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Integrative strategies to hybrid lamellar compounds: an integration challenge

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7
8 **Integrative strategies to hybrid lamellar compounds:**
9 **an integration challenge**

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1 **Abstract**

2 During the past decades, the potential derived from the hybridization of inorganic materials,
3 has been widely studied and presented. The capability of tuning materials' performances, not
4 only in terms of tailoring their physico-chemical properties to answer prerequisites of a given
5 application, but also regarding the elaboration of novel concepts, opened a door to a radical
6 new world in materials science. However, as a consequence of their diverse chemistry,
7 structure, envisaged applications and historical background, each subgroup of inorganic
8 lamellar compounds were usually discussed separately. This review intends to reflect upon the
9 different categories of lamellar compounds and their hybridization strategies, regardless of
10 their chemical and historical differences. The hybridization strategies of lamellar compounds
11 are divided and presented under two main categories. Firstly, the intercalation/exfoliation
12 approach, where the hybridization of lamellar compounds is operated in pre-formed inorganic
13 layered materials. Secondly, the *in-situ* synthesis methods, where the hybrid character of the
14 layered compound is imparted simultaneously along with the layered inorganic compounds
15 synthesis routes. Finally, in order to tackle the important question of "*the place and role of*
16 *hybrid lamellar compounds in consumer end-products, an integration challenge*", the proven
17 concepts and potential applications defined for these organic-inorganic compounds are
18 discussed.

19 **Table of abbreviations**

20 AMP: Aminopropyl-functionalized magnesium phyllosilicate

21 CSH: Calcium silicate hydrate

22 CPN: Clay polymer nanocomposite

23 DNA : Deoxyribonucleic acid

24 DS : Dodecylsulfate

25 LHDS: Layered hydroxyl double salts

26 LDH: layered double hydroxide

27 LHS: Layered hydroxide salts

- 1 LMC: Layered metal chalcogenides
- 2 Mt: Montmorillonite
- 3 PILC: Pillared interlayered clays
- 4 MX2: Metal dichalcogenides
- 5 MX3: Metal trichalcogenides

6 **1. Introduction**

7 Hybrid lamellar compounds are ubiquitous in materials science (Usuki et al., 1993; Giannelis,
8 1996; Leroux and Taviot-Guého, 2005; Ruiz-Hitzky et al., 2007; Sanchez et al., 2011). Their
9 widespread presence from laboratory benches to industrial plants is the image of a
10 fundamental research area that has profoundly impacted numerous applied domains. A quick
11 overview of the literature focused on lamellar hybrid materials show domains of application
12 as disparate as heterogeneous catalysis (Okada et al., 2012), adsorption (Lagadic et al., 2001),
13 nanocomposites (Ray and Okamoto, 2003), sensors (Aranda et al., 2006) or optics-related
14 materials (Mane and Pinna, 2006). Such variety of application has led to a consensus around
15 the idea that synthesizing hybrid compounds from their inorganic layered precursors is an
16 interesting strategy to tailor many of the latter properties.

17 Most of the advances on hybrid lamellar compounds elaboration have been led by research
18 groups previously working on the inorganic counterpart. As a consequence, much the
19 advances in hybrid lamellar compounds were led forward in different moments and by
20 researchers with different backgrounds. Such asynchronous interest on layered hybrid
21 materials justifies the heterogeneous state-of-the-art presently found in the literature, both in
22 their synthesis and their application. The clay community, for instance, has soon agreed on the
23 potentialities of hybrid clay compounds, following the pioneer works led by Gieseking
24 (1939), MacEwan (1948) and Jordan (1949) on organoclays. Such advances were
25 contemporary to the description of metal phosphates' cation exchange properties (Kraus and
26 Phillips, 1956; Alberti, 1978; Clearfield, 1988, 2012) which paved the way for the
27 development of phosphate and phosphonate hybrid materials (Cao et al., 1992). The first

1 systematic study of the intercalation of different organic and inorganic anionic species in the
2 interlayer space of layered double hydroxides (LDH) was not reported until the early 1980s
3 (Miyata, 1983).

4 Despite the history of lamellar compounds hybridization, the most salient feature in these
5 materials is a common and unifying factor: their *morphology*! Independent from the chemical
6 nature of the inorganic structure, the strategy used by the different research groups was, in
7 most cases, to modify the interlayer space of the inorganic layered host. Such approach arises
8 as a consequence of the two-dimensional morphology of inorganic layered compounds.
9 Numerous examples are available to strengthen this analysis: i) swelling of clay minerals
10 using caprolactam to perform *in situ* polymerization of Nylon (Fukushima and Inagaki, 1987);
11 ii) intercalation of polyoxymetalate anions in LDH to attain pillared structures (Dimotakis and
12 Pinnavaia, 1990) or iii) the delamination of α -zirconium phosphate crystals by the
13 intercalation of alkylammonium anions (Alberti et al., 1985, 2000). In each of the preceding
14 cases the common goal is to fine-tune the distance and relative order between the inorganic
15 layers by the nature of the guest chemical species. It is worth underlining that the lamellar
16 compounds are able to retain chemical species only with electrical charges compatible with
17 those of the layers. One of the major driving forces behind the intercalation of guest species in
18 the interlayer space of layered compounds relates to the affinity between both entities. Charge
19 matching naturally accounts for a very important part of such affinity. Organic cations are
20 likely to intercalate into negatively charged clay mineral layers, conversely, anionic species
21 are efficiently intercalated within the interlayer space of positively charged layered double
22 hydroxides lamellae. The electrostatic affinity can also be tailored by the insertion of excess
23 cations, switching the layered compound's affinity from an anion-exchanger to a cation-
24 exchanger or vice-versa.

25 If the hybridization of layered inorganic materials has become widespread across
26 materials-related disciplines (with quite few yet surprising exceptions), the integration of the
27 referred hybrid materials into devices and consumer end products is an entirely different
28 matter. This article addresses two dimensions of hybrid layered materials. First, it briefly
29 reviews the main strategies to fabricate hybrid layered compounds with new or improved
30 functionality; and second, it surveys how these new building blocks are being integrated from
31 both a conceptual and technologic point of view.

1 **2. Lamellar compounds**

2 Inorganic layered solids being the backbone of hybrid layered compounds, a brief description
3 of the different layered solids, under consideration in this review, is appropriate. Moreover,
4 since these compounds have been scarcely treated together (Nicolosi et al., 2013), the
5 overview of the different inorganic layered solids selected for this review intends to present a
6 collective analysis on their structures.

7 A layered compound is a crystalline material wherein the intralayer atoms are linked by
8 covalent, ionic, ionocovalent or metallic bonds, while the interlayer atoms interact through
9 weaker electrostatic forces mediated (when present) by interlayer species (Schoonheydt et al.,
10 1999). The interest of such brief explanation on the nature of bonds in inorganic layered
11 solids is two-fold. From a fundamental point-of-view, it describes the nature of the
12 interactions between the different atoms of the inorganic solid. In a more pragmatic look, it
13 highlights the energetic difference between the bonds within the inorganic layer and those in
14 between adjacent layers. This latter leads the reader to the logic behind the modification
15 strategies in this class of compounds.

16 In terms of lexicon, few precisions are needed, despite the different disciplines that have
17 treated the subject of layered structures. A single layer is called a lamella, slab, or sheet
18 (Alberti and Constantino, 1996), as a consequence, the terms interlayer and interlamellar are
19 used to define the gap between adjacent layers.

20 Clay minerals, layered metal hydroxides, layered simple hydroxides known as layered
21 hydroxy double salts, calcium silicate hydrates, layered metal oxides metal phosphonates,
22 metal phosphates and layered metal chalcogenides are the treated compounds in this section.
23 Simplified structures of these layered compounds are illustrated in figure 1.

24

25 *2.1. Clay minerals*

26 Clay minerals are at the epicenter of hybrid lamellar materials research. Even though their
27 origin and chemical nature have been perfectly identified for decades, their exact definition is
28 an ongoing subject of debate (Bergaya and Lagaly, 2006). The precise definition of a clay or a

1 clay mineral is not within the scope of this article but, given the wide variety of compounds
2 below the clay umbrella name, it is useful to discriminate which structures are referred to as
3 clay minerals throughout this work. Due to the layered nature/nano-morphology of the
4 materials under discussion, clay minerals displaying a fibrous habit such as sepiolite and
5 palygorskite, as well as clay minerals displaying rolled up inorganic layers such as halloysite
6 or chrysotile, fall out of the scope of this work and are not discussed. Within the layered clay
7 minerals this review focuses on planar hydrous phyllosilicates (Fig. 1a). No structural
8 difference will be pointed out between TO or TOT clay minerals, despite the interlayer charge
9 dissimilarity that derives from such structural differences (Auerbach et al., 2004; Bergaya et
10 al., 2006b).

11 The knowledge of the crystalline structure of clay minerals is the ultimate tool to rationally
12 design clay mineral-based materials. Insight on clay mineral structure followed the early
13 developments in X-ray diffraction (XRD) techniques in the transition between the XIX and
14 XX centuries (Bergaya et al., 2006a). In parallel with fundamental research on the structure of
15 clay minerals, a variety of new applications emerged. The most notable of which were linked
16 to the rheological (Stephenson, 1927), mechanical reinforcement of rubbers (Thies, 1925) and
17 their adsorption properties (Bradley, 1945), both closely related to the physical and chemical
18 phenomena occurring at the interlayer space of clay minerals. The most relevant features of
19 clay mineral regarding their potential use as hybrid lamellar compounds are thus the layered
20 morphology alongside with net layer charge per unit formula. Since the layer's charge varies
21 from neutral to negative, adjacent clay mineral layers are compensated by cations that
22 stabilize the clay particles. Knowing the cation exchange capacity (CEC) of clay minerals is
23 an effective method to estimate which species can be used and to what extent can the
24 interlayer space of clay minerals be modified.

25

26 2.2. *Layered Metal Hydroxides*

27 The simplest examples of this category of layered metal hydroxide compounds are brucite, *i.e.*
28 magnesium hydroxide and gibbsite, *i.e.* aluminium hydroxide. Brucite-like structures are
29 composed of divalent cations coordinated octahedrally by hydroxide ions, that is to say these
30 cations are placed in the center of octahedra with hydroxide groups located in vertices.

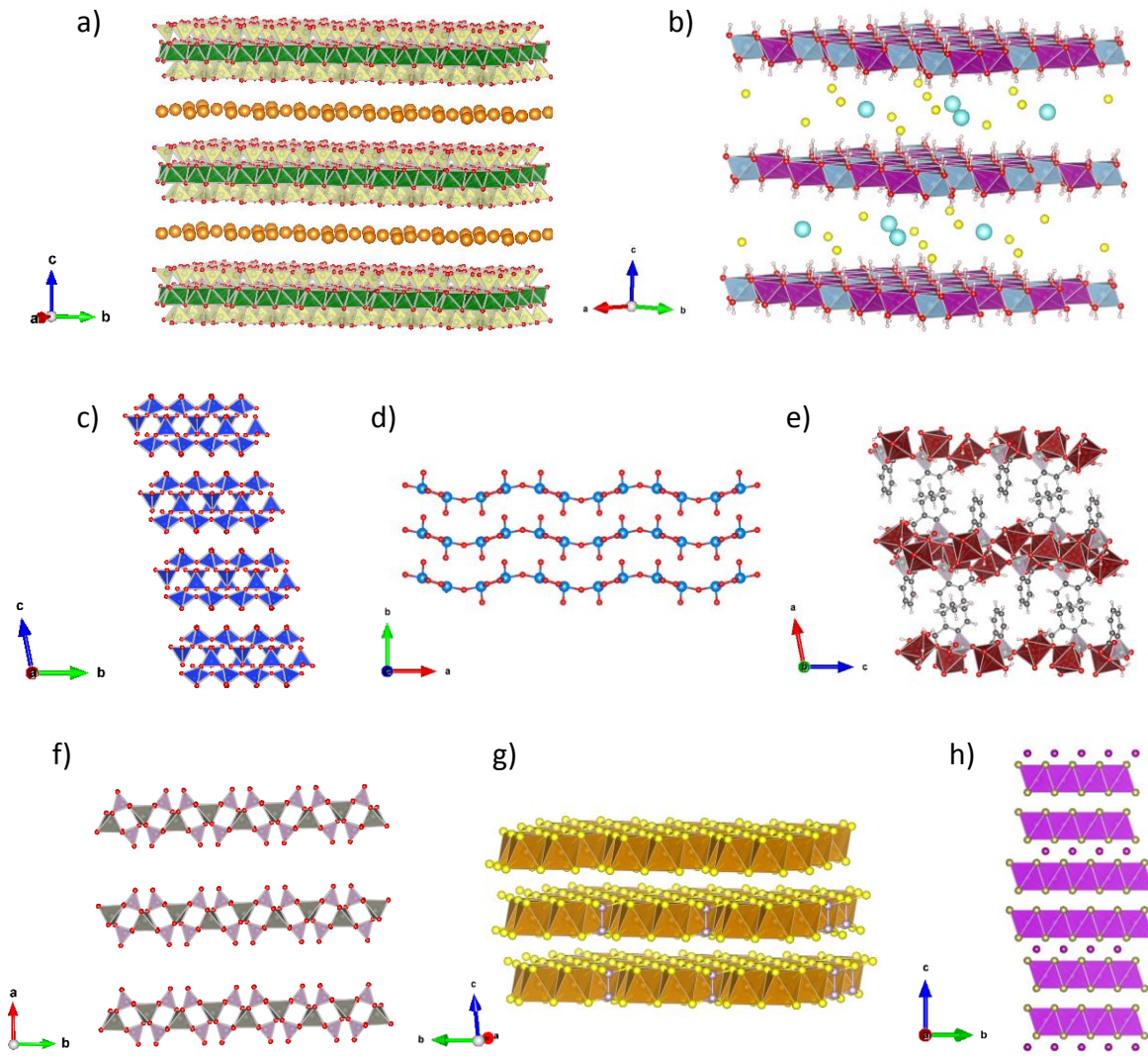
1 Octahedral units share edges to form infinite neutrally charged layers. Calcium, manganese,
2 iron, cobalt and nickel hydroxides are well-known examples of metal hydroxides with
3 brucite-like structures. The brucite structure can undergo chemical, as well as slight structural
4 modifications to form more complex metal hydroxides such as layered hydroxide salts (LHS),
5 layered double hydroxides (LDH) and layered hydroxy double salts (LHDS), also known as
6 “double hydroxide salts” (Arizaga et al., 2007).

