topotactic exchange of suitable chromophores in the organic-inorganic lattice. The second, by using the pillared materials with polyethylenoxa columns described above, constituted an excellent spider web to enshroud the oxygenphilic lanthanide metals and isolate them within the solid matrix. Additionally, the chromophores have been provided with chirality. The resulting materials exhibited circularly polarized luminescence (CPL) of lanthanides, an elusive property in the solid state which could find important applications in the technology of optical handling of information.

4.3. Gas and vapour storage

Hydrogen storage is attained by *physisorption* in porous matrices [4, 54] among other procedures. The attachment of polyphenyl or polyphenylethynyl diphosphonates to either of the ZrP phases (cf. **Figure 6** as an example) led to materials with slit-like ultramicropores of different length. Further exchange reactions allowed for the attachment of polar or non-polar

groups at both ends of the pores. This set of materials was tested for hydrogen storage. The best results were obtained with the material named αT60Li , $\alpha\text{-ZrP}$ with 60% of terphenyl-diphosphonates [6], the remainder phosphates bearing Li^+ as counterions. At 800 Torr and 77K, 1.7% w/w of hydrogen could be stored and the Department of Energy goal for 2010 (45 g of hydrogen per L of material) was thus attained below 2 atm. at 77K.

4.4. Building DSSCs

Phosphonate derivatives of the $\text{Ru}^{\text{II}}(\text{bpy})_3$ complex were attached to $\gamma\text{-ZrP}$ and placed side-by-side to different electron acceptors ranging from relatively simple viologens to more elaborated fullerene derivatives [55]. The first important observation was that the phosphorescence emission of the $\text{Ru}^{\text{II}}(\text{bpy})_3$ complex was heavily quenched by the presence of the electron-acceptor species, indicating that the pursued electron transfer took place. More recently, flash photolysis revealed some of these materials to have outstanding properties in that the separation of charges is long lived and the initially thought inert inorganic layer resulted in semiconducting, thus driving the separated electrons and/or holes along the material [56]. Additional results showed that these powders can be arranged as solar cells with promising efficiency [57].

4.5. Molecular confinement of drugs and dyes

Confinement of drugs into molecular matrices might be a good solution to their slow release at particular locations on the body [55]. Preliminary studies show that the erythromycin family antibiotics can intercalate into ZrP phases. The measurement of the interlayer distance versus the stoichiometry of the reactants shows that mono- and bilayers of erythromycin derivatives, as an example, may be enclosed between the inorganic lamellae.

On its part, dyes are an integral part of many technologies. For example, Malachite green (MG) is used in Gram's stain which is a technique used to classify bacteria. Also, it is used for anti-fungal purposes. However, many dyes are toxic and carcinogenic and have to be handled with special care if serious environmental contamination is to be avoided. Purification of water and air resources that contain even traces of dyes is an important technological challenge and has attracted wide attention. Dye-containing coloured water is of no use but appropriately bleached solutions may still be used for washing, cooling, irrigation and cleaning purposes. Materials able to efficiently entrap dyes are thus quite desirable. **ZrP** phases serve this purpose as well (**Figure 8**) [8, 9].

These preliminary results are a good omen regarding the high prospects of using ZrP phases in the uptake of different drugs and dyes like MG or its next-of-kin methyl- and crystal violet. They also show the importance of ZrP and its surfactant composites in the field of intercalation and inclusion chemistry of bioactive organic compounds within layered inorganic and organic-inorganic materials.

4.6. Metal uptake

One measure of water quality is its 'hardness' which is defined by its Mg^{2+} and Ca^{2+} ion contents. The synthesis and design of materials towards efficiently entrapping Ca^{2+} are of great

industrial importance because hard water, on being heated, precipitates calcium carbonate which clogs boilers and pipes. Moreover, Ca^{2+} reacts with soap and produces an insoluble product (soap scum). This scum is abrasive and may weaken clothes fibres.

λ -ZrP and its new ethylenediaminetetraacetic acid (EDTA)-functionalized derivative (λ -ZrPH₂Y) strongly complexes Ca^{2+} . The results are given in **Figure 9** [10].

