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▶ **To cite this version:**

Francisco M. Fernandes, H. Baradari, Clément Sanchez. Integrative strategies to hybrid lamellar compounds: an integration challenge. Applied Clay Science, 2014, 100, pp.2-21. 10.1016/j.clay.2014.05.013 . hal-01139001

HAL Id: hal-01139001

https://hal.sorbonne-universite.fr/hal-01139001

Submitted on 3 Apr 2015

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Manuscript submitted to

Applied Clay Science

Special Issue on Intercalated Nanomaterials:

From functional clays to advanced hybrid lamellar compounds

January, 2014

Integrative strategies to hybrid lamellar compounds: an integration challenge

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Abstract

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

Table of abbreviations

AMP: Aminopropyl-functionalized magnesium phyllosilicate

CSH: Calcium silicate hydrate

CPN: Clay polymer nanocomposite

DNA : Deoxyribonucleic acid

DS : Dodecylsulfate

LHDS: Layered hydroxyl double salts

LDH: layered double hydroxide

LHS: Layered hydroxide salts

LMC: Layered metal chalcogenides

Mt: Montmorillonite

PILC: Pillared interlayered clays

MX2: Metal dichalcogenides

MX3: Metal trichalcogenides

1. Introduction

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

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

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

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

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

2. Lamellar compounds

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

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

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

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

2.1. Clay minerals

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

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

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

2.2. Layered Metal Hydroxides

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

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

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

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

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

LHDS are synthetic layered materials with positively charged layers. Their general formula 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 divalent metals, such as Cu, Co, Ni, Mn, or Zn and X^{n-} is the exchangeable anion. The LHDS structure has also been described as an LHS containing two different cations (Arizaga et al., 2007). Generally speaking, their layers are composed of divalent metal ions stabilized in the two-dimensional lattice similar to the brucite structure with some vacant octahedral and a part of the metal ions are positioned above and below the vacant sites outside the hydroxide layer to form tetrahedral coordination (Petrov et al., 1987). This coordination results in the excess of positive charge of layers. Hence, the LHDS, similar to LDH, can accommodate anionic species within interlayer space to compensate the positive layer charge by anion-exchange reactions (Meyn et al., 1993; Tronto et al., 2006; Rojas et al., 2010). Their structure can be stabilized by electrostatic interaction between layers and anions or by a hydrogen bond network between water molecules, interlayer anions and interlayer hydroxyl groups.