7 Brucite-like structures can experience the substitution of a part of hydroxide groups by
8 appropriate anions or water molecules, resulting in formation of a structure called layered
9 hydroxide salt (LHS), also called layered simple hydroxides (LSH). The general formula of
10 LHS corresponds to $M^{2+}(OH)_{2-x}(A^{m-})_{x/m} \cdot nH_2O$ where M^{2+} is the metal cation (*e. g.* Mg^{2+} ,
11 Ni^{2+} , Zn^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+}) and A^{m-} is the anion (*e.g.* Cl^- , NO_3^- , SO_4^{2-} , dodecylsulfate,
12 dodecylsulfonate and acetate). Briefly speaking, their structure is composed of triangular
13 arrays of octahedral divalent cations, separated by anions, coordinating with metal ions and
14 interlayer water molecules. In this type of structures the anion is not grafted to the inorganic
15 layers by iono-covalent bonds to metal. Numerous organic molecules can be intercalated in
16 the interlayer space *via* anion-exchange and form divers layered hybrids (Ghose, 1964;
17 Stählin and Oswald, 1970; Petrov et al., 1989; Newman and Jones, 1999; Biswick et al., 2006;
18 Arizaga et al., 2007; Rogez et al., 2011). Numerous studies were focused on the synthesis of
19 transition-metal LHS, because of their interesting magnetic properties, which found out to be
20 tunable by the type and the length of organic molecules, present as counter-ion (Rabu et al.,
21 1993; Fujita and Awaga, 1996; Kurmoo et al., 2003; Forster et al., 2004; Kojima et al., 2007).

22 LDH are intriguing compounds. They display many physical and chemical properties that are
23 surprisingly similar to those of clay minerals (Forano et al., 2006). However LDH are not
24 silicates but metal hydroxides. They present bivalent and trivalent metallic cations on their
25 lamellae according to the following general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]$. These compounds can
26 also be described as a brucite-like structure which undergoes an isomorphic substitution of
27 cations, *i.e.* a part of divalent cations replaced by trivalent ones. Hence, the excess positive
28 charge of the layers permits the interlayer space of LDH hosting anionic species that
29 compensate the charge excess of the lamellae, according to the formula, $[X^{q-}]_{x/q} \cdot nH_2O$ (Fig. 1-
30 b). Such simple chemical definition explains three of the main characteristics of LDH. The
31 first derives from the multitude of compositions which are allowed to be intercalated between

1 the layers. Natural LDH can be found bearing a wide variety of bivalent metal cations such as
2 Mg^{2+} , Ni^{2+} , Ca^{2+} , Mn^{2+} , Zn^{2+} as well as various trivalent cations, Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} ,
3 Mg^{3+} . The second relates to the M^{II} to M^{III} ratio. LDH found in nature tend to present fairly
4 rigid ratio between both cations. Synthetic LDH are much more flexible in this regard
5 displaying M^{II} to M^{III} ratio between 1 and 5 (Forano et al., 2006). The last characteristic that
6 can be easily withdrawn from the general formula is that the layer charge of LDH layers is
7 positive and these are thus compensated by anions which can be easily exchanged. That is
8 why LDH have also been called “anionic clays”. The ensemble of characteristics referred to
9 this far would make LDH an excellent candidate for hybrid compounds design. However, one
10 last important feature renders LDH even more attractive, the multiplicity of synthetic
11 procedures. A profusion of methods is available to prepare LDH as has been thoroughly
12 surveyed elsewhere (He et al., 2006). It is, however, important to note that the diversity of
13 methods allowing to obtain LDH is one of the driving forces behind the advances in LDH-
14 derived hybrid materials and applications (Li and Duan, 2006).

15 LHDS are synthetic layered materials with positively charged layers. Their general formula
16 consists in $[(M^{2+}_{1-x}Me^{2+}_{1+x})(OH)_{3(1-y)}]X^{n-}_{(1+3y)/n} \cdot zH_2O$, where M^{2+} and Me^{2+} correspond to
17 divalent metals, such as Cu, Co, Ni, Mn, or Zn and X^{n-} is the exchangeable anion. The LHDS
18 structure has also been described as an LHS containing two different cations (Arizaga et al.,
19 2007). Generally speaking, their layers are composed of divalent metal ions stabilized in the
20 two-dimensional lattice similar to the brucite structure with some vacant octahedral and a part
21 of the metal ions are positioned above and below the vacant sites outside the hydroxide layer
22 to form tetrahedral coordination (Petrov et al., 1987). This coordination results in the excess
23 of positive charge of layers. Hence, the LHDS, similar to LDH, can accommodate anionic
24 species within interlayer space to compensate the positive layer charge by anion-exchange
25 reactions (Meyn et al., 1993; Tronto et al., 2006; Rojas et al., 2010). Their structure can be
26 stabilized by electrostatic interaction between layers and anions or by a hydrogen bond
27 network between water molecules, interlayer anions and interlayer hydroxyl groups.



1
 2 **Figure 1** - Simplified representations of several layered inorganic compounds: a) a calcium
 3 montmorillonite (Viani et al., 2002); b) shigaite $[AlMn_2(OH)_6]_3(SO_4)_2Na(H_2O)_6 \cdot 6H_2O$, a
 4 layered double hydroxide (Cooper and Hawthorne, 1996); c) tobermorite, a calcium silicate
 5 hydrate (Mrlino et al., 1999); d) vanadium pentoxide layered structure (Filonenko et al.,
 6 2004); e) schematic representation of $Co_3(^{2-}OOC_6H_4PO_3)_2(H_2O)_3 \cdot H_2O$ layered metal
 7 phosphonate featuring a 2-carboxyphenylphosphonic acid as organic building block, viewed
 8 along the b axis (Wang et al., 2011); f) a layered zinc phosphate (Choudhury et al., 2002) g) a
 9 layered iron hexathiohypodiphosphate, MPS_3 (Clement et al., 1986) and h) Bi_2MnTe_4
 10 chalcogenide displaying mixed interlayer space (Lee et al., 2013).

11
 12 **2.3. Calcium silicate hydrates**

13 Calcium silicate hydrates (CSH) are mainly discussed in cement science area, because this
 14 hydrated phase of major components of cement, *i.e.* calcium silicates, is the “glue” within

1 concrete. Formed during the hydration of cement grains, it plays the role of binding phase
2 between cement particles. CSH also occurs in nature *via* hydrothermal alteration of calcium
3 carbonate rocks and/or vesicle fillings in basalts (Taylor, 1989). Owing to their interesting
4 physicochemical properties, they were synthesized and used as catalysis for nuclear and
5 hazardous waste disposal (Komarneni and Breval, 1986), inorganic Portland cement
6 hardening additive (Thomas et al., 2010), to recover phosphorous from solutions (Okano et
7 al., 2013) and to develop orthopædic drug delivery systems (Wu et al., 2013). Different
8 phases and respective structures of CSH have been reviewed in detail by Richardson
9 (Richardson, 2008).

10 Briefly speaking, the smallest CSH unit has a layered structure, with unidirectional elongated
11 layers, resulting in a ribbon-like structure. Each layer consists in a central CaO sheet,
12 sandwiched between two linear chains of silica tetrahedra (Fig. 1-c). Among several structural
13 models for CSH, the most accepted and applied models are based on the crystal structures of
14 jennite and tobermorite minerals. The silicate chains of these minerals have *dreierkette*
15 structure. In this structure, each pair of silica tetrahedra, called pairing tetrahedra, shares O-O
16 edges with CaO octahedral of the central sheet and it is followed by a silica tetrahedron,
17 called bridging tetrahedron, sharing only O vertices with CaO. This pattern is repeated at
18 intervals of three silicate tetrahedra. In tobermorite CaO layers have bare Ca cations,
19 protonated bridging tetrahedra forming silanol groups and the interlayer spaces contain water
20 molecules and additional Ca cations to compensate the negative charge of the layer. In jennite
21 Ca cations of the CaO layers are monohydroxylated causing a considerable corrugation of
22 CaO layers; some of the O atoms in this layer are shared with dreierketten and the others with
23 water molecules and OH groups, creating Ca-OH bonds.

24 CSH share several features with smectites, such as layer morphology, intrinsic negative
25 charge of layers and hydrated interlayer spaces. However, compared to smectites, lateral
26 extension of the layers is limited, CSH have a high stacking disorder and cations of the
27 interlayer spaces are hardly exchangeable (Merlin et al., 2002; Van Damme and Gmira,
28 2006).

29

30 2.4. *Layered Metal Oxides*

1 Simple and mixed metal oxides are certainly the most heteroclite family of compounds
2 discussed in this review. Given the large array of compounds generally described by such
3 large definition, a large structural variability can be found. Metal oxides are commonly
4 arranged in bulk phase where some of them can, under adequate synthesis conditions, form
5 2D structures. Many examples of transition metal oxides according to the formula MO_2 ,
6 where M is a transition metal such as Sc, V, Cr, Mn, Fe, Ni, Mo, W, Ti, Nb, existe in 2D
7 morphology (Osada and Sasaki, 2009; Ataca et al., 2012). In the preceding cases, the metal is
8 hexa-coordinated giving rise to different arranged octahedral polyhedra, stacked to form
9 layered materials, with cations or water molecules between layers to compensate the charge.
10 According to the IUPAC definition of an oxide network (Alemán et al., 2007) and its 2D
11 morphology, vanadium pentoxide, V_2O_5 , is also a layered metal oxide. However it displays a
12 dramatically different layered waving structure composed of vanadium in square pyramidal
13 coordination (Fig. 1d) (Livage, 1991). Moreover, other authors have described the layered
14 metal oxides according to the general formula A_xMO_2 , where A is an alkali-metal ion and M
15 can be one or several ions with various oxidation states (Delmas et al., 1980). This
16 discrepancy in the basic lexicon of layered metal oxides is itself revelatory of the different
17 approaches to these materials as well as the different research fields involved.

18 Regardless of the different approaches and definitions one common factor is patent: a myriad
19 of applications such as catalysis (Kuhlenbeck et al., 2013), photocatalysis (Zou et al., 2001),
20 thermoelectric materials (Terasaki et al., 1997), solar cells (Kim et al., 1993) sensors or
21 superconductors (Takada et al., 2003), have been proposed for layered metal oxides.

22

23 2.5. *Metal Phosphonates*

24 Metal phosphonates with layered structures, classified as organic-inorganic hybrid solids,
25 (Fig. 1e) represent attractive features of both hybrid and layered materials. The metal-O-P and
26 P-C linkages, having quite good stability compared to silicon-based coupling agents, represent
27 a good alternative in organic-inorganic hybrid materials. The versatility of phosphorous
28 chemistry permits to tune characteristics of these materials and thus several applications such
29 as ion exchange, proton conduction, catalysis or sensing are well-known examples.

1 For most of metals, metal phosphonates have a layered structure, with organic group being
2 more or less perpendicular to the interlamellar space. One typical structure of divalent metal
3 phosphonates, with general formula of $MII(O_3PR) \cdot H_2O$, consists in parallel compact layers of
4 metal oxides, in octahedral configuration, sharing four corners with neighboring octahedra
5 and one corner and an edge with two phosphonate tetrahedra; the oxygen atoms of the
6 phosphonate tetrahedra are parallel with the inorganic layer and their organic moiety pointing
7 the interlayer space, forming an organic bilayer between inorganic lamella (Fig. 1e).
8 Therefore, the interlayer space distance, as well as its characteristics, is adjustable by the size
9 and nature of organic molecule. Simple alkyl phosphonates create van der Waals bonding
10 between the end groups of the alkyl chains of adjacent layers. Stronger interlayer bonding can
11 occur by incorporation of hydrogen bonding at the ends of the alkyl chains, e.g.,
12 $M(O_3PCH_2CH_2COOH)_2$. The lateral distance between organic groups can be altered by
13 changing the metal ion used in forming the solid.

14 Although this layered structure forms with most of the trivalent metals and it is the sole
15 existing layered structure for tetravalent metals, formation of a simple lamellar structure
16 largely depends on the size of the organic group. The reason behind this behavior is that the
17 structure of these materials depends on the type of bonding in the inorganic network, i.e.
18 metal-phosphonate bonding, which makes a scaffold for organic groups to lie on (Auerbach et
19 al., 2004; Vioux et al., 2004; Mutin et al., 2005).