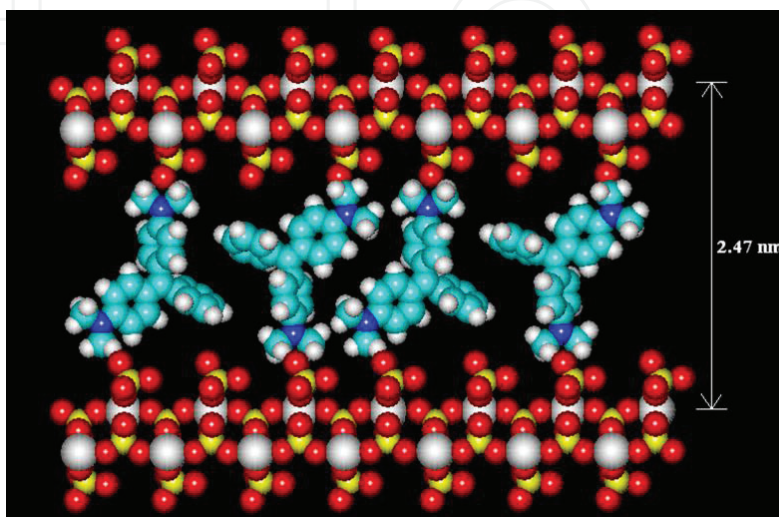


Figure 8. Possible arrangement of MG intercalated in γ -ZrP complying with the observed interlayer distance measured by XRD.

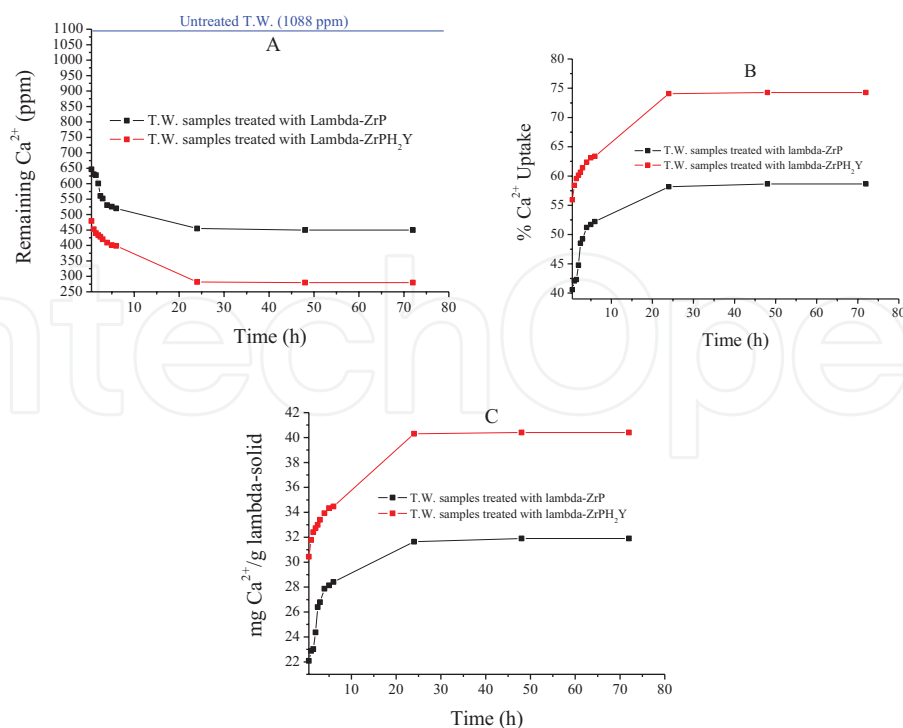


Figure 9. Kinetic curves of Ca^{2+} uptake from tap water samples (T.W.). (A) The remaining concentration of Ca^{2+} (ppm) in TW samples after treatment with λ -solids. (B) % Ca^{2+} uptake by λ -ZrP and λ -ZrPH₂Y. (C) Ca^{2+} uptake capacities of λ -ZrP and λ -ZrPH₂Y (mg g^{-1}).

Metal uptake reached the equilibrium after ca. 24 h, where the maximum Ca^{2+} uptake is obtained (32.0 and 40.4 mg Ca^{2+} /g λ -phase, respectively), corresponding to ca. 0.8 and 1.0 mmol Ca^{2+} /g λ -phase and % Ca^{2+} uptake of 60 and 74% (**Figure 9B**), respectively.

These positive results have stimulated the testing of λ -ZrP-EDTA material for the removal of toxic metals such as Cu^{2+} and Ni^{2+} from water. The results are summarized in **Figures 10** and **11** [58].

Equilibrium was reached for Cu^{2+} and Ni^{2+} after ca. 48 h, where the maximum uptake is obtained (72.0 and 93.5 mg M^{2+} /g λ -ZrPH₂Y, respectively). These uptake values correspond to ca. 4.58 and 5.49 mmol M^{2+} /g λ -ZrPH₂Y and % M^{2+} uptake of 58.0 and 76.6 %, respectively. This shows that λ -ZrPH₂Y has higher Ni^{2+} uptake capacity as compared to Cu^{2+} .