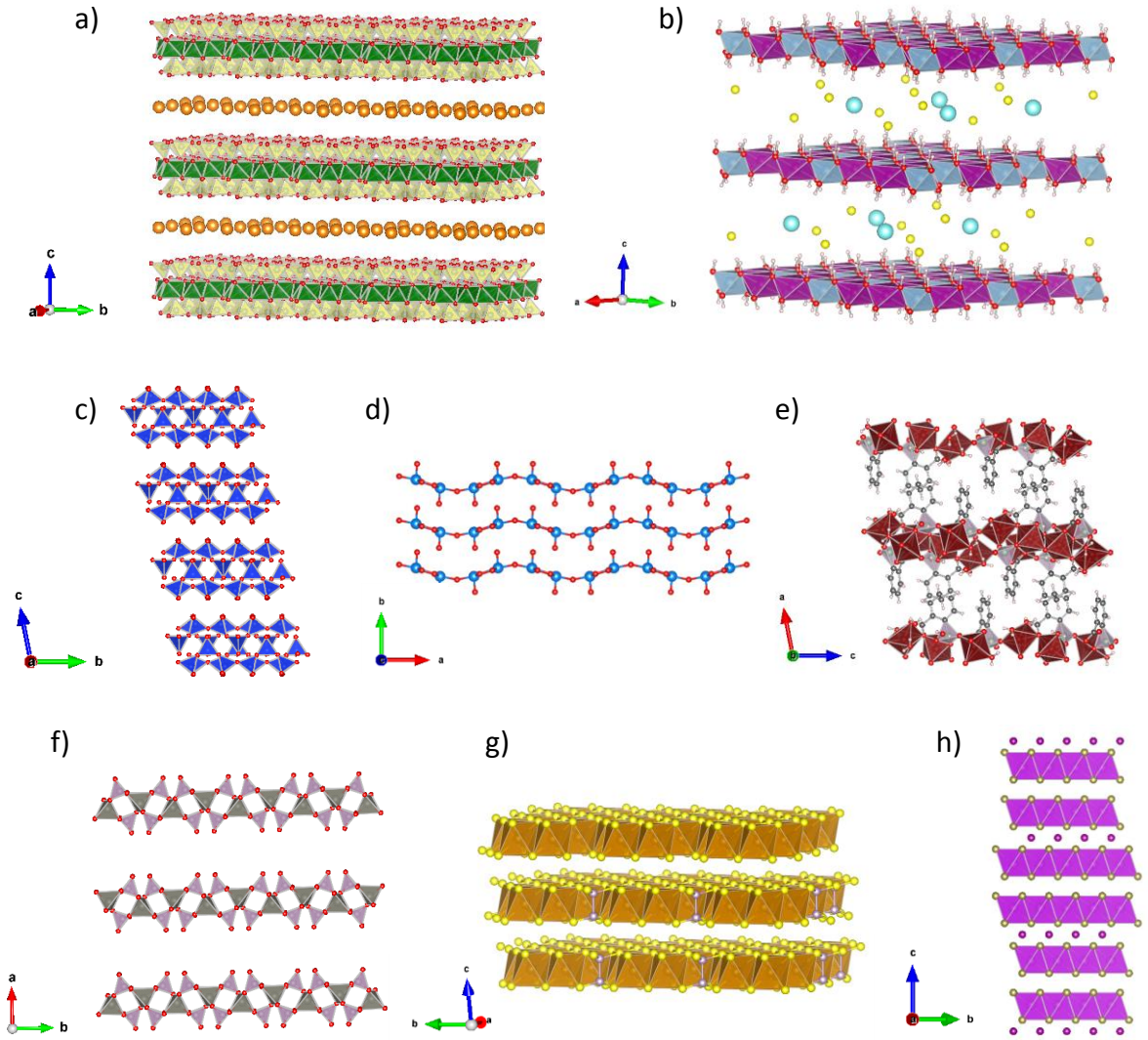


Figure 1 - Simplified representations of several layered inorganic compounds: a) a calcium montmorillonite (Viani et al., 2002); b) shigaite $[AlMn_2(OH)_6]_3(SO_4)_2Na(H_2O)_6.6H_2O$, a layered double hydroxide (Cooper and Hawthorne, 1996); c) tobermorite, a calcium silicate hydrate (Mrlino et al., 1999); d) vanadium pentoxide layered structure (Filonenko et al., 2004); e) schematic representation of $Co_3(^{2-}OOCC_6H_4PO_3)_2(H_2O)_3{\cdot}H_2O$ layered metal phosphonate featuring a 2-carboxyphenylphosphonic acid as organic building block, viewed along the b axis (Wang et al., 2011); f) a layered zinc phosphate (Choudhury et al., 2002) g) a layered iron hexathiohypodiphosphate, MPS_3 (Clement et al., 1986) and h) Bi_2MnTe_4 chalcogenide displaying mixed interlayer space (Lee et al., 2013).