20 2.6. *Layered Metal Phosphates*

21 Layered metal phosphates represent similar structural features as the layered metal
22 phosphonates. The structure of most of the known metal phosphonates is related to a purely
23 inorganic metal phosphate. Many of these layered materials with their rich chemistry are
24 excellent inorganic ion exchangers with a peculiar selectivity (Clearfield, 1988).

25 The structural motif of metal phosphates is composed of the planar di- or trivalent metal
26 cations, knitted together by phosphate oxygens above and below the layer plane (Cao et al.,
27 1992). Layered metal phosphates having similar structure (Fig. 1f and 1g), have been mostly
28 described with reference to the α -, γ - and λ -zirconium phosphates. Geometrically speaking,
29 each bi-dimensional layer is formed by concatenation through the vertices of polyvalent metal
30 octahedral and phosphate tetrahedral. The structures similar to that of the α -zirconium

1 phosphates are monoclinic, in which each tetrahedron bridges three different octahedral and
2 these latter bridge six tetrahedral. The arrangement of the pendent phosphate groups in the
3 interlayer space creates cavities, containing water molecules. In a typical γ -compound, metal
4 atoms are bonded by both phosphate tetrahedral and H_2PO_4 . The H_2PO_4 shares two oxygens
5 with two different metal atoms and points the remaining two OH groups to the interlayer
6 (Alberti et al., 1999). In the λ -structure, a layer is composed of four different metal atoms
7 bridged together with a tetrahedral phosphate group, compensating the residual positive
8 charge as well as completing the octahedral configuration of each metal atom with a
9 monovalent anionic ligand, Cl^- and a neutral monodentate ligand (Auerbach et al., 2004).

10

11 2.7. *Layered Metal Chalcogenides*

12 Owing to their interesting yet intriguing physico-chemical characteristics of these layered
13 two-dimensional (2D) materials, layered metal chalcogenides (LMC) attracted attentions of
14 researchers. Many interesting physical and chemical properties of LMC stem from the
15 anisotropic nature of the layers, resulting in technologically useful mechanical, electrical,
16 magnetic, and optical properties. MoS_2 , NbS_2 , and WS_2 are examples of LMCs which are
17 used both as solid lubricants and as additives in liquid lubricants in several technological
18 applications. Several transition metal dichalcogenides, such as MX_2 ($M = Ta, Ti, V, Mo,$ or
19 Cr ; $X = S$ or Se) were used as cathodic (positive) insertion electrode in rechargeable alkali
20 metal batteries. Transition metal trichalcogenides have demonstrated interesting
21 electrochemical properties for battery application. The group V transition metal
22 dichalcogenides MX_2 ($M=Ta$ or Nb ; $X=S, Se,$ or Te) are metallic superconductors.

23 LMC are usually categorized by their composition. They are either binary compounds,
24 including metal dichalcogenides (MX_2) and metal trichalcogenides (MX_3), or ternary
25 compounds, including AM_2S_5 , $(AS)_n(MS_2)_2$ (known as misfit layer) and metal phosphorus
26 trichalcogenides (MPX_3). LMC contain neutral layer structures except some compositions
27 which have negatively charged layers. An LMC is either semiconductor, or semimetallic or
28 metallic as a function of metal cation present in its structure. For example, MoS_2 , $MoSe_2$,
29 WS_2 , and WSe_2 are semiconductors, whereas MX_2 ($M=Ta$ or Nb ; $X=S, Se,$ or Te) are
30 metallic. While TiS_2 has a semiconductor–semimetallic phase transition, $TiSe_2$ is a semimetal.

1 Generally speaking, LMCs structure consists in layers of covalently bounded atoms with Van
2 der Waals interaction between layers. In each individual layer metal atoms arranged
3 hexagonally, sandwiched between two hexagonal sheets of chalcogen, forming a two-
4 dimensional electron bond layer. The individual 2D layers can self-assemble into
5 face-to-face-stacked layers, forming a LMC (Fig. 1h) (Auerbach et al., 2004).

6 **3. Lamellar compounds hybridization strategies and approaches**

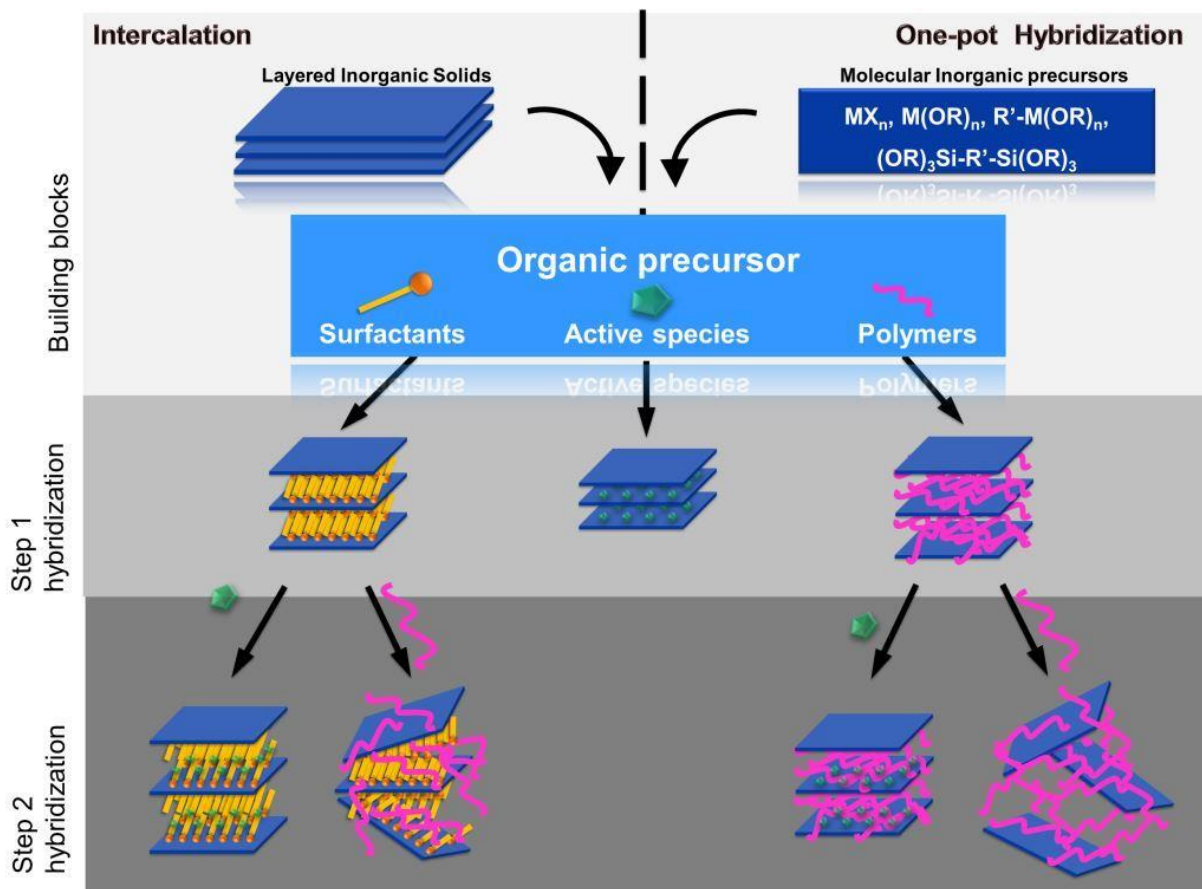
7 The picture of inorganic lamellar compounds beside each other, regardless of their chemical
8 composition (*c.f.* Figure 1), can easily lead keen eyes to the one common point between them:
9 their nano-morphology, composed of stacking inorganic layers which creates “the interlayer
10 space”. This important observation/conclusion on the structure of a lamellar compound,
11 notably the presence of weak electrostatic forces which governs the interlayer space
12 interactions, is the key idea behind the hybridization of lamellar compounds.

13 Taking advantage of the possibility of interlayer chemistry modification, the very first
14 strategy of organic modification of a lamellar compound was defined: inserting organic
15 species between layers, i.e. organic modification of the interlayer space. Later, this strategy
16 was also coined as hybridization of nano-building blocks (Sanchez et al., 2005).

17 The second hybridization strategy of lamellar compounds came with advent of organic-
18 inorganic hybrid materials concept. The advantages brought by sol-gel process, allowing
19 inorganic and organic precursors to mix at nanometric scale, was the origin of one-pot
20 synthesis strategies. The application of this strategy to obtain hybrid lamellar compounds will
21 be discussed in this paper.

22 Hybridization strategies of lamellar compounds can be depicted in two main categories:
23 hybridization by intercalation and by in-situ integration of a given organic moiety into the
24 forming inorganic layer (Fig. 2). While intercalation strategy consists in accommodating an
25 organic moiety between layers, after synthesizing the inorganic host, in-situ hybridization
26 implies self-assembly of organic and inorganic species together in the synthesis medium,
27 forming a layered texture, containing organic guests between inorganic layers.

1



2

3 **Figure 2-** Hybridization strategies of inorganic lamellar compounds

4

5 **3.1 Intercalation**

6 The most intuitive hybridization strategy for layered inorganic compounds relates to the
7 capacity that most layered structures display to accommodate molecular species in their
8 interlayer space (Hendricks, 1941; Hoffmann and Brindley, 1960, 1961; Hang and Brindley,
9 1970; Carrado et al., 1993; Lagaly, 2001; Forano et al., 2006; Beneš et al., 2012). In fact this
10 strategy might have been used in ancient Mayan civilization to prepare pigments such as
11 Maya Blue, a hybrid material consisting on indigo molecules stabilized inside the tunnels of
12 palygorskite, a fibrous clay mineral (Sanchez del Rio et al., 2011). Layered inorganic
13 compounds have also been used throughout history as adsorbents capable of stabilizing
14 organic molecular species. One of the most know examples is that of fuller's earth which has
15 served since the Roman civilization as a detergent due to the adsorption properties of the clay

1 fraction (Ruiz-Hitzky et al., 2010). Yet another example concerns the intercalation of urea
2 molecules that has been also used during the roman civilization to prepare hybrid layered
3 materials from decaying urines. (Rytwo, 2008) In fact, several centuries passed until Weiss
4 (1963) reported the intercalation of urea by layered silicates.

5 The first works about the intercalation of organic species in the interlayer space of layered
6 compounds have mostly focused on clay minerals and on the basic fundamental
7 understanding of the physical and chemical phenomena involved in the intercalation process,
8 cation exchange or dipolar interaction (MacEwan, 1946). The first organic-inorganic hybrid
9 layered materials have largely benefited from such fundamental works. The rationale behind
10 most of the hybrids prepared from an intercalation process was to protect a functional species
11 by inserting it into the interlayer space of inorganic layered solids. Although many examples
12 concern the modification of clay minerals, other inorganic layered solids have also been
13 modified according to the same strategy.

14

15 *3.1.1. Molecular guests*

16 Strongly motivated by the chromatic quality and chemical resistance of Maya Blue pigment,
17 the adsorption of colored dye molecules into the interlayered space of layered inorganic
18 compounds has soon seen important advances. Organic dyes are prone to UV degradation and
19 subsequent bleaching. The protective effect that inorganic layered hosts could induce has thus
20 been strongly sought after. Clays (Emodi, 1949; Hang and Brindley, 1970; Carrado et al.,
21 1993), metal layered oxides (Tagaya et al., 1993; Kuwahara et al., 2001), LDH (Miyata, 1983;
22 Hussein et al., 2004a; Forano et al., 2006) have proven to be extremely useful scaffolds to trap
23 and protect colored organic dyes.

24 One of the domains where many efforts were made in the intercalation was in the production
25 of new herbicide and pesticide formulations, where the active species (usually highly toxic) is
26 intercalated in the interlayer space of the layered compounds. The first understanding of the
27 potential of clay minerals to act as a reservoir, was unveiled by Bailey and White (1964) in
28 the context of soil science. This approach soon became widely studied. In the case of
29 clay-herbicide hybrids, one of the biggest concerns is the reduction of herbicide leaching.
30 Nennemann *et al.* (2001) have addressed this issue by adsorbing metolachlor in different

1 layered inorganic hosts from aqueous and/or alcohol solutions. Their results indicate that raw
2 bentonites and montmorillonites can integrate up to $200 \mu\text{g}\cdot\text{g}^{-1}$ metolachlor. Moreover, the
3 inorganic host is capable of tuning the release kinetics of herbicide to attain formulations that
4 have systematically surpassed commercial formulation of metolachlor containing compounds
5 over growth inhibition of green foxtail (*Setaria viridis*). While clay minerals seem especially
6 well-suited for the adsorption and controlled release of cationic species, LDH do the reverse.
7 Due to their positive layer charge, they display important anion-exchange capacity that can be
8 useful in the adsorption of negatively charged species (Pavlovic et al., 2005; Nejati et al.,
9 2013; Otero et al., 2013). Interestingly, in the case of LDH, the mechanism of adsorption does
10 not seem to fully reproduce the diffusion-controlled ion exchange observed in the interlayer
11 space of clay minerals. Since LDH have the ability to exfoliate and restack in solution
12 (reconstruction), the adsorption of the different pesticides seems to pass through a disordered
13 phase (where the cationic sites are easily available to the anionic pesticides) followed by the
14 reconstruction of the LDH-pesticide hybrid (Pavlovic et al., 2005). These authors have
15 reported very high adsorption values of $2500 \mu\text{mol/g}$ and $1035 \mu\text{mol/g}$ for the pesticides
16 Clopyralid (3,6-dichloropycolinic acid) and Picloram
17 (4-amino-3,5,6-trichloropyridine-2-carboxylic acid), respectively.