These experiments showed that EDTA was successfully incorporated inside the interlayer gallery of λ -ZrP by means of topotactic carboxylate/Cl ligand exchange reaction. The resulting

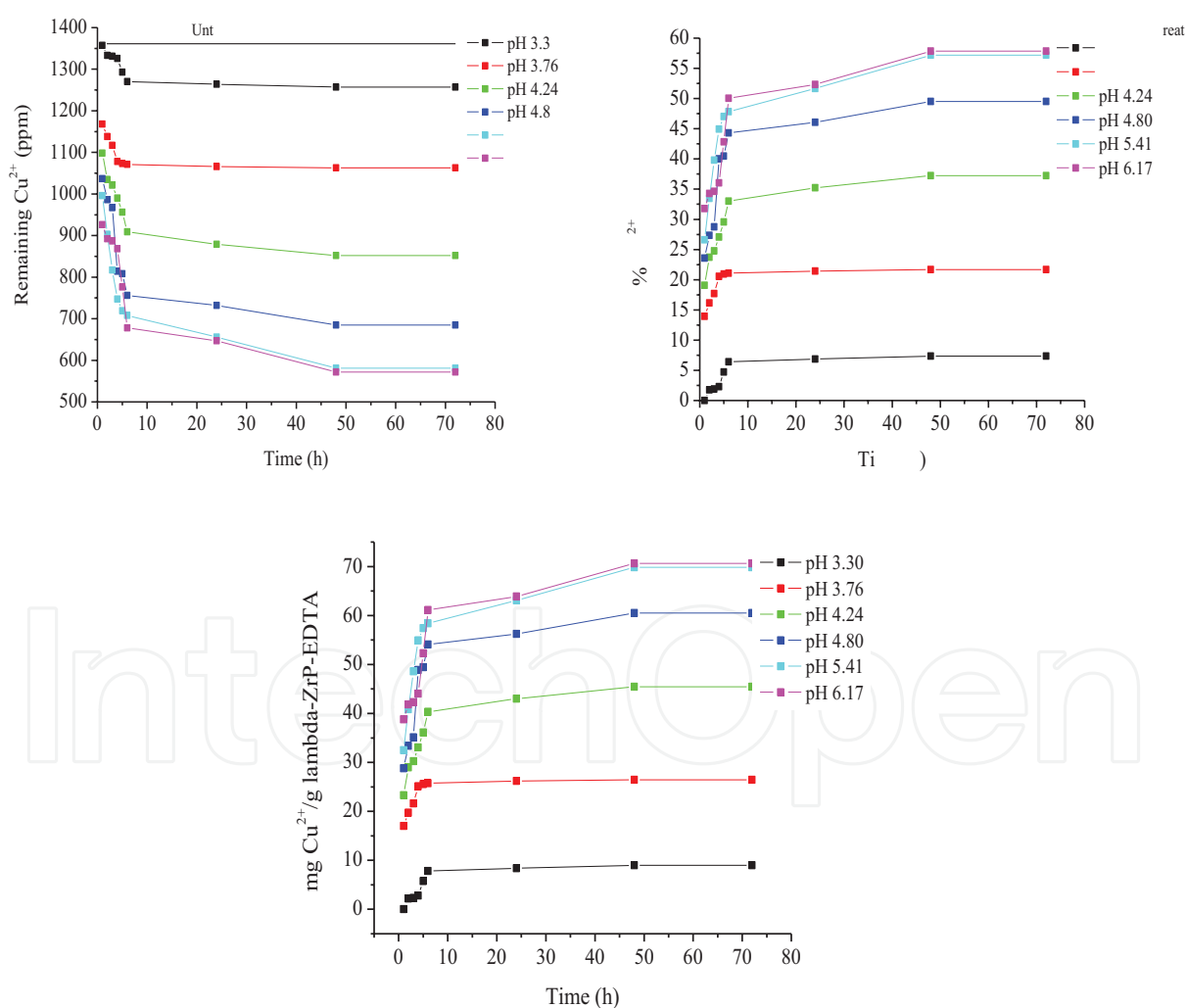


Figure 10. Kinetic curves of Cu^{2+} uptake from aqueous solutions: The remaining concentration of Cu^{2+} (ppm) in samples after treatment with λ -ZrPH₂Y (top left). % Cu^{2+} uptake by λ -ZrPH₂Y (top right). Cu^{2+} uptake capacities of λ -ZrPH₂Y (mg g^{-1}) (bottom).