2.3. Calcium silicate hydrates

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

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

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

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

2.4. Layered Metal Oxides

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

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

2.5. Metal Phosphonates

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

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

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

2.6. Layered Metal Phosphates

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

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

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

2.7. Layered Metal Chalcogenides

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

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

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

3. Lamellar compounds hybridization strategies and approaches

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

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

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

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

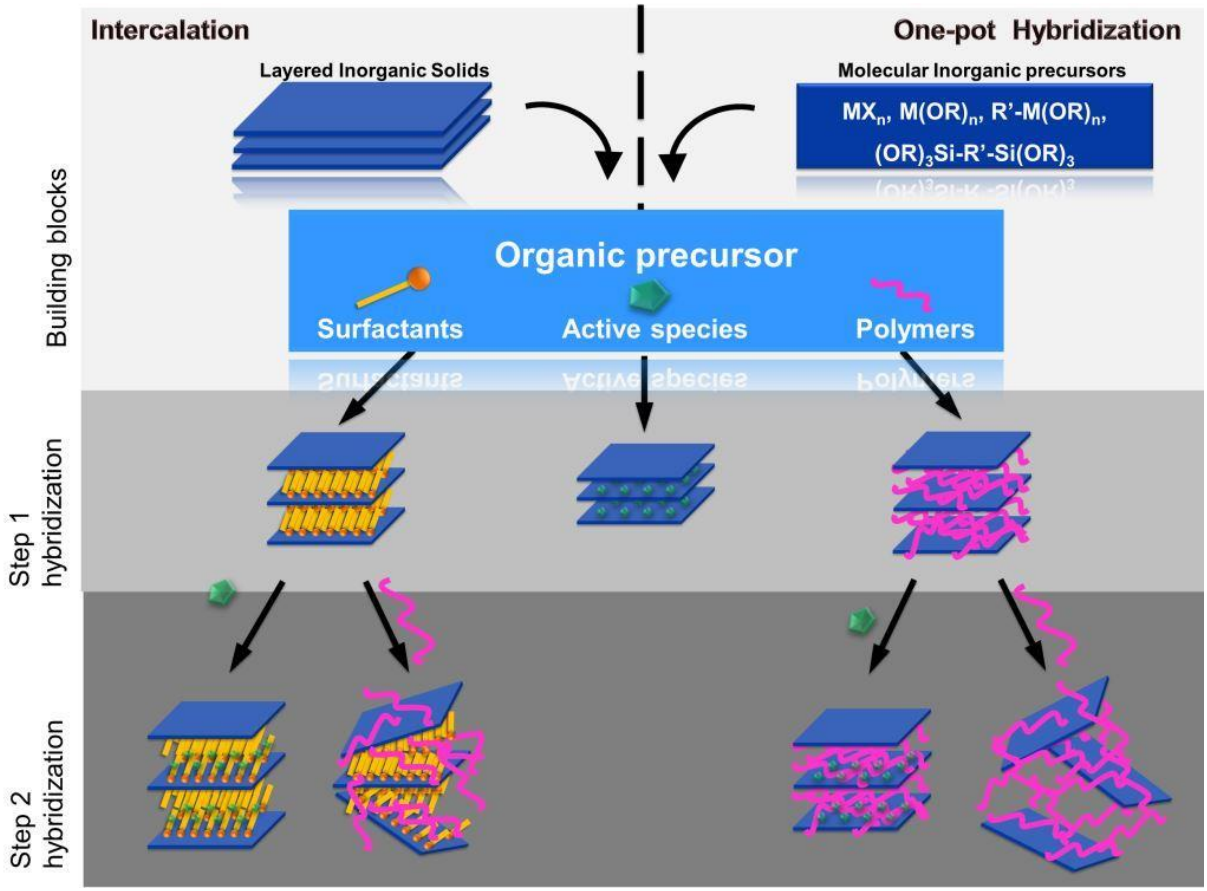


Figure 2- Hybridization strategies of inorganic lamellar compounds

3.1 Intercalation

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

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

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

3.1.1. Molecular guests

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

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

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

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

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

Besides above mentioned considerations on layered inorganic hosts, *i.e.* reservoir, protecting shell and/or confined reactor, the combination of intrinsic properties of these hosts with a similar characteristic of an organic guest permits to accentuate a demanded property. This combination mode has been significantly used to modulate the magnetic or optical properties of layered metal hydroxides (Rueff et al., 2004; Delahaye et al., 2009). Several examples of these types of molecular magnets have been presented by different authors. A heterometallic layered structure magnet was obtained by intercalation of chiral and non-chiral salen-type Ni(II) complexes into copper and cobalt layered simple hydroxides. Pre-intercalated cobalt and copper hydroxides, *i.e.* $Cu_2(OH)_3(DS)$ and $Co_2(OH)_3(DS0)$, where DS is dodecylsulfate and DS0 is dodecylsulfonate, were used as host materials and salen-Ni(II) complexes were used as guest molecules to induce chirality in a non-chiral magnetic system (Delahaye et al., 2010). Intercalation of peptides by anion-exchange reactions into pre-intercalated Cu(II) and Co(II) LSH interlayer space (Copper acetate monohydrate ($Cu(CH_3COO)_2.H_2O$), cobalt acetate tetrahydrate ($Co(CH_3COO)_2.4H_2O$)), resulted in bio-hybrid compounds. Among these compounds, the copper-based tyrosine LSH bio-hybrids showed an antiferromagnetic behavior whereas the cobalt-based analogues were ferrimagnets (Si et al., 2012).

3.1.2 Molecular modifiers of the interlayer space of layered materials

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

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

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

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

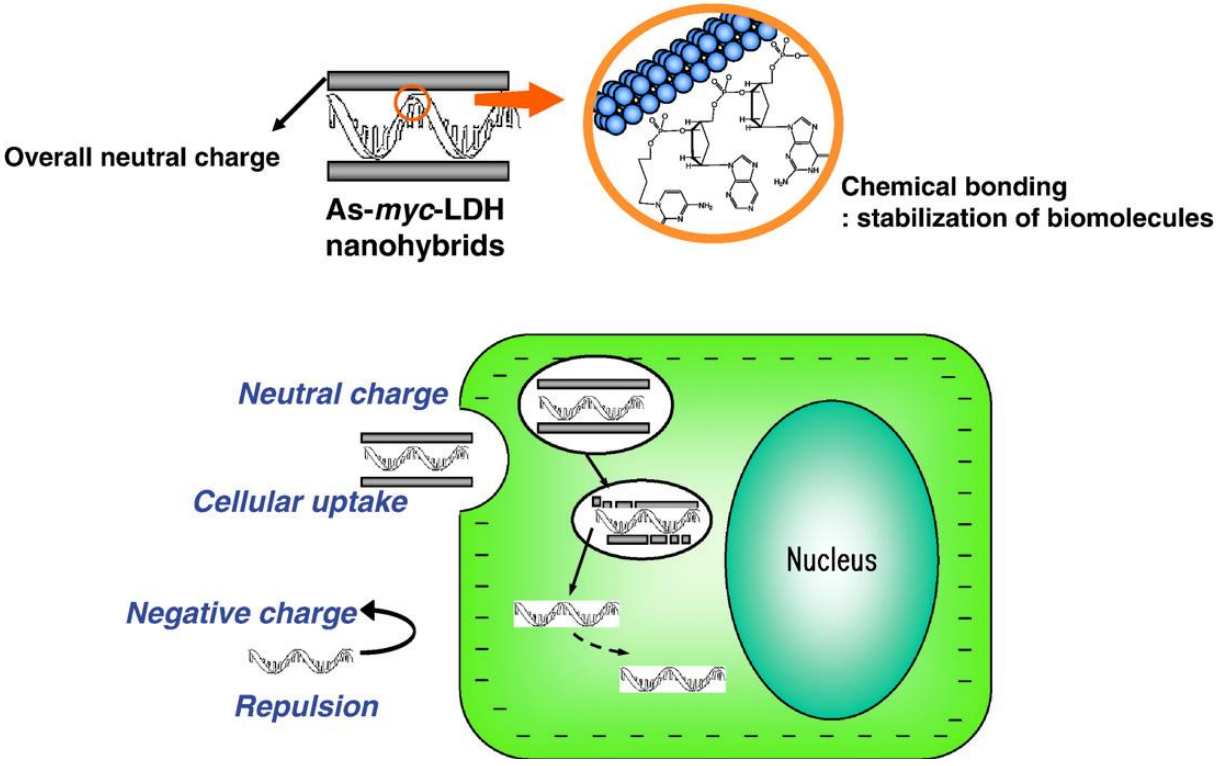


Figure 3 – Schematic representation of DNA transfection by Layered double hydroxides (Choy et al., 2007). Reproduced with permission from Elsevier Ltd.