18 Regardless of the obvious differences, there is a strong resemblance between materials
19 devised for soils and materials that are designed for drug delivery systems. In both cases the
20 role of the prepared material is to deliver a specific functional species (a pesticide in soils, a
21 drug in medical applications) to a very complex system. Delivery to such a complex medium
22 necessitates protection of the functional species from undue delivery or degradation both in
23 drug delivery systems, and in soil science. Hybrid layered materials have been intensively
24 explored in this field of application owing to their two important characteristics: first, their
25 capacity of accommodation a molecular specie of different nature in the interlayer space, and
26 second the non-toxicity of many inorganic layered structures such as LDH (Forano et al.,
27 2006; Li and Duan, 2006; Delhoyo, 2007) and clays (Carretero et al., 2006; Choy et al.,
28 2007; Darder et al., 2007; Ruiz-Hitzky et al., 2010). These compounds have served as hosts
29 for the controlled delivery of a wide variety of active principles such as methotrexane, a
30 potent anti-cancer drug; diclofenac, ibuprofen and naproxen, non-steroid anti-inflammatories
31 or vitamin C, for cosmetics (Forano et al., 2006; Li and Duan, 2006; Choy et al., 2007; Ruiz-
32 Hitzky et al., 2010).

1 The polymer community, strongly motivated by the potential impact of inorganic layered
2 compounds in the mechanical reinforcement of polymer-based nanocomposites, has soon
3 embraced the layered inorganic materials field. The first works, reported by Blumstein (1965),
4 focused on the adsorption and subsequent polymerization of different monomers by Mt such
5 as acrylonitrile, methyl methacrylate, vinyl acetate, styrene and isoprene. This work reported
6 the changes in basal spacing of the clay mineral according to the intercalated monomers
7 monolayer followed by their polymerization. Despite the fundamental approach (Blumstein
8 was interested in the study of two-dimensional polymerization phenomena more than in the
9 preparation of materials) his findings constitute a milestone in the preparation of hybrid
10 lamellar compounds. According to Blumstein's approach, the interlayer space in inorganic
11 compounds could be understood not only as a reservoir of organic molecules, but also as a
12 confined reactor capable of modulating the outcome of chemical reactions. This approach was
13 followed by researchers working in conductive polymers such as polyaniline and other
14 inorganic layered structures such as vanadium pentoxides (Kanatidis et al., 1989; Wu et al.,
15 1996) aiming at the preparation of conductive composite materials.

16 Besides above mentioned considerations on layered inorganic hosts, *i.e.* reservoir, protecting
17 shell and/or confined reactor, the combination of intrinsic properties of these hosts with a
18 similar characteristic of an organic guest permits to accentuate a demanded property. This
19 combination mode has been significantly used to modulate the magnetic or optical properties
20 of layered metal hydroxides (Rueff et al., 2004; Delahaye et al., 2009). Several examples of
21 these types of molecular magnets have been presented by different authors. A heterometallic
22 layered structure magnet was obtained by intercalation of chiral and non-chiral salen-type
23 Ni(II) complexes into copper and cobalt layered simple hydroxides. Pre-intercalated cobalt
24 and copper hydroxides, *i.e.* $\text{Cu}_2(\text{OH})_3(\text{DS})$ and $\text{Co}_2(\text{OH})_3(\text{DSO})$, where DS is dodecylsulfate
25 and DSO is dodecylsulfonate, were used as host materials and salen-Ni(II) complexes were
26 used as guest molecules to induce chirality in a non-chiral magnetic system (Delahaye et al.,
27 2010). Intercalation of peptides by anion-exchange reactions into pre-intercalated Cu(II) and
28 Co(II) LSH interlayer space (Copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), cobalt
29 acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$)), resulted in bio-hybrid compounds. Among these
30 compounds, the copper-based tyrosine LSH bio-hybrids showed an antiferromagnetic
31 behavior whereas the cobalt-based analogues were ferrimagnets (Si et al., 2012).

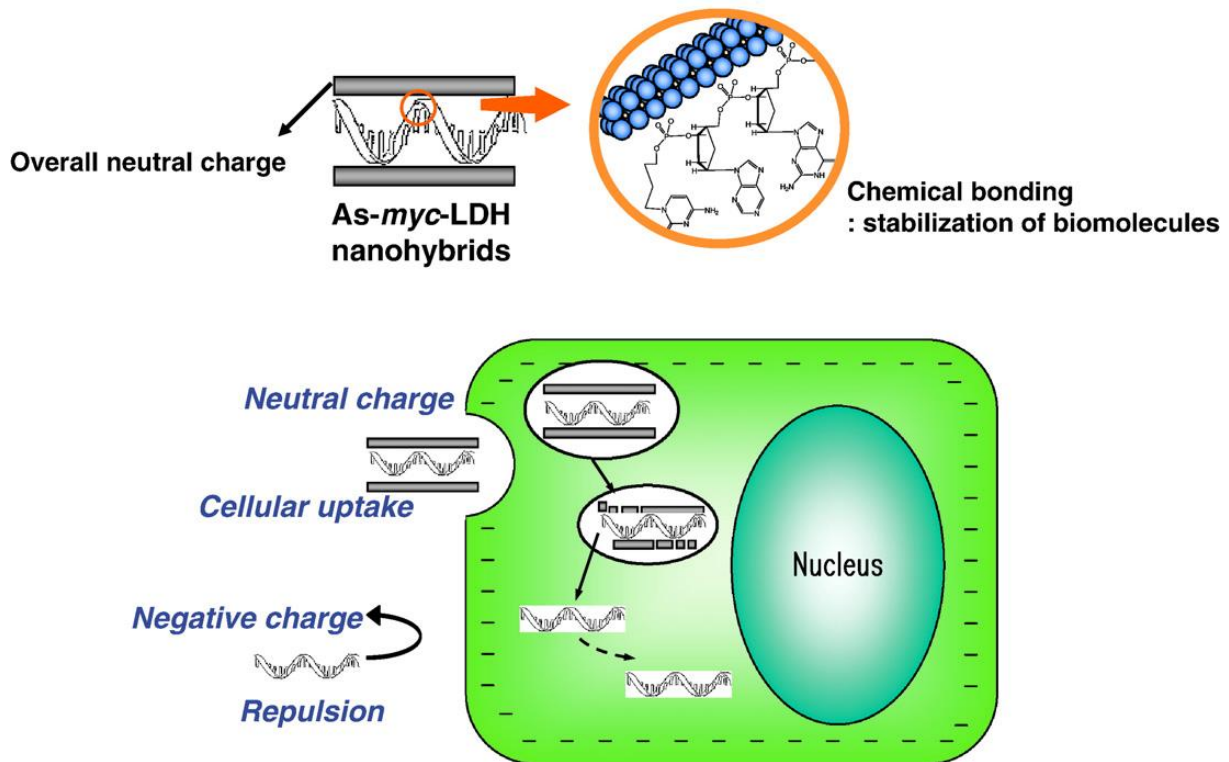
1 3.1.2 *Molecular modifiers of the interlayer space of layered materials*

2 The following step in the modification of inorganic layered systems was based on the
3 enhancement of a guest molecule intercalation by the pre-adsorption of compounds which can
4 modify the chemical environment of the interlayer space, mostly due to the use of surfactant
5 species. Historically, alkylammonium ions were the first compounds used to render the
6 interlayer space of clay minerals hydrophobic (Giesecking, 1939; Jordan, 1949). Such strategy
7 finds numerous examples in the literature where the same rationale has been applied. It was
8 applied to vanadium oxide using the same alkylammonium organocations (Livage, 1991), to
9 copper and cobalt simple layered hydroxides using alkyl sulfate derivatives (Eyele-Mezui et
10 al., 2012), to layered clay minerals using phospholipids (Wicklein et al., 2010) among many
11 other examples.

12 The most outstanding feature of this approach regards the capacity for highly amphiphilic
13 molecules to self-assemble (mostly due to the interaction between alkyl chains) in a
14 cooperative manner, thus significantly increasing the basal distance of the layered systems.
15 This separation creates, as previously mentioned, a different chemical environment
16 responsible for the enhanced adsorption of non-polar molecules (Miyata, 1983; Jaynes and
17 Vance, 1999; Kwolek et al., 2003; Kozak and Domka, 2004; Rytwo et al., 2005; de Paiva et
18 al., 2008; ; Moscofian and Airoidi, 2008; Ruiz-Hitzky et al., 2010; Wicklein et al., 2010).

19 Another important feature of the basal spacing augmentation is its impact on the confinement
20 of the subsequently adsorbed species. Fukushima et al., in a series of ground-breaking works,
21 have fully understood the potential to effectively exfoliate inorganic layered materials by
22 polymerizing monomers such as caprolactam and methyl methacrylate in between previously
23 expanded clay mineral layers (Fukushima and Inagaki, 1987; Fukushima et al., 1988; Kojima
24 et al., 1993; Usuki et al., 1993; Fukushima and Tani, 1995). The result was an outstanding
25 dispersion of the clay mineral layers within the polymer matrix, displaying a dramatic effect
26 over the mechanical properties of the material, a clay polymer nanocomposite. Numerous
27 contributions on the CPN field followed (Messersmith and Giannelis, 1993, 1995; Giannelis,
28 1996; Bafna et al., 2003; Ruiz-Hitzky and Van Meerbeek, 2006; Podsiadlo et al., 2007; Chen
29 et al., 2008; Annabi-Bergaya, 2008; Paul and Robeson, 2008), being at present one of the
30 fields where hybrid layered compounds have established their way into consumer end
31 products.

1 Beside advances in *in-situ* polymerization of adsorbed monomers into modified interlayer
 2 space of a given clay mineral, another thrived approach concerns the diffusion of polymers
 3 directly into the modified clay minerals. This latter, technically much simpler, allows direct
 4 integration into processing units such as melt compounders or extrusion units. The rationale
 5 behind this methodology lies on the enhanced dispersibility of clay mineral particles induced
 6 by shear as well as the maximization of polymer chain mobility with temperature in
 7 thermoplastics. These two phenomena, together with an appropriate interlayer space
 8 modification, allow to fully disperse organoclays stacks to individual layers throughout the
 9 CPN (Vaia et al., 1995; Giannelis, 1996; Gilman, 1999; Lagaly, 1999; LeBaron et al., 1999;
 10 Alexandre and Dubois, 2000; Suprakas Sinha Ray and Okamoto, 2003; Lagaly et al., 2006;
 11 Tjong, 2006).



12

13 **Figure 3** – Schematic representation of DNA transfection by Layered double hydroxides (Choy et al., 2007).
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15

16 **3.1.3 Polymer diffusion in raw inorganic layered materials**

17 Another strategy devoted to the production of hybrid layered materials that has recently found
 18 an impressive development, concerns the diffusion of polymers directly into the interlayer

1 space. Given the hydrophilic nature of most inorganic layered materials, such diffusion is
2 widely favored in aqueous conditions, which in turn dramatically reduces the array of
3 polymers that are concerned by this modification approach.

4 Within the water-soluble polymers many have been used to produce CPN for different
5 applications, from lithium insertion batteries to DNA transfection (Fig. 3) (Ruiz-Hitzky and
6 Aranda, 1990; Aranda and Ruiz-Hitzky, 1992; Ray and Okamoto, 2003; Darder et al., 2005b;
7 Ray and Bousmina, 2005; Ruiz-Hitzky et al., 2005, 2010, 2011; Choy et al., 2007; Zhuang et
8 al., 2007; Chivrac et al., 2009; Ojijo and Ray, 2013). Analyzing these materials, one
9 conclusion is apparent. Most of the water-soluble polymers that diffuse into the inorganic
10 layered materials are of biological origin. In fact, the assembly of biopolymers with inorganic
11 nanomaterials has been recently coined as bionanocomposites (Darder et al., 2007; Ruiz-
12 Hitzky et al., 2008). These materials are presently under intensive research using a multitude
13 of inorganic hosts such as vanadium pentoxide (Carn et al., 2010), clay minerals (Darder et
14 al., 2008; Ruiz-Hitzky and Fernandes, 2013), LDH (Darder et al., 2005b) or phosphates
15 (Darder et al., 2006). The strategy behind the preparation of these materials is not different
16 from hybrid materials prepared by diffusion of molecular species. Biopolymers are usually
17 adsorbed within the interlayer space of the inorganic host. The intercalation is often followed
18 by the complimentary information provided by the adsorption isotherm as well as XRD
19 patterns that clearly identifies the basal spacing changes induced by the adsorption. This
20 technique implies a very high affinity between the inorganic host and the macromolecule
21 being adsorbed. When the inorganic host displays a layer charge such as in the case of clay
22 minerals or LDH, the adsorption mechanism is mediated by an ion-exchange process. One of
23 the most prominent results concerning the direct intercalation of biopolymers within an
24 inorganic lamellar host is that of DNA (Fig. 3) (Choy et al., 1999, 2007).