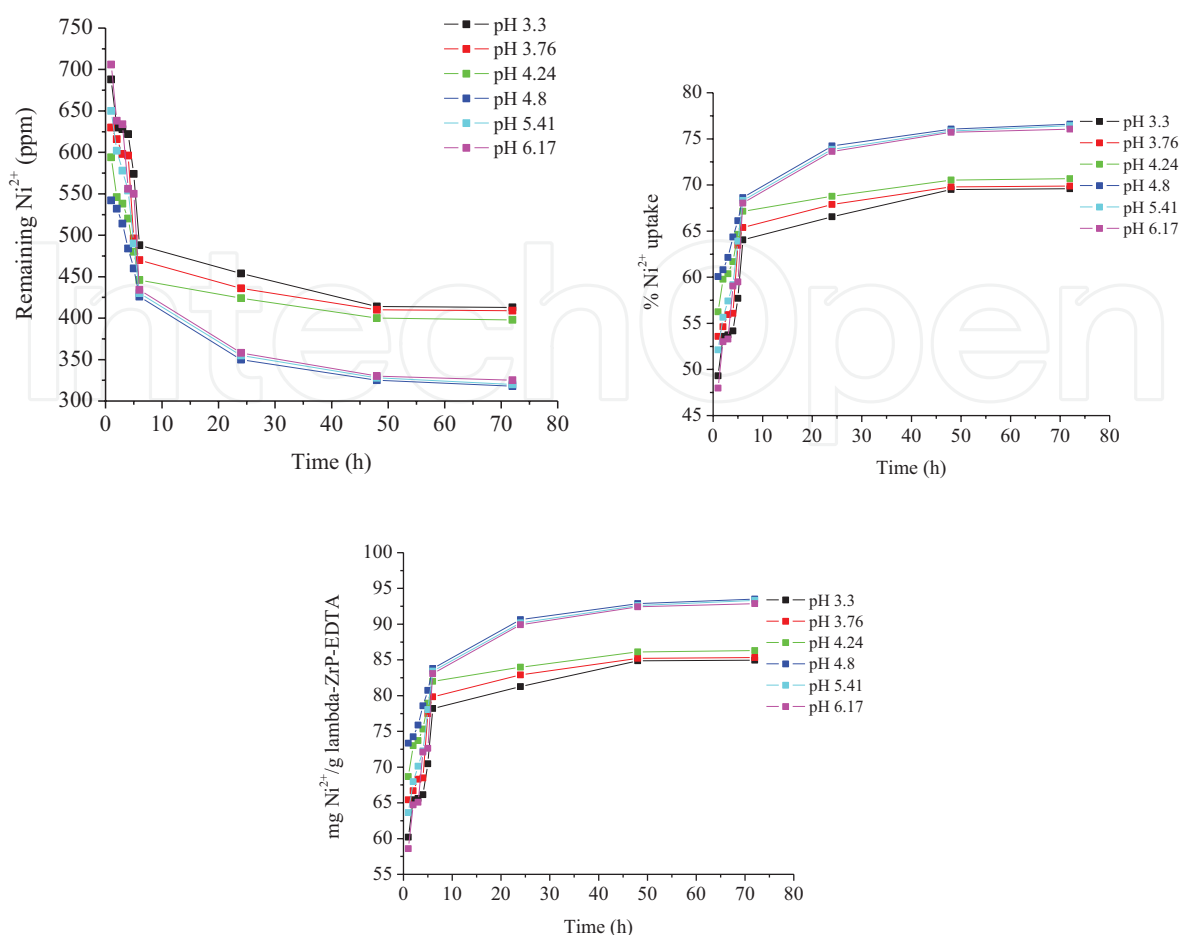


Figure 11. Kinetic curves of Ni^{2+} uptake from aqueous solutions (initial conc. 1375 ppm): The remaining concentration of Ni^{2+} (ppm) in samples after treatment with $\lambda\text{-ZrPH}_2\text{Y}$ (top left). % Ni^{2+} uptake by $\lambda\text{-ZrPH}_2\text{Y}$ (top right). Ni^{2+} uptake capacities of $\lambda\text{-ZrPH}_2\text{Y}$ (mg g^{-1}) (bottom).

composite phase, $\lambda\text{-ZrPH}_2\text{Y}$, exhibited high potential for the extraction of various metal ions from water samples.

5. Conclusion and prospects

Phosphoric acid chemistry has limitless features. In this article, we have gathered a collection of eloquent experimental facts where the primordial phosphoric acid, combined with Zr metal and other chemicals, led to the building of inorganic-organic 2D and 3D structures that can play a crucial role in numerous research areas. The number of rather complex composites that can be figured out from the presented rationale is inexhaustible and only limited by the imagination and chemical needs of the researcher. Moreover, the confinement of organic molecules within the ZrP frameworks would confer them new properties at the supramolecular level and give rise to many surprises driven by the high level of *serendipity* that was and will be found in this field.