3.1.3 Polymer diffusion in raw inorganic layered materials

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

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

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

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

$Mg_2Al(NO_3)$ LDH. LDH have proven effective materials to host DNA without inducing conformational or compositional changes in the DNA strands. Moreover, since the net charge of the hybrid compound is positive the electrostatic repulsion between the cell walls and DNA was circumvented.

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

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

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

3.1.4 Interlayered metal nanoparticles

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

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

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

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

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

3.2 In situ integration of organic guest molecule

Intercalation of organic species/guest molecules in the interlayer space of the lamellar compounds at the end of the 1950's, not only opened the discussion about the feasibility of hybridization of such inorganic hosts, but also it answered an important question: how to make the most of the lamellar compounds. Later on, in the mid 1990's, inspired by the vast possibilities given by sol-gel chemistry obtained from polycondensation of organosilanes and metal alkoxides, researchers started to pave a new road toward organic-inorganic hybrid layered materials. Shortly after, procedures based on the self-assembly of amphiphilic organic molecules in the synthesis medium and in presence of an inorganic precursor, allowed to synthesize hybrid materials with layered textures (Sanchez et al., 2005, 2011).
Sol-gel process, co-precipitation at room temperature or at hydrothermal or solvothermal conditions, are the most common one-pot synthesis methods used to elaborate hybrid layered materials.

3.2.1 Sol-gel process

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

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

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

organo-metal phyllosilicates. Although this latter makes the structural characterization of these compounds difficult, the admitted structure for inorganic layer of organo-metal phyllosilicates consists in metallic cations centered in octahedral sites, coordinated by oxygen atoms, which are sandwiched between silicate tetrahedral sheets. The organic chains are attached to tetrahedral R-Si-O_3 group of the inorganic layer *via* Si-C bonds, pointing to the interlayer space (Burkett et al., 1997; Fonseca et al., 1999, 2004). Depending on the organic group bonded to Si, interlayer distance ranges from 11 to 38 Å (Richard-Plouet et al., 2004).

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

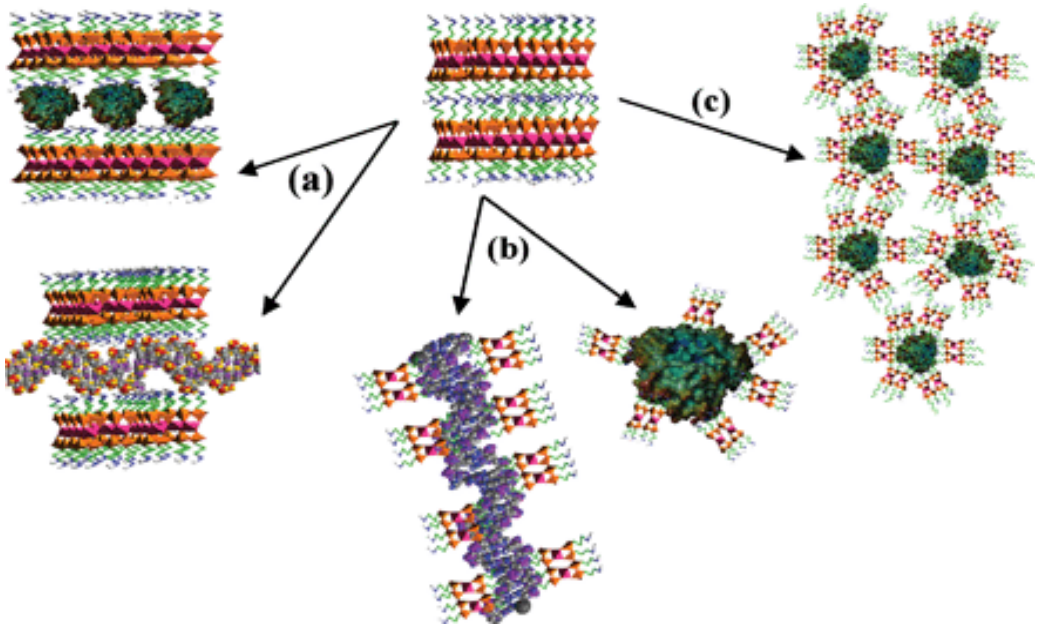


Figure 4 – (center) Proposed structure for aminopropyl-functionalized magnesium phyllosilicate (AMP) composed of a central layer of brucite $Mg(OH)_2$ octahedra connected on both sides to a tetrahedral silicate layer comprising covalently linked aminopropyl moieties that are positioned in the interlayer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

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

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

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

3.2.2 Co-precipitation method

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

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

A wide range of organic molecules were integrated between LDH layers *via* co-precipitation method. By mixing a solution of commercially blue dye molecules (Evan blue, Chicago sky blue, Niagara blue) with aqueous solutions of $ZnCl_2$ and $AlCl_3$, Marangoni *et al.* synthesized successfully an organic-inorganic LDH assembly, applied as filler for polystyrene, resulted in a blue plastic nanocomposite film (Marangoni et al., 2008). A ‘‘bio-assisted’’ nanocomposite of Zn_2Al/alginate was precipitated from a mixed solution of alginic acid and Zn and Al salts at room temperature (Leroux et al., 2004). Hybrid UV absorbent-LDH nanocomposites were also obtained from a mixed aqueous solution of caffeic acid (or sinapic acid or 4-nitro-2-(trifluoromethyl)bezoic acid), Zn $(NO_3)_2.6H_2O$, and $Al(NO_3)_3.9H_2O$ (Khan et al., 2011). LDH were also considered as nano-drug carriers for drug delivery systems and the hybrid LDH drug nanocomoposite can also be obtained by this direct synthesis method (Choi et al., 2008). Désigaux *et al.* (2006) described co-precipitation method as a proper chemical synthesis, enabling DNA molecules entrapment into a supramolecular assembly.