25 Gene therapy concerns the treatment of a variety of diseases by transfection, *i.e.* delivering
26 genetic material within the intracellular space so it can interact with the cells' own genes. To
27 achieve this goal two criteria must be taken into account. The first one relates to the
28 degradability of DNA and the second to the need to overcome the charge repulsion that is
29 established between the cell walls and the DNA strands (both charged negatively). The most
30 known strategy to address transfection consists in the use of viral capsids to penetrate the cell
31 wall and deliver the therapeutic genetic material to the nucleus. To produce non-viral vectors
32 for gene delivery, Choy *et al.* (1999, 2007) have adsorbed nucleotides and DNA within

1 Mg₂Al(NO₃) LDH. LDH have proven effective materials to host DNA without inducing
2 conformational or compositional changes in the DNA strands. Moreover, since the net charge
3 of the hybrid compound is positive the electrostatic repulsion between the cell walls and DNA
4 was circumvented.

5 Another noteworthy example of biopolymer diffusion in the interlayer space of raw inorganic
6 layered compounds regards the intercalation of chitosan in the interlayer space of Mt. Darder
7 *et al.* (2003) have shown that the intercalation of a biopolymer can be pushed beyond the
8 adsorption of a monolayer in the interlayer space of the clay mineral. Based on XRD and
9 adsorption data, the authors have demonstrated the formation of a bilayer of positively
10 charged chitosan macromolecules in the interlayer space of the clay mineral. The result of
11 such massive intercalation was the transformation of Mt chitosan, a cation exchanger into an
12 anionic exchanger when the chitosan to Mt reached 5:1, respectively. This feature has been
13 demonstrated in the form of a sensor displaying potentiometric cross-sensitivity.

14 Finally, another remarkable application for bionanocomposites prepared from layered hybrid
15 materials concerns the mechanical reinforcement provided by the inorganic moiety to the
16 biopolymer matrix. The key idea behind the preparation of clay polymer bionanocomposites
17 for structural applications does not differ from the classical CPN. It is based on the difference
18 between the mechanical properties of the inorganic layers and those of biopolymers.
19 Moreover, the elevated aspect ratio of inorganic layers obtained by the delamination of
20 lamellar compounds alongside with the potential to disperse thoroughly the inorganic layers
21 has naturally attracted the interest of researchers. The strategy is, again, no different from the
22 previous examples. The biopolymers are adsorbed into the interlayer space of clay minerals
23 (Darder *et al.*, 2008), oxides (Carn *et al.*, 2010) or LDH (Darder *et al.*, 2006) inducing the
24 basal spacing augmentation until the interactions between adjacent layers are comparable to
25 the interaction with the biopolymers. This process, usually performed in aqueous solution is
26 normally followed by shaping by solution casting, foaming or spinning techniques. Alongside
27 with the mechanical reinforcement, bionanocomposite materials benefit from the
28 biocompatibility of the used biopolymer. This is why bionanocomposites have special impact
29 in two sensitive domains, health and food packaging (Armentano *et al.*, 2013). Due to the
30 resemblance between the nature of bionanocomposites and bone composition (a natural
31 bionanocomposite made out of collagen and nanometric hydroxyapatite sheets), these
32 materials are often discussed in the context of tissue engineering (Armentano *et al.*, 2013;

1 Okamoto and John, 2013; Sowmya et al., 2013). However, the domain, where
2 bionanocomposites are perceiving increasing attention, is that of food packaging (Armentano
3 et al., 2013; Raquez et al., 2013; Reddy et al., 2013; Rhim et al., 2013).

4

5 3.1.4 Interlayered metal nanoparticles

6 One of the most interesting domains discussed in the context of layered materials regards the
7 role of such inorganic structures in the development of prebiotic life (Ponnamperuma et al.,
8 1982). In fact this hypothesis is supported by the wide availability of inorganic layered
9 materials such as silicates along with the morphological characteristics of layered materials
10 that can act as confined reactors for an eventual prebiotic synthesis. Yet, the catalytic effect of
11 the inorganic layers themselves is often overseen. In fact the inorganic layers of clay minerals
12 such as Mt have been used to catalyze the synthesis of biomolecules from prebiotic conditions
13 (Brack, 2006).

14 Modern catalysts however depend on far more complex systems due to strict technical
15 demands in terms of efficiency, selectivity and reusability. To achieve suitable catalysts one
16 of the most common approaches consists in the deposition of active nanometric catalytic
17 centers on a substrate to maximize the contact between the active center and the species to be
18 catalyzed (*i.e.* heterogeneous catalyst systems). Metallic centers displaying catalytic activity
19 such as Ni, Pd or Cu have been introduced in the interlayer space of layered systems in form
20 of nanoparticles (Martínez-Ortiz et al., 2003; Patakfalvi et al., 2003; Tichit et al., 2006;
21 Gérardin et al., 2008) in the case of LDH, and as pillared structures bridging the gap between
22 adjacent clay layers in clay minerals (Ohtsuka, 1997).

23 The main routes of synthesizing metal/LDH catalysts consist in 1) impregnation and/or
24 exchange of $M^{II}(M^{III})O$ with metal precursor, 2) partial or total substitution of M^{II} or M^{III} with
25 transition metal *via* co-precipitation, and 3) intercalation by anion-exchange of preformed
26 metal colloid (Tichit et al., 2006). Palladium nanoparticle loaded LDH were synthesized using
27 these mentioned routes. The obtained results demonstrated that the catalytic system obtained
28 from a palladium colloid nanocomposite precursor resulted in the higher performances in the
29 one-pot synthesis of 2-methyl-3-phenyl-propanal from benzaldehyde and propanal (Tichit et
30 al., 2007). The richness of this system concerns the diversity of active centers available inside

1 the interlayer space of the nanocomposite material. Basic sites induce the condensation of
2 benzaldehyde and propanal to attain a reaction intermediary, acid sites are capable of
3 dehydrating the reaction intermediary and finally, the palladium reactive centers selectively
4 hydrogenate the carbon double bond. The same system has been applied to the
5 dehydrogenation of 2-butyne-1,4-diol to 1,4 butanediol (Tichit et al., 2007).

6 As previously stated clay minerals are also capable of forming catalysis-relevant materials.
7 However, most of the catalysts prepared using clay minerals as support concern pillaring the
8 layers together via the adsorption and subsequent condensation of the catalyst center (pillared
9 interlayered clays, PILC) to form a microporous solid. Despite the loss of the layered nature
10 of the initial materials, (PILC materials are actually considered as two-dimensional zeolites)
11 these materials are a paradigmatic example of the potentialities of layered systems even in the
12 development of 3D functional materials.

13

14 3.2 *In situ integration of organic guest molecule*

15 Intercalation of organic species/guest molecules in the interlayer space of the lamellar
16 compounds at the end of the 1950's, not only opened the discussion about the feasibility of
17 hybridization of such inorganic hosts, but also it answered an important question: how to
18 make the most of the lamellar compounds. Later on, in the mid 1990's, inspired by the vast
19 possibilities given by sol-gel chemistry obtained from polycondensation of organosilanes and
20 metal alkoxides, researchers started to pave a new road toward organic-inorganic hybrid
21 layered materials. Shortly after, procedures based on the self-assembly of amphiphilic organic
22 molecules in the synthesis medium and in presence of an inorganic precursor, allowed to
23 synthesize hybrid materials with layered textures (Sanchez et al., 2005, 2011).

24 Sol-gel process, co-precipitation at room temperature or at hydrothermal or solvothermal
25 conditions, are the most common one-pot synthesis methods used to elaborate hybrid layered
26 materials.

27

28 3.2.1 *Sol-gel process*

1 Sol-gel route has been widely used to synthesize hybrid layered silicates. The idea of using
2 this method and its vast application stem from the self-directed assembly potential of
3 alkoxysilanes ($\text{Si}(\text{OR})_4$) and organoalkoxysilanes ($\text{R}_n\text{Si}(\text{OR})_{4-n}$), where R can be an organic
4 group. Considering each organoalkoxysilane molecule as an amphiphilic unit (depending on
5 the length of organic moiety chain) as well as the sol-gel processing conditions, they can be
6 self-assembled to form inorganic layers composed of silicate chains, between which organic
7 chains are placed (Sanchez and In, 1992; Sanchez and Ribot, 1994; Judeinstein and Sanchez,
8 1996; Mann et al., 1997; Kuroda et al., 2014). Based on the mechanisms involved in sol-gel
9 reaction, several organic-inorganic layered compounds have been successfully synthesized.
10 Clay minerals analogous metal phyllosilicates (Fonseca et al., 1999, 2000, 2004; Jaber et al.,
11 2002, 2003, 2005; Gallégo et al., 2008; Jaber and Miehé-Brendlé, 2008), CSH, oxides and
12 metal phosphonates are well-discussed examples.

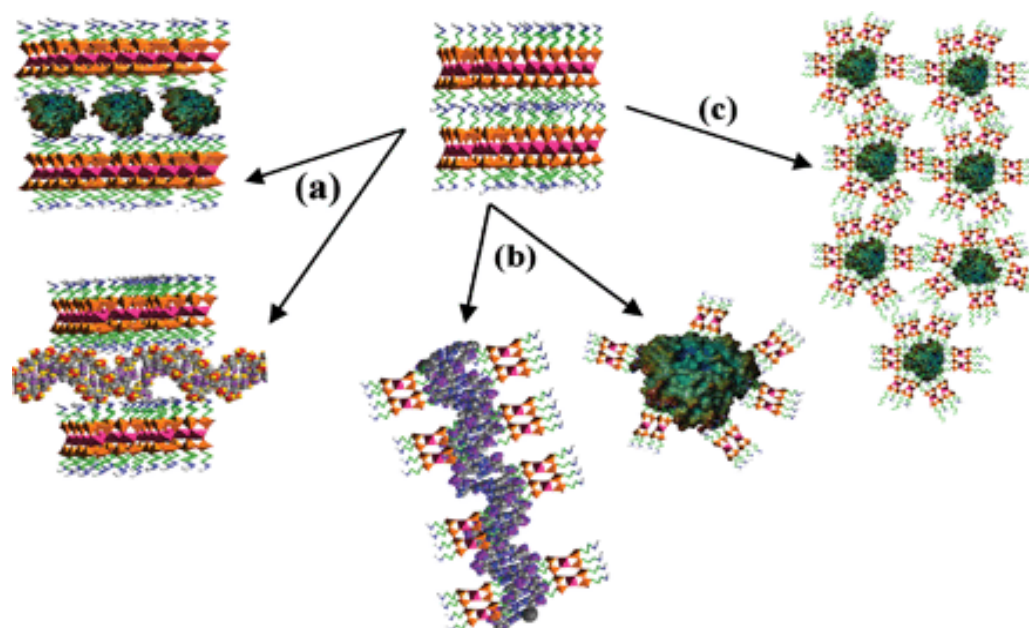
13 The advent of sol-gel synthesis of organic-inorganic hybrid metal phyllosilicate was in 1995,
14 by Fukushima *et al.*, using an organosilane as silica precursor (Fukushima and Tani, 1995).
15 The common point between numerous existing protocols for synthesizing layered
16 organic-inorganic metal phyllosilicates through this process relies on chemical reaction
17 between a wide variety of metal salt solutions (magnesium, aluminum, copper, zinc, calcium,
18 lithium, nickel, etc.) and organotrialkoxysilane precursors, in basic medium. Several different
19 alkoxysilanes were used to synthesize these compounds, including methyltriethoxysilane,
20 octyltriethoxysilane, phenyltriethoxysilane, phenethyltrimethoxysilane,
21 aminopropyltrimethoxysilane, N-phenylaminomethyltrimethoxysilane,
22 (3-mercaptopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, [N-(2-aminoethyl)-3-
23 aminopropyl]trimethoxysilane, [(10-amino)-4,7-diazanonyl]trimethoxysilane,
24 (3-(methacryloxy)propyl)trimethoxysilane, (3-acryloxypropyl)trimethoxysilane (Burkett et
25 al., 1997, Carrado et al., 2001; Fujii et al., 2003; Fonseca et al., 2004; Lagadic, 2006; Gallégo
26 et al., 2008; Badshah and Airoidi, 2011).

27 These organo-metal phyllosilicates were obtained in aqueous or water-solvent mixed media,
28 at room temperature or at higher temperatures. The mechanisms invoking the formation of
29 metal organo-phyllosilicates *via* sol-gel route depend not only on the synthesis conditions, *e.g.*
30 pH and temperature, but also on the intrinsic characteristics of applied organotrialkoxysilane,
31 *e.g.* organic moiety chain length/ hydrophobicity and hydrolysis and condensation kinetics
32 (Richard-Plouet et al., 2004). This synthesis route resulted majorly in poorly crystalline

1 organo-metal phyllosilicates. Although this latter makes the structural characterization of
2 these compounds difficult, the admitted structure for inorganic layer of organo-metal
3 phyllosilicates consists in metallic cations centered in octahedral sites, coordinated by oxygen
4 atoms, which are sandwiched between silicate tetrahedral sheets. The organic chains are
5 attached to tetrahedral R-Si-O₃ group of the inorganic layer *via* Si-C bonds, pointing to the
6 interlayer space (Burkett et al., 1997; Fonseca et al., 1999, 2004). Depending on the organic
7 group bonded to Si, interlayer distance ranges from 11 to 38 Å (Richard-Plouet et al., 2004).