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References

- [1] Brunet E, Alhendawi H, Juanes O, Jiménez L, Rodríguez-Ubis JC. Luminescence of Lanthanides in Pillared Zirconium Phosphate. *J. Mater. Chem.* 2009; **19**:1-10. DOI: 10.1039/b817317f
- [2] Brunet E, Alhendawi H, Juanes O, Rodríguez-Ubis JC. The Quest for Relationships between Conformation and Chiroptical Properties: From Solution to Solid State. *J. Mex. Chem. Soc.* 2009; **53**(3):155-162. DOI: 47512154013
- [3] Brunet E, de la Mata MJ, Juanes O, Alhendawi H, Cerro C, Rodríguez-Ubis JC. Solid-State Reshaping of Nanostructured Crystals: Supramolecular Chirality of Layered Materials Derived from Polyethylenoxa-Pillared Zirconium Phosphate. *Tetrahedron: Asymmetry* 2006; **17**(3):347-354. DOI: 10.1016/j.tetasy.2006.01.014
- [4] Brunet E, Alhendawi H, Cerro C, de la Mata MJ, Juanes O, Rodríguez-Ubis JC. Hydrogen Storage in a Highly Porous Solid Derived from γ -Zirconium Phosphate. *Angew. Chem. Int. Edit.* 2006; **45**:6918-6920. DOI: 10.1002/anie.200602445
- [5] Brunet E, Alhendawi H, Cerro C, de la Mata MJ, Juanes O, Rodríguez-Ubis JC. Creating Libraries of Porous Materials Derived from γ -Zirconium Phosphate: Pillaring with Polyphenylethynyl Diphosphonates. *Micropor. Mesopor. Mat.* 2011; **138**:75-85. DOI: 10.1016/j.micromeso.2010.09.027
- [6] Brunet E, Alhendawi H, Cerro C, de la Mata MJ, Juanes O, Rodríguez-Ubis JC. Easy γ -to- α Transformation of Zirconium Phosphate/Polyphenylphosphonate Salts: Porosity and Hydrogen Physisorption. *Chem. Eng. J.* 2010; **158**:333-344. DOI: 10.1016/j.cej.2010.01.040

- [7] Brunet E, Alhendawi H, Alonso M, Cerro C, Jiménez L, Juanes O, de la Mata MJ, Salvador A, Victoria M, Rodríguez-Payán E, Rodríguez-Ubis JC. The Use of Laminar Inorganic Salts to Make Organic Molecules Display New Properties at the Supramolecular Level in the Solid State. *J. Phys.: Conf. Ser.* 2010; **232**:012017. DOI: 10.1088/1742-6596/232/1/012017
- [8] Alhendawi H. Intercalation of Malachite Green ($[\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2]\text{Cl}$) in Layered γ -Zirconium Phosphate. Effect of Cationic Surfactants. *J. Mater. Chem.* 2011; **21**:7748-7754. DOI: 10.1039/c0jm04147e
- [9] Alhendawi H, Brunet E, Rodríguez Payán E, Juanes O, Rodríguez Ubis JC, Al-Asqalany M. Surfactant-assisted Intercalation of Crystal Violet in Layered γ -Zirconium Phosphate. Dye uptake from aqueous solutions. *J. Incl. Phenom. Macrocycl. Chem.* 2012; **73**:387-396. DOI: 10.1007/s10847-011-0076-6
- [10] Alhendawi H, Brunet E, Juanes O, Idhair S, Hammouda H, Rodríguez Payán E, de Victoria Rodríguez M. Functionalization of lambda-zirconium phosphate with ethylenediaminetetraacetic acid: Synthesis, characterization and applications. *J. Chem. Sci.* 2014; **120**(6):1721-1727. DOI: 10.1007/s12039-014-0726-5
- [11] Clearfield A. Metal phosphate chemistry. In: Karlin KD, editor. *Progress in Inorganic Chemistry*. New York: Wiley; 1998. p. 373-510. DOI: 10.1002/978-0-471-24039-6
- [12] Brunet E, de Victoria-Rodríguez M, García-Patrón LJ, Hindawi H, Rodríguez-Payán E, Rodríguez-Ubis JC, Juanes O. Tales from the unexpected: chemistry at the surface and interlayer space of layered organic-inorganic hybrid materials based on γ -zirconium phosphate. In: Brunet E, Colón JL, Clearfield A, editors. *Tailored Organic-Inorganic Materials*. Hoboken: Wiley; 2015. p. 45-82. DOI: 10.1002/978-1-118-77346-8
- [13] Clearfield A, Stynes JA. The Preparation of Crystalline Zirconium Phosphate and Some Observations on its Ion Exchange Behavior. *J. Inorg. Nucl. Chem.* 1964; **26**:117-129.
- [14] Clearfield A, Blessing RH, Stynes JA. New Crystalline Phases of Zirconium Phosphate Possessing Ion-Exchange Properties. *J. Inorg. Nucl. Chem.* 1968; **30**:2249-2258.
- [15] Poojary DM, Zhang B, Clearfield A. Synthesis and Crystal Structure of a New Layered Zirconium Phosphate Compound, $\text{Zr}(\text{PO}_4)\text{F}(\text{OSMe}_2)$. *J. Chem. Soc. Dalton Trans.* 1994; **16**:2453-2456. DOI: 10.1039/DT9940002453
- [16] Whittingham MS, Jacobson AJ, editors. *Intercalation Chemistry*. New York: Academic Press; 1982. 614 p. DOI: 10.1016/0022-0728(82)90079-9
- [17] Tomita I, Takeo C. Synthesis of γ -Zirconium Phosphate by Fluoro-Complex Method and Intercalation Behavior of Some α -Dimines. *J. Incl. Phenom. Mol.* 1990; **9**:315-325.
- [18] Feng Y, He W, Zhang X, Jia X, Zhao H. The Preparation of Nanoparticle Zirconium Phosphate. *Mater. Lett.* 2007; **61**:3258-3261. DOI: 10.1016/j.matlet.2006.11.132
- [19] Clearfield A, Costantino U. Layered Metal Phosphates and Their Intercalation Chemistry. In: Alberti G, Bein T, editors. *Comprehensive Supramolecular Chemistry*. New York: Pergamon; 1996. p. 107-149. DOI: 10.1016/B0-08-091254-7