Beside integration of individual organic molecules by co-precipitation method, polymer incorporation between LDH layers, *via* the same method has been reported too (Leroux and Taviot-Guého, 2005; Vieille et al., 2004, 2003). LDH containing Poly(acry1ic acid), poly(vinylsu1fonate) and poly(styrenesulfonate) were synthesized by reacting mixed aqueous salt solutions with a basic solution containing dissolved polymer. The obtained sheets of LDH, composing of $M_{1-x}A1_x(OH)_2^+$ (M = Mg, Ca, Co) and Zn_{1-x} M' $_x$ $OH)_2^+$ (M'= Al, Cr), were grown in a solution containing the desired polymer with polymer bilayers between them (Oriakhi et al., 1996).

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

(methyl orange (MO) and orange II) hybrid was precipitated from a mixture of $ZnCL_2$ and each dye aqueous solutions (da Silva et al., 2012). A simple direct reaction between cobalt hydroxide and ethanedisulfonic acid under hydrothermal conditions resulted in crystalline $Co_7(H_2O)_2(OH)_{12}(C_2H_4S_2O_6)$ with ethanedisulfonate anions packed tightly between the layers (Forster et al., 2004).

One-pot synthesis of hybrid layered metal chalcogenides followed mainly an approach consisting in using metal complexes as structure-directing agents (Ralph Stähler, 2001; Stähler et al., 2003). Zheng *et al.* (2005) obtained a layered chalcogenide framework structure templated by a chiral complex, by mixing the aqueous solutions of GeO_2, $Zn(NO_3)_2.6H_2O$, sulfur and tris(2-aminoethyl)amine. The obtained structure consisted in a layered framework with the composition of $[Ge_3S_6Zn(H_2O)S_3Zn(H_2O)]^{2-}$ and a divalent charge-balancing complex ion (*i.e.*, $Zn(C_6N_4H_{18})(H_2O)^{2+}$) in the interlayer space. $(Haep)_2{\cdot}Ga_2Sb_2S_7$ bimetallic layered sulfide, where aep = 1-(2-aminoethyl)piperazine, is another example of these hybrid layered chalcogenides, synthesized by dissolving and homogenizing Ga, Sb and S in 1-(2-aminoethyl)piperazine, reacted at 443 K during 7 days. The inorganic layers of the obtained structure had $[Ga_2Sb_2S_7]^{2-}$ composition, with two monoprotonated aep cations per formula unit (Lin et al., 2010). A mild solvothermal reaction between $Co(Ac)_2.H_2O$ and Na_2SeO_3 in a mixed solution, composed of deionized water and diethylenetriamine, resulted in the formation of $CoSe_2$-amine(protonated) nanocomposite belts with multiple stacked layers of CoSe2 slabs and protonated amine (Gao et al., 2009).

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

4. Integration of hybrid lamellar compounds

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

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

accounts for the fine tuning of clay mineral intercalation and exfoliation is held simultaneously with the standard top-down approach of shaping the melt into a solid of desired dimensions and properties. This integrative approach allows for the multi-scale architecture of the CPN while ensuring its processing cost-effectiveness (Backov, 2006; Scaffaro et al., 2013). Other materials, regardless of their implantation on the market, have forwarded this integrative approach (Pradhan et al., 2012; Birjega et al., 2013; Yoshitake et al., 2013). For instance, Coiai *et al.* (2011) fabricated low-density polyethylene/layered double hydroxide (LDPE/LDH) nanocomposites with intercalated/exfoliated morphology *via* melt extrusion. The fabricated materials showed a remarkable increase of the thermal-oxidative stability even with a low LDH concentration, and a reduction of oxygen permeability mainly depending on the aspect ratio. Tang *et al.*, (2003) have increased the adsorption affinity between clay mineral layers and polyelectrolytes through an automated layer-by-layer procedure. Such approach allowed developing macroscopic bionanocomposite films with controlled nanometric ordering and extraordinary mechanical properties (Tang et al., 2003). Likewise, Posati *et al.* (2014) developed transparent bionanocomposite films, composed of Zn_2Al LDH-silk fibroin by drop casting of a dispersion of hydrotalcite-like compound in silk fibroin solution with remarkably enhanced mechanical resistance.