8 One-pot synthesis of a hybrid layered metal phyllosilicate by applying an
9 organotrialkoxysilane *via* sol-gel route can result in the modified structures and chemical
10 characteristics which permit these compounds integrating various functional guest
11 biomolecules to form bio-inorganic hybrids (Patil and Mann, 2008). Exfoliation of an
12 aminopropyl-functionalized magnesium phyllosilicate (AMP) in water resulted in
13 delaminated layers of 30 to 150 nm in size and about 2 nm thickness, which corresponds to a
14 positively charged (due to protonation of aminopropyl chains) single layer of organoclay
15 framework. Afterward, the addition of negatively charged myoglobin or glucose oxidase to
16 the exfoliated AMP dispersion resulted in immediate re-assembly and restacking of layers,
17 forming protein intercalated lamellar metal organophyllosilicate (Fig. 4a) (Patil et al., 2005).
18 In order to obtain organoclay DNA-AMP (Patil et al., 2007) and organoclay drug-AMP
19 (Holmström et al., 2007) nanocomposites the same logic were used. The organoclay layers
20 restacking depends on the size and charge of the applied biomolecules. A positively charged
21 biomolecule or a large negatively charged one, did not result in a lamellar bio-hybrid structure
22 (Patil et al., 2005). Leaning on the synthetic metal organophyllosilicates potentials,
23 synthesizing other bio-inorganic nanocomposites can be conceivable. Oligomers of a
24 positively charged exfoliated AMP obtained after AMP layers exfoliation in water, followed
25 by gel chromatography of the delaminated material. Adding solutions of biomolecules such as
26 myoglobin and glucose oxidase to stable sols of the oligomeric organoclays resulted in
27 wrapping of biomolecules by these organoclay clusters (Fig. 4b). Modification of organic
28 moieties of metal organophyllosilicate in order to have pendent long-chain hydrophobic
29 moieties attached to silicate layers can result in bio-inorganic nanocomposite with a high
30 order superstructure (Fig. 4c) (Patil et al., 2004). Using similar AMP oligomers dispersion,
31 added to λ -DNA solutions, organoclay DNA nanowires were obtained (Fig. 4b) (Patil et al.,
32 2007).

1



2

3 **Figure 4** – (center) Proposed structure for aminopropyl-functionalized magnesium
4 phyllosilicate (AMP) composed of a central layer of brucite $Mg(OH)_2$ octahedra connected on
5 both sides to a tetrahedral silicate layer comprising covalently linked aminopropyl moieties
6 that are positioned in the interlayer spaces, (a) exfoliated cationic AMP sheets after
7 electrostatically induced reassembly of the organoclay layers with biomolecule and DNA, (b)
8 wrapped negatively charged proteins (bottom centre right) or DNA (bottom centre left) with
9 cationic organoclay clusters, (c) superstructures of organoclay-enveloped biomolecules (Patil
10 and Mann, 2008).

11

12 Using the same logic to synthesize a hybrid layered component, *i.e.* incorporation of an
13 organic group covalently bonded to a silicate layer *via* sol-gel process, Minet *et al.* (2004)
14 synthesized hybrid CSH. Such hybrids are obtained from co-precipitation of both
15 organotrialkoxysilane and tetraethoxysilane together with calcium salt in aqueous/ethanolic
16 solution, in basic medium. CSH accommodated the small sized organic groups, linked to
17 silicate chains, by co-condensation of tetraethoxysilane and trialkoxysilanes, such as
18 ethyltriethoxysilane, n-butyltrimethoxysilane or 3-aminopropyltriethoxysilane (Minet *et al.*,
19 2006). However, using only organotrialkoxysilanes with alkyl chains (from methyl to
20 octadecyl) as both silicon and organic group precursors, Minet *et al.* obtained a hybrid layered
21 calcium silicate with smectite-like layer, rather than the parent inorganic CSH structure
22 (Minet *et al.*, 2004).

1 Sol-gel route has also found its place in synthesizing multifunctional hybrid metal oxide and
2 hydroxide nanoparticles. Pinna *et al.* (2005) presented a new hybrid layered yttria-based
3 nanomaterial, composed of alternating layers of crystalline yttrium oxide and benzoate
4 molecules between the layers. The synthesis procedure consisted in a non-aqueous sol-gel
5 process, involving the reaction between yttrium alkoxide and benzyl alcohol at relatively low
6 temperatures. Later, applying the same procedure, *i.e.* non-aqueous sol-gel reaction between
7 Ln III (Ln = Gd, Sm, Nd) isopropoxide and benzyl alcohol, they succeeded to obtain
8 lanthanide-base well-crystallized lamellar nanohybrids, composed of crystalline lanthanide
9 oxide layers regularly separated from each other by organic layers of intercalated benzoate
10 molecules (Karmaoui and Ferreira, 2006; Karmaoui and Mafra, 2007; Karmaoui et al., 2007).
11 This one-pot “benzyl alcohol route overcomes the main drawback of aqueous sol-gel
12 chemistry, that is to say the low crystallinity of the final product, without the need for any
13 template (Pinna, 2007).

14 Owing to the formation of both P–C and P–O–C stable bonds during hydrolysis of
15 organophosphorus molecules, sol-gel route has been applied to synthesize metal phosphonates
16 and hybrid metal phosphates. The precursor of organophosphorous molecules are usually
17 acids, *i.e.* alkylphosphoric, phosphonic and phosphinic acids or mono and diesters of
18 phosphoric acid. Briefly speaking, the synthesis of metal phosphonates *via* sol-gel route
19 consists in a non-hydrolytic step followed by a hydrolytic step. First, a mixture of
20 metal-alkoxide precursor and a solution of organophosphorous acid in an organic solvent go
21 through the heterocondensation between P-OH and M-OR groups with release of alcohol.
22 Then, by adding water, M-O-M bonds form *via* hydrolysis/condensation of residual alkoxide
23 groups (Vioux et al., 2004; Mutin et al., 2005). Titanium oxide/phenylphosphonate hybrids
24 (Guerrero et al., 2000) and layered zinc phenylphosphonate (Deemie et al., 1999) are two
25 examples of these materials obtained by sol-gel process.

26

27 3.2.2 Co-precipitation method

28 This well-known method is widely used to synthesize hybrid materials, layered compounds
29 included. It is the major one-pot synthesis method defined and applied to obtain layered
30 compounds such as LMH and LMC.

1 A wide variety of hybrid LDH were synthesized *via* co-precipitation method (Whilton et al.,
2 1997; Hussein et al., 2004b; Roland-Swanson et al., 2004; Tronto et al., 2004a, 2004b; Leroux
3 and Taviot-Guého, 2005). A simple scheme of hybrid LDH synthesis through co-precipitation
4 consists in mixing a solution of organic precursor with that of bi-and trivalent metallic cation
5 salts in a basic medium. In some cases, in order to accommodate organic specie between LDH
6 layers, one should overcome the guest selectivity of LDH interlayer space, determined by the
7 charge and the size of anions. Using metal hydroxides as inorganic precursors in hybrid-LDH
8 synthesis by co-precipitation is one of the applied solutions (Ogawa and Asai, 2000).

9 A wide range of organic molecules were integrated between LDH layers *via* co-precipitation
10 method. By mixing a solution of commercially blue dye molecules (Evan blue, Chicago sky
11 blue, Niagara blue) with aqueous solutions of ZnCl₂ and AlCl₃, Marangoni *et al.* synthesized
12 successfully an organic-inorganic LDH assembly, applied as filler for polystyrene, resulted in
13 a blue plastic nanocomposite film (Marangoni et al., 2008). A “bio-assisted” nanocomposite
14 of Zn₂Al/alginate was precipitated from a mixed solution of alginic acid and Zn and Al salts
15 at room temperature (Leroux et al., 2004). Hybrid UV absorbent-LDH nanocomposites were
16 also obtained from a mixed aqueous solution of caffeic acid (or sinapic acid or
17 4-nitro-2-(trifluoromethyl)benzoic acid), Zn (NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O (Khan et al.,
18 2011). LDH were also considered as nano-drug carriers for drug delivery systems and the
19 hybrid LDH drug nanocomposite can also be obtained by this direct synthesis method (Choi
20 et al., 2008). Désigaux *et al.* (2006) described co-precipitation method as a proper chemical
21 synthesis, enabling DNA molecules entrapment into a supramolecular assembly.

22 Beside integration of individual organic molecules by co-precipitation method, polymer
23 incorporation between LDH layers, *via* the same method has been reported too (Leroux and
24 Taviot-Guého, 2005; Vieille et al., 2004, 2003). LDH containing Poly(acrylic acid),
25 poly(vinylsulfonate) and poly(styrenesulfonate) were synthesized by reacting mixed aqueous
26 salt solutions with a basic solution containing dissolved polymer. The obtained sheets of
27 LDH, composing of M_{1-x}Al_x(OH)₂⁺ (M = Mg, Ca, Co) and Zn_{1-x}M'_x(OH)₂⁺ (M' = Al, Cr),
28 were grown in a solution containing the desired polymer with polymer bilayers between them
29 (Oriakhi et al., 1996).

30 Using the same method, other hybrid metal hydroxides were also synthesized and applied in
31 different domains. Namely, layered zinc hydroxide salts (zinc LHS) - anionic orange azo dyes

1 (methyl orange (MO) and orange II) hybrid was precipitated from a mixture of ZnCl_2 and
2 each dye aqueous solutions (da Silva et al., 2012). A simple direct reaction between cobalt
3 hydroxide and ethanedisulfonic acid under hydrothermal conditions resulted in crystalline
4 $\text{Co}_7(\text{H}_2\text{O})_2(\text{OH})_{12}(\text{C}_2\text{H}_4\text{S}_2\text{O}_6)$ with ethanedisulfonate anions packed tightly between the layers
5 (Forster et al., 2004).

6 One-pot synthesis of hybrid layered metal chalcogenides followed mainly an approach
7 consisting in using metal complexes as structure-directing agents (Ralph Stähler, 2001;
8 Stähler et al., 2003). Zheng *et al.* (2005) obtained a layered chalcogenide framework structure
9 templated by a chiral complex, by mixing the aqueous solutions of GeO_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,
10 sulfur and tris(2-aminoethyl)amine. The obtained structure consisted in a layered framework
11 with the composition of $[\text{Ge}_3\text{S}_6\text{Zn}(\text{H}_2\text{O})\text{S}_3\text{Zn}(\text{H}_2\text{O})]^{2-}$ and a divalent charge-balancing
12 complex ion (*i.e.*, $\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})^{2+}$) in the interlayer space. $(\text{Haep})_2 \cdot \text{Ga}_2\text{Sb}_2\text{S}_7$ bimetallic
13 layered sulfide, where aep = 1-(2-aminoethyl)piperazine, is another example of these hybrid
14 layered chalcogenides, synthesized by dissolving and homogenizing Ga, Sb and S in 1-(2-
15 aminoethyl)piperazine, reacted at 443 K during 7 days. The inorganic layers of the obtained
16 structure had $[\text{Ga}_2\text{Sb}_2\text{S}_7]^{2-}$ composition, with two monoprotonated aep cations per formula
17 unit (Lin et al., 2010). A mild solvothermal reaction between $\text{Co}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ and Na_2SeO_3 in a
18 mixed solution, composed of deionized water and diethylenetriamine, resulted in the
19 formation of CoSe_2 -amine(protonated) nanocomposite belts with multiple stacked layers of
20 CoSe_2 slabs and protonated amine (Gao et al., 2009).

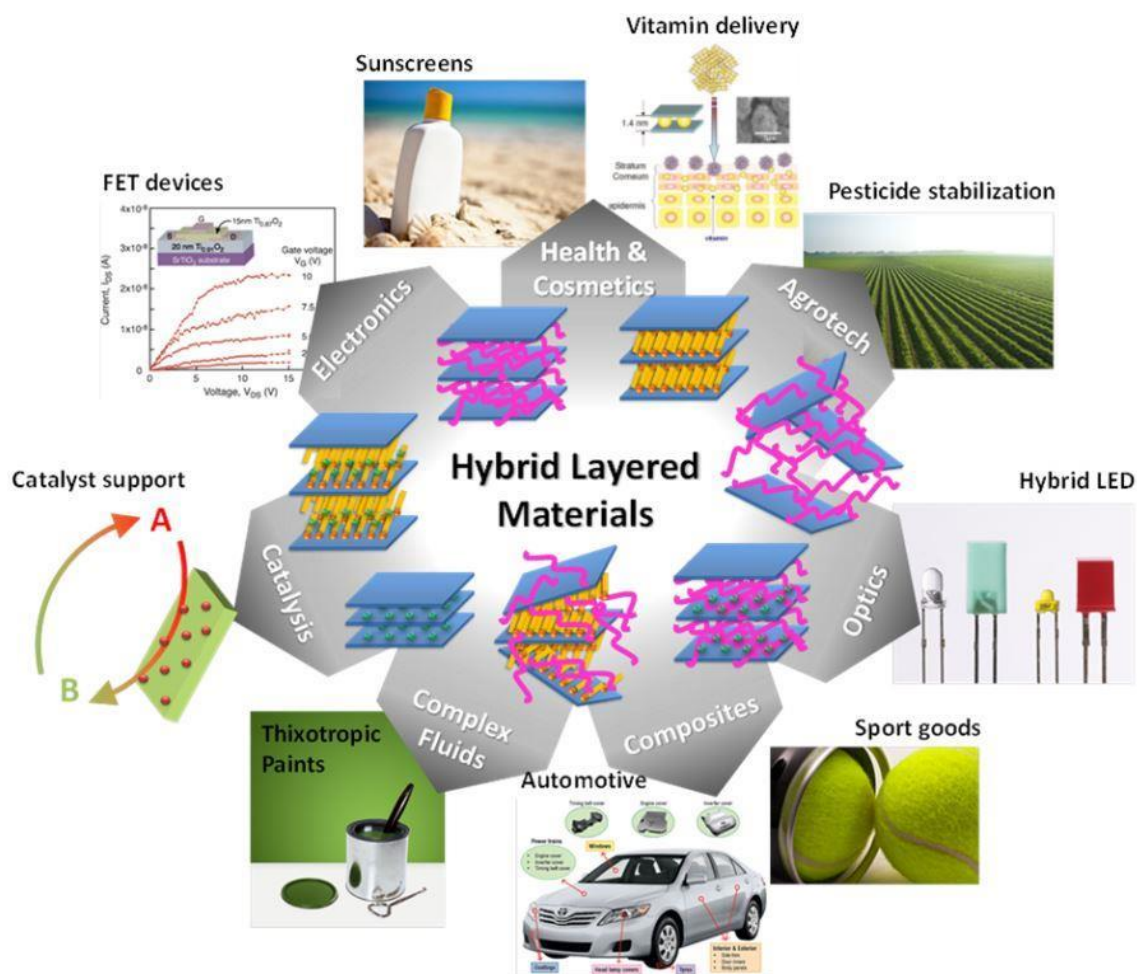
21 Some organic-inorganic metal organophosphonates were also successfully synthesized *via*
22 co-precipitation method, usually in hydrothermal conditions (Frink et al., 1991; Malaman et
23 al., 2010; Lagadic et al., 2012). This method consisted in mixing the metal salt (*i.e.* carbonate,
24 chloride or nitrate) with the phosphonic acid in aqueous media, with the right stoichiometric
25 ratio and placing the mixture in an autoclave, heating it around 140–190°C. The details of this
26 synthesis method, obtained materials and their characteristics are presented and discussed
27 elsewhere (Bellitto et al., 2008).