- [20] Alhendawi H. Synthesis and Structural Characterization of Zirconium Phosphate Adipate Dimethyl Sulfoxide: A New Lambda-Type Organic-Inorganic Layered Material. *J. Chem. Sc.* 2014; **126**(4): 975-979. DOI: 10.1007/s12039-014-0634-8
- [21] Liu J, Boo WJ, Clearfield A, Sue HJ. Intercalation and Exfoliation: A Review on Morphology of Polymer Nanocomposites Reinforced By Inorganic Layer Structures. *Mater. Manuf. Process.* 2006; **20**:143-151. DOI: 10.1081/AMP-200068646
- [22] Alberti G, Dionigi C, Giontella E, Murcia-Mascarós S, Vivani R. Formation of Colloidal Dispersions of Layered γ -Zirconium Phosphate in Water/Acetone Mixtures. *J. Colloid Interf. Sci.* 1997; **188**:27-31. DOI: org/10.1006/jcis.1996.4679
- [23] Alberti G, Casciola M, Costantino U. Inorganic Ion-Exchange Pellicles Obtained By Delamination of α -Zirconium Phosphate Crystals. *J. Colloid Interf. Sci.* 1985; **107**: 256-263. DOI: org/10.1016/0021-9797(85)90169-9
- [24] Vivani R, Alberti G, Costantino F, Nocchetti M. New Advances in Zirconium Phosphate and Phosphonate Chemistry: Structural Archetypes. *Micropor. Mesopor. Mater.* 2008; **107**:58-70. DOI:10.1016/j.micromeso.2007.02.029
- [25] Alberti G, Vivani R, Marmottini F, Zappelli P. Microporous Solids Based on Pillared Metal(IV) Phosphates and Phosphonates. *J. Porous Mater.* 1998; **5**:205-220. DOI: 10.1023/A:1009678120336
- [26] Alberti G. Bidimensional Structures Based on Metal Phosphates and their Applications. *Sci. Tech.* 1998; **80**:607-614. DOI: 29062316
- [27] Alberti G, Casciola M, Costantino U, Vivani R. Layered and Pillared Metal(IV) Phosphates and Phosphonates. *Adv. Mater.* 1996; **8**:291-303. DOI: 10.1002/adma.19960080405
- [28] Nakato T, Miyamoto N. Sol-Gel Transition of Nanosheet Colloids of Layered Niobate $K_4Nb_6O_{17}$. *J. Mater. Chem.* 2002; **12**:1245-1246. DOI: 10.1039/B202000A
- [29] Miyamoto N, Nakato T. Liquid Crystalline Colloidal System Obtained by Mixing Niobate and Aluminosilicate Nanosheets: A Spectroscopic Study Using a Probe Dye. *Langmuir* 2003; **19**:8057. DOI: 10.1021/la0268449
- [30] Miyamoto N, Kuroda K, Ogawa M. Exfoliation and Film Preparation of a Layered Titanate, $Na_2Ti_3O_7$, and Intercalation of Pseudocyanine Dye. *J. Mater. Chem.* 2004; **14**:165-170. DOI: 10.1039/B308800F
- [31] Geng F, Ma R, Ebina Y, Yamauchi Y, Miyamoto N, Sasaki T. Gigantic Swelling of Inorganic Layered Materials: A Bridge to Molecularly Thin Two-Dimensional Nanosheets. *J. Am. Chem. Soc.* 2014; **136**:5491-5500. DOI: 10.1021/ja501587y
- [32] Alhendawi H, Brunet E, Hammouda H, Rodríguez Payán E. Intercalation of Primary Alkylamines into Lambda-Zirconium Phosphate. Lambda-Type Materials with Extended Interlayer Separation. *J. Porous. Mater.* 2016; **23**:1519-1526. DOI: 10.1007/s10934-016-0212-1