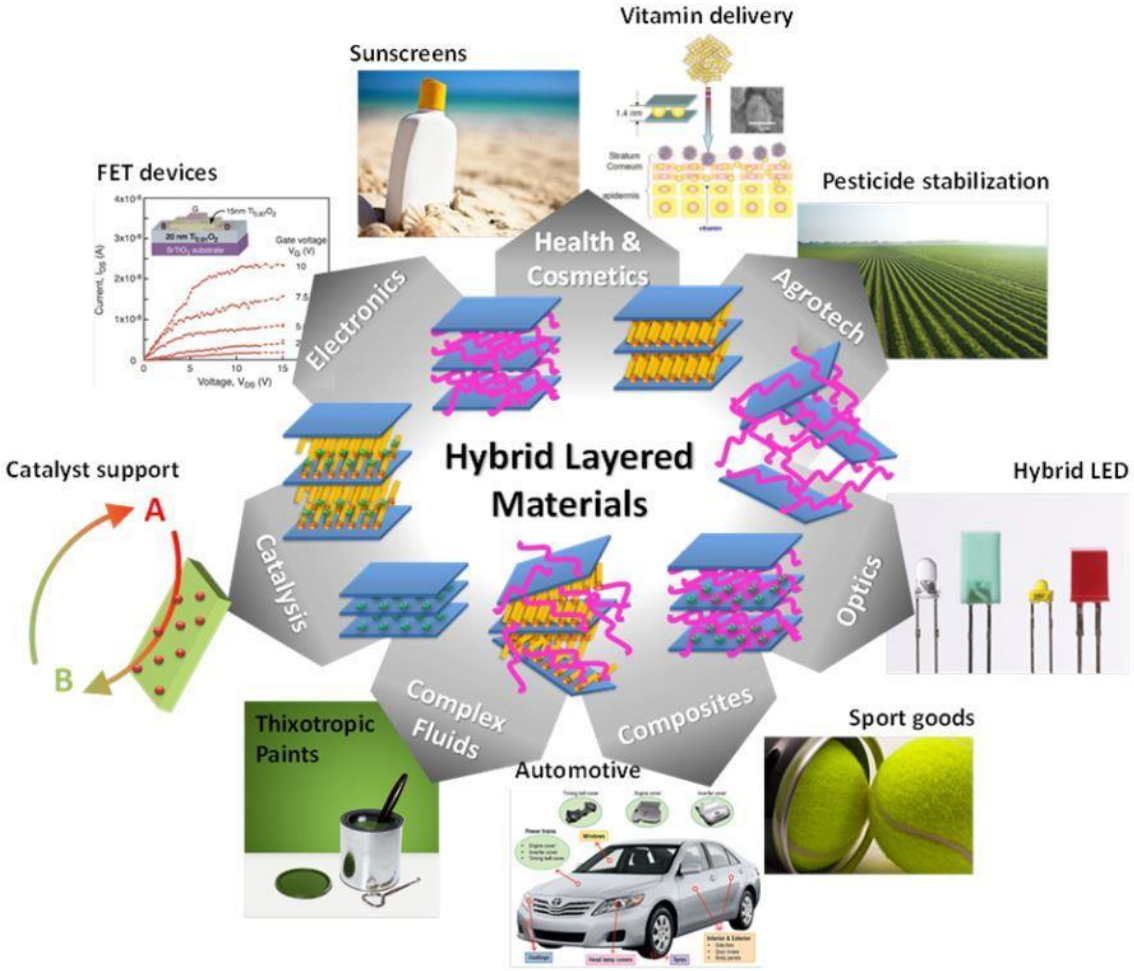


Figure 5 – Major applications and technological sectors using hybrid layered compounds.

The focus in the field of electronics, historically, is on top-down approaches such as patterning through ion-beam lithography. Following this approach, hybrid lamellar compounds have been elaborated to be integrated in different type of devices. The nanocomposites of LMC-polymer were proven to be potentially good choices to develop hybrid-photovoltaic materials (Saikia et al., 2011). Maier *et al.* (2011) synthesized CdS- and ZnS-P3EBT (poly(3-(ethyl-4-butanoate)thiophene)) composites, trough *in-situ* formation of inorganic nanostructures within the polymer matrix. The substrate was spin coated by the polymer-inorganic precursor solutions and subsequently integrated in a solar cell showing the desirable photovoltaic activity. Xu and Mitzi (2003) obtained a non-perovskite-based semiconductor lamellar hybrid $[CH_3(CH_2)_{11}NH_3]SnI_3$ which can be solution-processed into thin films at ambient temperatures. Recently, increasing attention is devoted to the delamination of different layered oxides for direct device integration as can be seen in Fig. 6