1 **4. Integration of hybrid lamellar compounds**

2 Inorganic lamellar compound is a large definition comprising compounds that display
3 different chemistry, different intrinsic properties and even a different history. Moreover, these
4 compounds have been addressed by actors from different domains of knowledge, which
5 justifies their asymmetric development. However, the emergence of hybrid materials, has led
6 to extraordinary advances in the manipulation of the interlayer space of layered compounds
7 and eventually to the development of hybrid layered compounds. This new class of
8 compounds, composed of an inorganic layered structure in close connection with an organic
9 moiety, has widened the range of potential applications of inorganic materials. Surprisingly,
10 this approach has had different feedbacks in the different research communities. While clays
11 and LDH have been widely hybridized, few research efforts have been directed towards the
12 development of other types of hybrid layered compounds. Table 1 briefly analyses the
13 development of hybrid layered materials and their applications as a function of the inorganic
14 host. Regardless of the heterogeneous development of organic-inorganic hybrid lamellar
15 materials, these compounds have found their place in different domains of application as is
16 illustrated in figure 5. Composites, electronics and optics, catalysis, health, cosmetics and
17 environment are the major discussed areas of application. However, the distance between
18 potential applications of hybrid lamellar compounds and technologically ready materials is
19 still considerably large. The main purpose of this section is thus to discuss processing of
20 hybrid lamellar compounds, (*i.e.* their integration as consumer-end products) *via* underlining
21 the major potential applications and their bottlenecks.

22 Among the materials that are actually applied in day to day objects, the most successful are
23 clearly CPN. They can be found from the gas-tight rubber in tennis balls to automobile engine
24 covers and their market value is expected to reach \$2.4 billion by 2016 (Ciesla and Werner,
25 2012). Most of the other layered hybrid materials however have not been industrialized. It is
26 instructive to analyze the differences between these outcomes from a technological
27 perspective. CPN are most frequently prepared by shearing the organoclay in the polymer
28 melt in a compounder or and extrusion unit, *i.e.* during the polymer processing. The ability to
29 prepare an enhanced material without dramatically changing the processing, accounts for the
30 huge success behind these materials. In fact, the key is the integration of the outcome of years
31 of research directly into the shaping of the material. Somehow, the bottom-up process that

1 accounts for the fine tuning of clay mineral intercalation and exfoliation is held
2 simultaneously with the standard top-down approach of shaping the melt into a solid of
3 desired dimensions and properties. This integrative approach allows for the multi-scale
4 architecture of the CPN while ensuring its processing cost-effectiveness (Backov, 2006;
5 Scaffaro et al., 2013). Other materials, regardless of their implantation on the market, have
6 forwarded this integrative approach (Pradhan et al., 2012; Birjega et al., 2013; Yoshitake et
7 al., 2013). For instance, Coiai *et al.* (2011) fabricated low-density polyethylene/layered
8 double hydroxide (LDPE/LDH) nanocomposites with intercalated/exfoliated morphology *via*
9 melt extrusion. The fabricated materials showed a remarkable increase of the thermal-
10 oxidative stability even with a low LDH concentration, and a reduction of oxygen
11 permeability mainly depending on the aspect ratio. Tang *et al.*, (2003) have increased the
12 adsorption affinity between clay mineral layers and polyelectrolytes through an automated
13 layer-by-layer procedure. Such approach allowed developing macroscopic bionanocomposite
14 films with controlled nanometric ordering and extraordinary mechanical properties (Tang et
15 al., 2003). Likewise, Posati *et al.* (2014) developed transparent bionanocomposite films,
16 composed of Zn₂Al LDH-silk fibroin by drop casting of a dispersion of hydrotalcite-like
17 compound in silk fibroin solution with remarkably enhanced mechanical resistance.
18



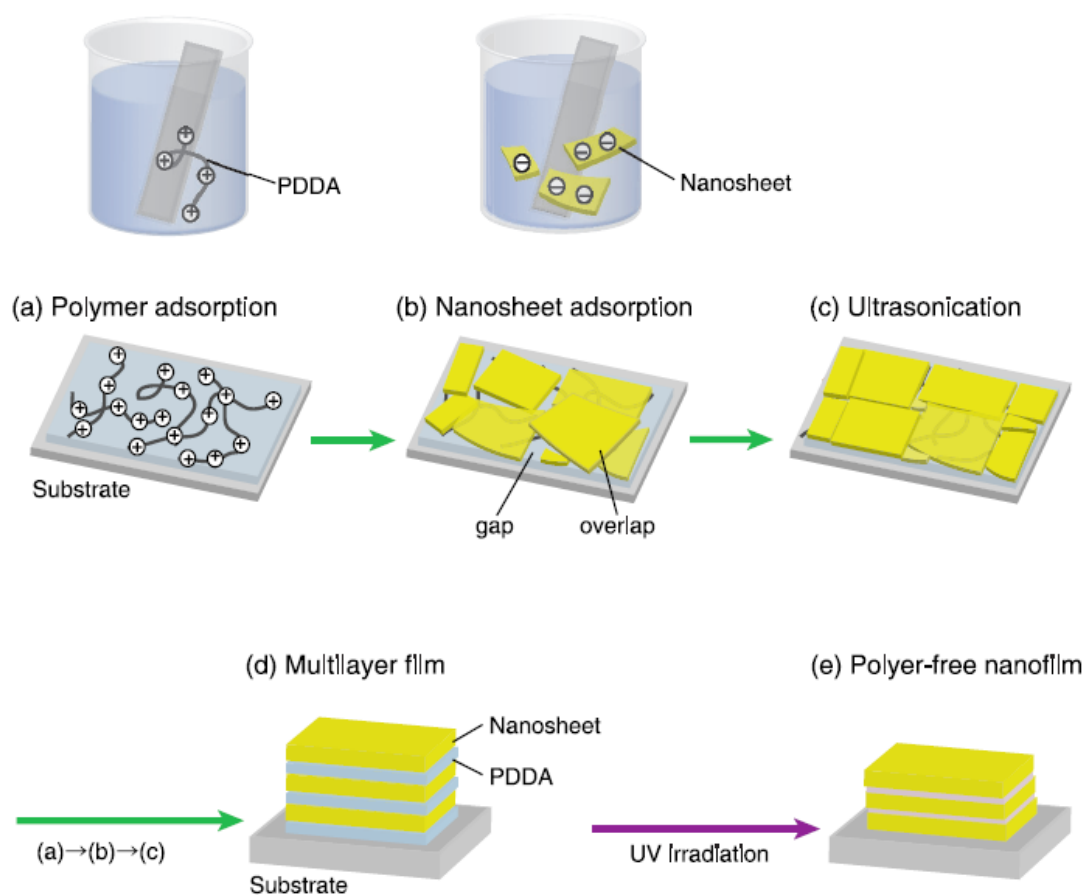
1
 2 **Figure 5** – Major applications and technological sectors using hybrid layered compounds.
 3

4 The focus in the field of electronics, historically, is on top-down approaches such as
 5 patterning through ion-beam lithography. Following this approach, hybrid lamellar
 6 compounds have been elaborated to be integrated in different type of devices. The
 7 nanocomposites of LMC-polymer were proven to be potentially good choices to develop
 8 hybrid-photovoltaic materials (Saikia et al., 2011). Maier *et al.* (2011) synthesized CdS- and
 9 ZnS-P3EBT (poly(3-(ethyl-4-butanoate)thiophene)) composites, through *in-situ* formation of
 10 inorganic nanostructures within the polymer matrix. The substrate was spin coated by the
 11 polymer-inorganic precursor solutions and subsequently integrated in a solar cell showing the
 12 desirable photovoltaic activity. Xu and Mitzi (2003) obtained a non-perovskite-based
 13 semiconductor lamellar hybrid $[\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3]\text{SnI}_3$ which can be solution-processed into
 14 thin films at ambient temperatures. Recently, increasing attention is devoted to the
 15 delamination of different layered oxides for direct device integration as can be seen in Fig. 6

1 (Osada and Sasaki, 2009, 2012). Using this approach, thin films based on alternate assembly
2 of zinc phthalocyanine complex and LDH monolayers, with enhanced optical properties, were
3 obtained. Exfoliated Mg-Al-LDH monolayers and zinc tetrasulfophthalocyanine, having long
4 fluorescent lifetimes and high quantum yields, were used as building blocks and were
5 assembled by layer-by-layer method. This integrated approach resulted thin films with
6 properties such as polarized luminescence, while LDH monolayers functioning as an energy
7 well layer, were applied to various opto-electrical devices (Yan et al., 2010). Although several
8 organic-inorganic hybrid lamellar compounds with interesting electric, magnetic and/or optic
9 characteristics have been presented, they have not found their way to be processed and
10 applied to electronic, opto-electronic or magneto-electronic devices, yet. The case of hybrid
11 LHS with important magnetic and optical properties is a striking example. A considerable
12 number of research works were dedicated to study different synthesis methods of various
13 functional molecules and metal complexes into metal hydroxide layers. Other studies
14 succeeded to define mechanisms which govern magnetic and optical characteristics of these
15 hybrid layered compounds. The correlations between the layered structures and magnetic
16 properties of these hybrid layered compounds were also established (Drillon and Panissod,
17 1998; Laget et al., 1998; Rogez et al., 2011). Nevertheless, they are still not processed to be
18 used as magnetic devices.

19

1



2

3 **Figure 6** – Mixed layer-by-layer and ultrasound strategies for the preparation of layered
 4 perovskites superlattices. Reproduced with permission from the Wiley (Osada and Sasaki,
 5 2012).

6 Hybrid lamellar compounds have also shown remarkable catalytic characteristics and thus
 7 some of them, LDH and clay minerals, have been extensively studied as catalysts. LDH are
 8 well-known precursors for elaboration of multifunctional catalysts. These materials can
 9 potentially possess acid, basic and redox sites. A proper LDH synthesis method potentially
 10 results in formation of mixed oxides that exhibit a homogeneous inter dispersion of the
 11 elements, high specific surface areas and basic required properties (Tichit et al., 2006).
 12 Moreover, after appropriate treatments these mixed oxides contain well dispersed metal
 13 particles in strong interaction with the mixed oxide support (*e.g.* Pd/ Mg(Al)O) (Takehira and
 14 Shishido, 2007; Tichit et al., 2007; Gérardin et al., 2008; Shi et al., 2012; Cunha et al., 2013).
 15 However, hybridized lamellar compounds have been merely used as catalyst precursor. LDH
 16 have been hybridized by organic molecules to enhance the catalytic activity of some organic
 17 molecules. The intercalation of thiamine pyrophosphate (TPP) into Zn–Al and Mg–Al LDH