- [33] Caneschi A, Gatteschi D, Sangregorio C, Vaz MGF, Costantino U, Nocchetti M, Vivani R. Intercalation of a Nitronyl Nitroxide Radical into Layered Inorganic Hosts. Preparation and Physico-Chemical Characterization. *Inorg. Chim. Acta.* 2002; **338**:127-132. DOI: [org/10.1016/S0020-1693\(02\)01026-5](https://doi.org/10.1016/S0020-1693(02)01026-5)
- [34] Alhendawi H, Brunet E, Juanes O, Hammouda H, Idhair S, Rodríguez Payán E, de Victoria Rodríguez M. New Soft Porous Frameworks Based On Lambda-Zirconium Phosphate And Aliphatic Dicarboxylates: Synthesis And Structural Characterization. *J. Phys. Chem. Sol.* 2015; **86**:95-100. DOI: [org/10.1016/j.jpcs.2015.06.021](https://doi.org/10.1016/j.jpcs.2015.06.021)
- [35] Alhendawi H, Brunet E, Rodríguez Payán E, Shurrah N, Juanes O, Idhair S, Al-Asqalany M. A New Layered Zirconium Biphosphonate Framework Covalently Pillared with N,N'-Piperazinebis(Methylene) Moiety: Synthesis And Characterization. *J. Porous Mater.* 2013; **20**(5):1189-1194. DOI: [10.1007/s10934-013-9702-6](https://doi.org/10.1007/s10934-013-9702-6)
- [36] Alberti G, Murcia-Mascarós S, Vivan R. Preparation and Characterization Of Zirconium Phosphate Diphosphonates with the γ -Structure: A New Class Of Covalently Pillared Compounds. *Mater. Chem. Phys.* 1993; **35**:187-192. DOI: [org/10.1016/0254-0584\(93\)90129](https://doi.org/10.1016/0254-0584(93)90129)
- [37] Brunet E, de la Mata MJ, Alhendawi H, Cerro C, Alonso M, Juanes O, Rodriguez-Ubis JC. Engineering of Microcrystalline Solid-State Networks Using Cross-Linked γ -Zirconium Phosphate/Hypophosphite with Nonrigid Polyethylenoxadiphosphonates. Easy Access to Porously Dynamic Solids with Polar/Nonpolar Pores. *Chem. Mater.* 2005; **17**:1424-1433. DOI: [10.1021/cm048754q](https://doi.org/10.1021/cm048754q)
- [38] Alberti G, Brunet E, Chiara D, de la Mata MJ, Juanes O, Rodríguez-Ubis JC, Vivan R. Shaping Solid-State Supramolecular Cavities: Chemically Induced Accordionlike Movement of gamma-Zirconium Phosphate Containing Polyethylenoxide Pillars. *Angew. Chem. Int. Ed.* 1999; **22**(38):3351-3353. DOI: [10.1002/\(SICI\)1521-3773\(19991115\)38:22<3351::AID-ANIE3351>3.0.CO;2-V](https://doi.org/10.1002/(SICI)1521-3773(19991115)38:22<3351::AID-ANIE3351>3.0.CO;2-V)
- [39] Alberti G, Costantino U, Marmottini F, Vivani R, Valentini C. Ion Exchange Properties of α -Zirconium Phosphate Modified by a Process of Intercalation/De-Intercalation with Monoamines. In: Williams PA, Hundson MJ editors. *Recent Development in Ion Exchange*. London: Elsevier Applied Sciences; 1987. p. 233-248. DOI: [978-94-010-8044-6](https://doi.org/10.1016/0021-9517(86)90224-1)
- [40] Wan BZ, Anthony RG, Peng GZ, Clearfield A. Characterization of Organically Pillared Zirconium Phosphates. *J. Catal.* 1986; **101**:19-27. DOI: [10.1016/0021-9517\(86\)90224-1](https://doi.org/10.1016/0021-9517(86)90224-1)
- [41] Alberti G, Costantino U. Recent Progress in The Intercalation Chemistry of Layered α -Zirconium Phosphate And Its Derivatives, And Future Perspectives For Their Use In Catalysis. *J. Mol. Catal.* 1984; **27**:235-250. DOI: [org/10.1016/0304-5102\(84\)85083-X](https://doi.org/10.1016/0304-5102(84)85083-X)
- [42] Cao G, Garcia ME, Alcalá M, Burgess LG, Mallouk TE. Chiral Molecular Recognition in Intercalated Zirconium Phosphate. *J. Am. Chem. Soc.* 1992; **114**: 7574-7575. DOI: [10.1021/ja00045a046](https://doi.org/10.1021/ja00045a046)
- [43] Mallouk TE, Gavin JA. Molecular Recognition in Lamellar Solids and Thin Films. *Acc. Chem. Res.* 1998; **31**:209-217. DOI: [10.1021/ar970038p](https://doi.org/10.1021/ar970038p)