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

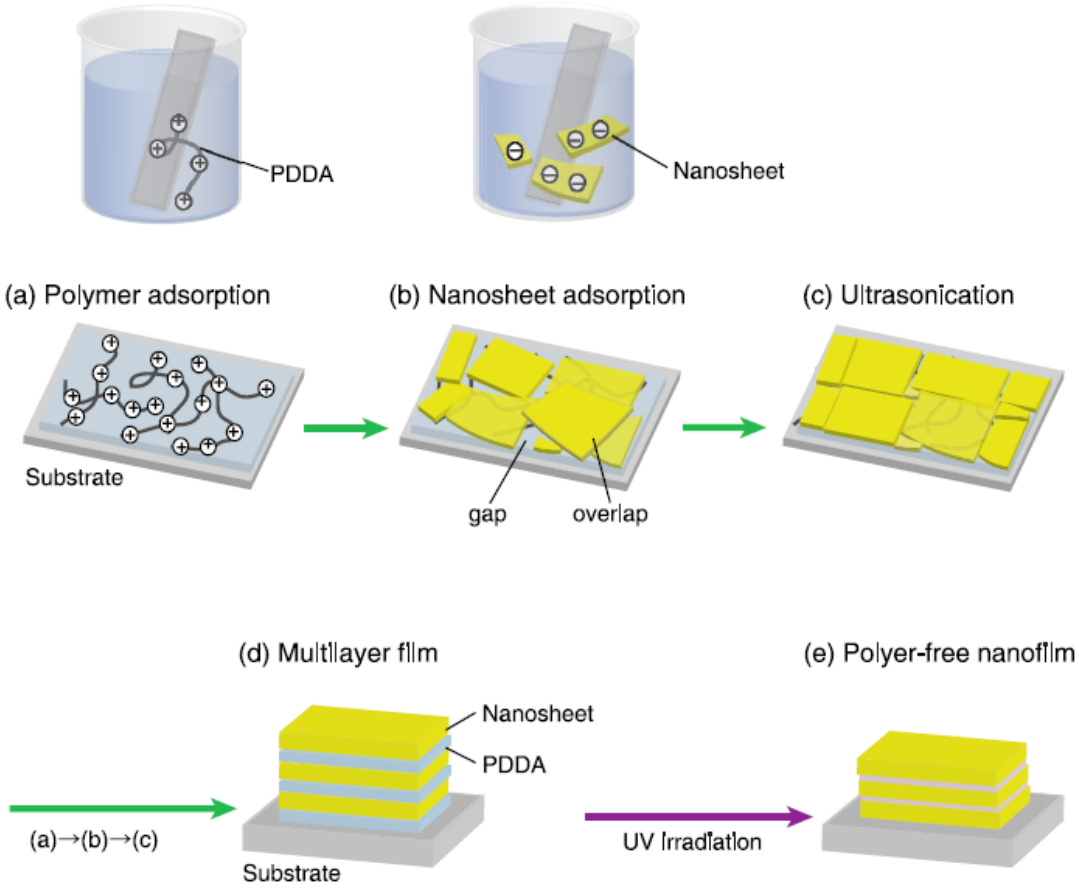


Figure 6 – Mixed layer-by-layer and ultrasound strategies for the preparation of layered perovskites superlatices. Reproduced with permission from the Wiley (Osada and Sasaki, 2012).

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

resulted in high catalytic activity of pyruvate decarboxylation as an active biocatalyst (Baikousi et al., 2013). The preparation of $[Ni(C_6O_7H_3)_x(OH)]_y^{y(3x-1)-}$-LDH nanocomposites by anion exchange between Mg/Al LDH host structure and $Ni(C_6O_7H_3)_x(OH)]_y^{y(3x-1)-}$ clusters, permitted to control both the Ni loading and the size of the particles in Ni^0/Mg(Al)O metal supported catalysts after the nanocomposite reduction (Gérardin et al., 2008).

In this context, also clay minerals can be engineered into various functional solid catalysts. Depending on the design and their preparation, clay minerals can play four major roles: (1) catalytic activity of the framework of clay, (2) exchangeability of the interlayer ions for catalysis purpose, (3) interlayer modification by functional nanoparticles and (4) the use of clay minerals or their derivatives used as catalyst supports (Zhou, 2011; Zeng et al., 2013). Hybrids of clay- manganese species, obtained from the adsorption of manganese (III) salen complexes, showed a good activity to catalyse water oxidation (Berends et al., 2011) and epoxidation of olefins (Kuźniarska-Biernacka et al., 2011). Another example consisted of cyclic poly(L-lactide) (PLLA) used as stabilizer of palladium nanoparticles to prepare PLLA-clay hybrid material as recyclable catalyst support. The obtained nanocomposite was reported to be a highly efficient and recyclable catalyst for the aminocarbonylation reactions of aryl halides with various amines (Prasad et al., 2013). Despite the advances shown by the isolated proofs of concept, the absence of an integrative strategy (that could transfer the reported results into the relevant context) hampers an extended application of these advances.

Owing to their biocompatibility, ion-exchange ability, and low cytotoxicity, LDHs and clays have also found great potential application as inorganic nanoparticles for drug delivery. Different ionic pharmaceutically active molecules can be intercalated into the interlayer space of LDHs and clays by ion-exchange. The interlayer space of these materials can be considered as a reservoir for drug, protecting it from the reaction of light and oxygen. After the cellular uptake of these particles by clathrin-mediated endocytosis, the drug may be released through a deintercalation process because of anion exchange or displacement reactions. The drug release can be controlled by tuning the host–guest interactions, which can be obtained by hybridizing clay minerals or LDH. The synthesis and potential applications of these hybrid lamellar drug carriers are discussed in detail in other review articles (Li and Duan, 2006; Patil and Mann, 2008; Zhao et al., 2012; Ruiz-Hitzky et al., 2013). A good example in this area is the research work of Miao *et al.* (2012) concerning a drug delivery system based on the fibers of LDH/biopolymer. Ibuprofen intercalated Mg-Al LDH was dispersed in polycaprolactone (PCL) or polylactide (PLA) solutions, obtaining electrospinning suitable solutions. The