1 resulted in high catalytic activity of pyruvate decarboxylation as an active biocatalyst
2 (Baikousi et al., 2013). The preparation of $[\text{Ni}(\text{C}_6\text{O}_7\text{H}_3)_x(\text{OH})]_y^{y(3x-1)-}$ -LDH nanocomposites
3 by anion exchange between Mg/Al LDH host structure and $[\text{Ni}(\text{C}_6\text{O}_7\text{H}_3)_x(\text{OH})]_y^{y(3x-1)-}$ clusters,
4 permitted to control both the Ni loading and the size of the particles in $\text{Ni}^0/\text{Mg}(\text{Al})\text{O}$ metal
5 supported catalysts after the nanocomposite reduction (Gérardin et al., 2008).
6 In this context, also clay minerals can be engineered into various functional solid catalysts.
7 Depending on the design and their preparation, clay minerals can play four major roles: (1)
8 catalytic activity of the framework of clay, (2) exchangeability of the interlayer ions for
9 catalysis purpose, (3) interlayer modification by functional nanoparticles and (4) the use of
10 clay minerals or their derivatives used as catalyst supports (Zhou, 2011; Zeng et al., 2013).
11 Hybrids of clay- manganese species, obtained from the adsorption of manganese (III) salen
12 complexes, showed a good activity to catalyse water oxidation (Berends et al., 2011) and
13 epoxidation of olefins (Kuźniarska-Biernacka et al., 2011). Another example consisted of
14 cyclic poly(L-lactide) (PLLA) used as stabilizer of palladium nanoparticles to prepare PLLA-
15 clay hybrid material as recyclable catalyst support. The obtained nanocomposite was reported
16 to be a highly efficient and recyclable catalyst for the aminocarbonylation reactions of aryl
17 halides with various amines (Prasad et al., 2013). Despite the advances shown by the isolated
18 proofs of concept, the absence of an integrative strategy (that could transfer the reported
19 results into the relevant context) hampers an extended application of these advances.
20 Owing to their biocompatibility, ion-exchange ability, and low cytotoxicity, LDHs and clays
21 have also found great potential application as inorganic nanoparticles for drug delivery.
22 Different ionic pharmaceutically active molecules can be intercalated into the interlayer space
23 of LDHs and clays by ion-exchange. The interlayer space of these materials can be considered
24 as a reservoir for drug, protecting it from the reaction of light and oxygen. After the cellular
25 uptake of these particles by clathrin-mediated endocytosis, the drug may be released through a
26 deintercalation process because of anion exchange or displacement reactions. The drug
27 release can be controlled by tuning the host–guest interactions, which can be obtained by
28 hybridizing clay minerals or LDH. The synthesis and potential applications of these hybrid
29 lamellar drug carriers are discussed in detail in other review articles (Li and Duan, 2006; Patil
30 and Mann, 2008; Zhao et al., 2012; Ruiz-Hitzky et al., 2013). A good example in this area is
31 the research work of Miao *et al.* (2012) concerning a drug delivery system based on the fibers
32 of LDH/biopolymer. Ibuprofen intercalated Mg-Al LDH was dispersed in polycaprolactone
33 (PCL) or polylactide (PLA) solutions, obtaining electrospinning suitable solutions. The

1 electrospun fibers of ibuprofen-LDH/biopolymer, comparing to ibuprofen/LDH system,
2 brought a remarkably enhanced control over the *in vitro* ibuprofen release.

3 Except for composite materials that are steadily growing as a fully operational domain, most
4 of the classes of hybrid layered materials discussed in this review article have not passed the
5 “proof of concept” stage. As an example (*c.f.* table 1), an important feature of hybrid lamellar
6 compounds such as hybrid metal phyllosilicates, hybrid LDH or hybrid zirconium phosphate,
7 is their capacity of heavy metal cation adsorption from water. This characteristic led these
8 materials to be presented as potential water decontaminants. However, a glance at actual
9 water decontamination technologies shows the absence of hybrid layered materials among
10 them. We believe that further efforts should be oriented towards the mutual adaptation
11 between the scientific breakthroughs and the practical technological aspects of each domain.
12 This convergent movement should facilitate the advancement of the present state of the art in
13 hybrid layered materials.

14 Another interesting point in the context of layered materials consists on a, until now, fairly
15 discrete domain: the intersection between physical processing techniques and chemical
16 synthetic routes. New approaches, using monolayer deposition of materials that are usually
17 obtained in bulk, are bringing new and exotic layered materials to the game of hybrid layered
18 compounds (Ohtomo et al., 1999; Umar and Hahn, 2006). This perspective will not only
19 strengthen the role of physical processing routes in the development of new materials, but will
20 surely widen the range of materials and applications that can be envisaged by hybrid materials
21 research.

22

Host inorganic structure	Guest molecule	Integration method	Properties	Applications / Status	References
Clays					
Mt	Organocations	Intercalation	Enhanced dispersion in polymer matrices, enhanced adsorption of hydrophobic molecules.	Additive for composite materials / Fully commercial (Nanocor, Southern Clay Products, Clariant, Laviosa Chimica Mineraria, etc.)	(Patel and Mahajan, 2012) (Scaffaro et al., 2013)
	Organocations + thermoplastics	Intercalation / exfoliation	Mechanical reinforcement and flame retardant properties	Structural nanocomposites / Fully commercial (Toyota, Dupont, LyondellBasel, Ube Industries, etc.)	(Patel and Mahajan, 2012)
	Organocations + Elastomers	Intercalation / exfoliation	Structural properties, abrasion resistance,	Tyres reinforcement / Fully commercial	(Patel and Mahajan, 2012)
	Polyethylene oxide	Intercalation	Ion conductivity	Fundamental	(Aranda and Ruiz-hitzky, 1992)
	Chitosan	Intercalation	Conductive anionic and cationic exchanger	Potentiometric sensors / POC	(Darder et al., 2005)
	Sucrose	Intercalation In situ polymerization	Electrical conductivity	Fundamental	(Darder and Ruiz-Hitzky, 2005)
	(3-mercaptopropyl)trimethoxysilane)	Intercalation / grafting	Heavy metal adsorption	Pb, Zn, Cd adsorption / POC	(Mercier and Detellier, 1995)
Metal phyllosilicates					
Mg-phyllosilicate	N-trimethoxysilylpropylthiopropamide	Sol-gel	Heavy metal cation sorption	POC	(Badshah and Airoidi, 2013)
	Organosiloxanes	Sol-gel	Gold nano-particle synthesis	POC	(Burkett et al., 1997)
	Mercaptopropyltri-methoxysilane	Sol-gel	Heavy metals adsorption	POC	(Lagadic et al., 2001)

	2-aminophenyldisulfid	Sol-gel	Heavy metal absorbent	POC	(Moscofian and Airoldi, 2008)
Ni-phyllsilicate	3-aminopropyltriethoxysilane + Cu phthalocyanine	Hydrothermal	Magnetic properties	Fundamental	(Richard-Plouet et al., 2002)
	New silyating agent with ethanolamine and diethanolamine functions	Sol-gel	Barium adsorption	POC	(Melo et al., 2008)

Layered Metal Hydroxides

LHS					
$\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{CO}_2)\text{H}_2\text{O}$	Olygothiophenecarboxylates	Hydrothermal	Magnetic properties	POC	(Demessence et al., 2010)
$\text{Co}_2(\text{OH})_3\text{NO}_3$					
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Oligophenylenevinylene	Ion-exchange	Magnetic & photoluminescence properties	POC	(Rueff et al., 2004)
$\text{Co}_2(\text{OH})_3(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}$	Diarylethene	Ion-exchange	Photomagnetism	POC	(Kojima et al., 2007)
LDH					
Mg_2Al	5-fluorouracil (5-Fu)	Co-precipitation	Drug encapsulation	Drug Delivery System / POC	(Choi et al., 2008)
	Nucleoside monophosphates	Ion-exchange	Encapsulation	Gene Delivery System / POC	(Choy et al., 1999)
	Deoxyribonucleic acid (DNA)				
	Dodecyl sulfate	Microemulsion method	Rheological properties of DLH dispersion in polypropylene	Fundamental	(Wang et al., 2012)
$\text{Mg}_2\text{Al}, \text{Mg}_2\text{Fe}, \text{Mg}_2\text{Ga}$	DNA	Co-precipitation	Encapsulation	Gene Delivery System / POC	(Desigaux et al., 2006)
Zn_2Al	4[12-(methacryloylamino)dodecanoylamino] benzenesulfonate acid	Co-precipitation	Thermal and rheological properties of DLH dispersion in polystyrene	Fundamental	(Illaik et al., 2008), (Leroux et al., 2009)

	3,4-dihydroxycinnamic acid, 4-hydroxy-3,5-dimethoxycinnamic acid, 3-amino-5-trifluoromethylbenzoic acid	Co-precipitation	UV-absorption	Sunscreen / POC	(Khan et al., 2011)
CSH	acrylic acid, 2-(phosphonoxy)-ethyl-methacrylate	Co-precipitation	Cement additive	Cement hardening acceleration / Fully commercialized	(Nicoleau et al., 2013)
Oxides					
Vanadium oxide	Piperidinium	Intercalation	Magnetic properties	Fundamental	(Zhang et al., 1998)
Vanadium oxide	poly(N-[5-(8-hydroxyquinoline)methyl]aniline)	In situ polymerization	Electrically conductive and fluorescence properties	Fundamental	(Wang et al., 2009)
Vanadium oxide	Phenylacetate	Co-precipitation	High electrical charge storage, good dispersion in electrolyte	Li ion batteries / POC	(Sun et al., 2011)
Vanadium pentoxide xerogel	Poly(ethylene oxide)	Intercalation	Electrochemical properties	Li ion batteries / POC	(Guerra et al., 2006)
Lanthanide oxide (Y, Gd, Er)	Benzoate molecules	Sol-gel	Optical properties	Fundamental	(Sá Ferreira et al., 2006) (Karmaoui et al., 2007)
Lanthanide oxide (Gd, Sm, Nd)	Benzoate molecules	Sol-gel	Optical properties	Fundamental	(Karmaoui and Ferreira, 2006)
	Biphenyl molecules	Sol-gel	Optical properties	Tunable the emission chromaticity / POC	(Karmaoui and Mafra, 2007)
γ -ZrP	n-Alkyl Monoamines	Intercalation	Enhanced adsorption capacity	Fundamental	(Alberti et al., 2000)
α -ZrP	Polyaniline	Intercalation, in-situ polymerization	Electric properties	Fundamental	(Takei et al., 2006)
Cobalt phosphonate	Carboxylates	Co-precipitation	Magnetic properties	Fundamental	(Yang et al., 2008)

Hydrated vanadyl phosphate	Polyaniline	Intercalation	Proton conductivity	Fundamental	(De et al., 2007)
M-hydroxyl-carboxylate-phosphonates (M= Mn, Fe, Co)	[(CH(OH)(CO ₂)(PO ₃ H))(H ₂ O) ₂] ⁻	Co-precipitation	Antiferromagnetic properties	Fundamental	(Ruibiao Fu, et al., 2005)
Zirconium phosphite	Bis(triphenylphosphine)palladium(II) dichloride complex	Co-precipitation	Supported catalyst	POC	(Villemin et al., 1997)
Bimetallic sulfides (M ₁ =Ga or Mn, M ₂ =Sb)	1-(2-aminoethyl)piperazine 1,10-phenanthroline	Co-precipitation	Good semiconductors, photoluminescent and antiferromagnetic properties	POC	(Lin et al., 2010)
MPS ₃ (M=Mn, Cd, Zn)	4-[4- (dimethylamino)-R-styryl]- 1-methylpyridinium iodide	Intercalation	Non-linear optics	POC	(Coradin et al., 1996)

*POC: Proof of Concept

1

1 **5. Concluding remarks**

2 The number of research works dedicated to understanding old and new lamellar compounds,
3 the efforts made in integrating organic guests in between the different inorganic layered hosts,
4 as well as the conceptual and technological framework that surrounds these materials is
5 breathtaking! In no more than half a century, researchers from different domains have
6 constructed a solid collection of knowledge and have started to conceive materials that are (in
7 variable degree) present in our day-to-day life.

8 Hybrid layered materials benefit from a vast research community with diverse background
9 and objectives. This has led to the development of **new ideas** for hybrid layered materials.
10 Mann *et al.* for instance, went farther than uniquely modifying the interlayer space of talc like
11 compounds; they have addressed the size of formed two-dimensional hybrid building blocks
12 (Burkett *et al.*, 1997; Patil *et al.*, 2005). By separating the layered nanobuilding blocks by size
13 they were able to wrap around different biological entities providing *ad-hoc* protecting
14 structures around enzymes, DNA or proteins. Also Tang *et al.* (2003) have instilled new
15 breath to the preparation of layer-by-layer bionanocomposite material with a structure
16 resembling that of mother of pearl (Tang *et al.*, 2003). Charge matching between clay
17 lamellae in dispersion and the selected biopolymer, plus the alternating layer-by-layer
18 procedure, allowed developing bioinspired nanocomposites with morphological control in the
19 nanometer range. In both cases their making of hybrid lamellar compounds was compatible
20 with processing tools/techniques and *vice versa* which led to exciting new results.

21 Another important landmark in the context of hybrid layered materials concerns **new**
22 **materials** related to the discipline. Graphene and graphene-like materials, which can still be
23 considered as emerging materials, are of dramatic importance to the advancement of hybrid
24 layered materials. The prescient work by Kyotani *et al.* (1988) who carbonized
25 polyacrylonitrile to form graphite (or most likely few layers of graphene) in the interlayer of
26 clay mineral has paved the way to develop new hybrids displaying tunable chemistry and
27 physical properties (Darder and Aranda, 2010; Ruiz-Hitzky *et al.*, 2011). Also graphene-like
28 materials such as fluorographene, boron nitride, molybdenum disulphide, silicene or
29 germanene are capturing increasing attention in materials science (Radisavljevic *et al.*, 2011;

1 Geim and Grigorieva, 2013; Xu et al., 2013). The association of these materials with
2 “traditional” inorganic layered compounds as well as their hybridizations opens up new
3 exciting perspectives in the field of layered materials.

4 Finally, a deep survey on the state of the art of hybrid layered compounds shed light on the
5 considerable gap between the proven concepts of potential applications and consumer
6 products. Bridging this gap depends on the ability to integrate the new materials in
7 technologically relevant contexts according to the requirements of each domain. In one word,
8 the challenge is integration!

9

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