- [44] Brunet E. Asymmetric Induction Under Confinement. *Chirality* 2002; **14**:135-143. DOI: 10.1002/chir.10054
- [45] Vivani R, Masci S, Alberti G. Anionic Ligand Exchange on $\text{ZrPO}_4\text{Cl}(\text{dmsO})$: Alkoxide and Carboxylate Derivatives. *Inorg. Chem.* 2004; **43**:368-374. DOI: 10.1021/ic034695r
- [46] Alhendawi H. Lambda-Zirconium Phosphate Covalently Pillared with 1,4-Biphenyldicarboxylate: A New Rigid Mesoporous Framework. *J. Incl. Phenom. Macrocycl. Chem.* 2016; **85**:187-192. DOI 10.1007/s10847-016-0618-z
- [47] Alhendawi H. Synthesis and Structural Characterization Of A New Chiral Porous Hybrid Organic-Inorganic Material Based On Γ -Zirconium Phosphates and L-(+)-Phosphoserine. *J. Solid State Chem.* 2013; **201**:24-28. DOI: org/10.1016/j.jssc.2013.02.025
- [48] Alberti G, Bartocci M, Santarelli M, Vivani R. Zirconium Phosphate Chloride Dimethyl Sulfoxide, a Reactive Precursor of a Large Family of Layered Compounds. *Inorg. Chem.* 1997; **36**:3574-3575. DOI: 10.1021/ic9704389
- [49] Alberti G, Masci S, Vivani R. Layered Zirconium Phosphate Chloride Dimethyl Sulfoxide as a Two-Dimensional Exchanger of Anionic Ligands. Part I. Substitution of Chloride with Inorganic Monodentate Ligands. *Inorg. Chem.* 2002; **41**:1913-1919. DOI: 10.1021/ic010643v
- [50] Brunet E, Huelva M, Rodriguez-Ubis JC. Covalent Bonding of Aza-18-Crown-6 to γ -Zirconium Phosphate. A New Layered Ion-Exchanger with Potential Recognition Capabilities. *Tetrahedron. Lett.* 1994; **35**:8697-8700. DOI: org/10.1016/S0040-4039(00)78475-9
- [51] Brewster JH. A Useful Model of Optical Activity. I. Open Chain Compounds. *J. Am. Chem. Soc.* 1959; **81**:5475-5483. DOI: 10.1021/ja01529a056
- [52] Eliel EL, Brunet E. Quantitative Relationship Between Optical Rotation And Conformation. *J. Org. Chem.* 1991; **56**:1668-1670. DOI: 10.1021/jo00004a059
- [53] Brunet E, Juanes O, Rodriguez-Ubis JC. Supramolecularly Organized Lanthanide Complexes for Efficient Metal Excitation and Luminescence as Sensors in Organic and Biological Applications. *Curr. Chem. Biol.* 2007; **1**:11-39. DOI: 10.2174/2212796810701010011
- [54] Brunet E, Cerro C, Juanes O, Rodriguez-Ubis JC, Clearfield A. Hydrogen Storage in Highly Microporous Solids Derived From Aluminium Biphenyldiphosphonate. *J. Mater. Sci.* 2008; **43**(3):1155-1158. DOI 10.1007/s10853-007-2377-0
- [55] Salonen J, Kaukonen AM, Hirvonen J, Lehto VP. Mesoporous Silicon in Drug Delivery Applications. *J. Pharm. Sci.* 2008; **97**(2):632-653. DOI: 10.1002/jps.20999
- [56] Brunet E, Alonso M, Quintana MC, Atienzar P, Juanes O, Rodriguez-Ubis JC, Garcia H. Laser Flash-Photolysis Study of Organic-Inorganic Materials Derived from Zirconium Phosphates/Phosphonates of $\text{Ru}(\text{bpy})_3$ and C_{60} as Electron Donor-Acceptor Pairs. *J. Phys. Chem. C* 2008; **112**(15):5699-5702. DOI: 10.1021/jp800026r

- [57] Teruel L, Alonso M, Quintana MC, Salvador A, Juanes O, Rodriguez-Ubis JC, Brunet E, Garcia H. Photovoltaic Activity of Layered Zirconium Phosphates Containing Covalently Grafted Ruthenium Tris(Bipyridyl) and Diquat Phosphonates as Electron Donor/Acceptor Sites. *Phys. Chem. Chem. Phys.* 2009; **11(16)**:2922-2927. DOI: 10.1039/B816698F
- [58] Alhendawi H, Brunet E, Hammouda H, Abu Tuha G, Rodríguez Payán E. To be published.