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

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

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

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-phyllosolicate	N-trimethoxysilylpropylthiopropanamidomethylacrylamide	Sol-gel	Heavy metal cation sorption	POC	(Badshah and Airoldi, 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-phyllosilicate	3-aminopropyltriethoxysilane + Cu phthalocyanine	Hydrothermal	Magnetic properties	Fundamental	(Richard-Plouet et al., 2002)
	New syliating agent with ethanolamine and diethanolamine functions	Sol-gel	Barium adsorption	POC	(Melo et al., 2008)
Layered Metal Hydroxides					
LHS					
$Cu_2(OH)_3(CH_3CO_2)H_2O$ $Co_2(OH)_3NO_3$	Olygothiophenecarboxylates	Hydrothermal	Magnetic properties	POC	(Demessence et al., 2010)
$Ni(NO_3)_2.6H_2O$	Oligophenylenevinylene	Ion-exchange	Magnetic & photoluminescence properties	POC	(Rueff et al., 2004)
$Co_2(OH)_3(CH_3COO).H_2O$	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 Deoxyribonucleic acid (DNA)	Ion-exchange	Encapsulation	Gene Delivery System / POC	(Choy et al., 1999)
	Dodecyl sulfate	Microemulsion method	Rheological properties of DLH dispersion in polypropylene	Fundamental	(Wang et al., 2012)
Mg_2Al, Mg_2Fe, Mg_2Ga	DNA	Co-precipitation	Encapsulation	Gene Delivery System / POC	(Desigaux et al., 2006)
Zn_2AL	4[12-(methacryloylamino)dode-canoylamino] 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-triflouromethylbenzoi	Co-precipitation	UV-absorption	Sunscreen / POC	(Khan et al., 2011)
CSH	acrylic acid, 2-(phosphonooxy)-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_3H))($H_2O)_2$]$^-$	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**

5. Concluding remarks

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

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

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

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

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

References

Alberti, G., 1978. Syntheses,Crystalline Structure, and Ion-Exchange Properties of Insoluble Acid Salts of Tetravalent Metals and Their Salt Forms. Acc. Chem. Res. 11, 163–170.

Alberti, G., Constantino, U., 1996. Solid-State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Compounds, in: Alberti, G., Bein, T. (Eds.), Compreensive Chemistry. Pergamon-Elsevier, Oxford, pp. 1–23.

Alberti, G. Casciola, M., Constantino, U., 1985. Inorganic Ion-Exchange Pellicles Obtained by Delamination of o-Zirconium Phosphate Crystals 107, 256–263.

Alberti, G., Marmottini, F., Cavalaglio, S., Severi, D., 2000. Intercalation Processes of n-lkyl Monoamines in γ-Zirconium Phosphate. Langmuir 16, 4165–4170.

Alberti, G., Grassi, A., Lombardo, G.M., Pappalardo, G.C., Vivani, R., Chimica, D., Elce, V., Chimiche, S., Generale, C., Doria, V.A., April, R. V, 1999. Derivation of Force Field Parameters , and Force Field and Quantum Mechanical Studies of Layered r- and γ-Zirconium Phosphates. Inorg. Chem. 38, 4249–4255.

Alemán, J., Chadwick, A. V., He, J., Hess, M., Horie, K., Jones, R.G., Kratochvíl, P., Meisel, I., Mita, I., Moad, G., Penczek, S., Stepto, R.F.T., 2007. Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials. Pure Appl. Chem. 79, 1801–1829.

Alexandre, M., Dubois, P., 2000. Polymer-layered silicate nanocomposites : preparation, properties and uses of a new class of materials 28, 1–63.

Annabi-Bergaya, F., 2008. Microporous and Mesoporous Mater., 107, 141-148

Aranda, P., Ruiz-hitzky, E., 1992. Poly (ethylene oxide)-Silicate Intercalation Materials. Chem. Mater. 4, 1395–1403.

Aranda, P., Darder, M., Fernandez-Saavedra, R., Lopez-Blanco, M., Ruiz-Hitzky, E., 2006. Relevance of polymer- and biopolymer-clay nanocomposites in electrochemical and electroanalytical applications. Thin Solid Films 495, 104–112.

Arizaga, G., Satyanarayana, K., Wypych, F., 2007. Layered hydroxide salts: Synthesis, properties and potential applications. Solid State Ionics 178, 1143–1162.

Ataca, C., Sahin, H., Ciraci, S., 2012. Stable, single-layer MX2 transition-metal oxides and dichalcogenides in a honeycomb-like structure. J. Phys. Chem. C 116, 8983–8999.

Auerbach, S., Carrado, K., Dutta, P., 2004. Handbook of layered materials. Marcel Dekker Inc., New York.

Backov, R., 2006. Combining soft matter and soft chemistry: integrative chemistry towards designing novel and complex multiscale architectures. Soft Matter 2, 452.

Badshah, S., Airoldi, C., 2011. Layered organoclay with talc-like structure as agent for thermodynamics of cations sorption at the solid/liquid interface. Chem. Eng. J. 166, 420–427.

Badshah, S., Airoldi, C., 2013. Layered inorganic–organic hybrid with talc-like structure for cation removal at the solid/liquid interface. Thermochim. Acta 552, 28–36.

Bafna, A., Beaucage, G., Mirabella, F., Mehta, S., 2003. 3D Hierarchical orientation in polymer-clay nanocomposite films. Polymer 44, 1103–1115.

Baikousi, M., Stamatis, Ag., Louloudi, M., Karakassides, M. A., 2013. Thiamine pyrophosphate intercalation in layered double hydroxides (LDHs): An active bio-hybrid catalyst for pyruvate decarboxylation. Appl. Clay Sci. 75-76, 126–133.

Bailey, G.W., White, J.L., 1964. Soil-Pesticide Relationships, Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity. J. Agric. Food Chem. 12, 324–332.

Bellitto, C., Bauer, E.M., Righini, G., 2008. On the crystal structures and magnetism of some hybrid organic–inorganic metal organophosphonates. Inorganica Chim. Acta 361, 3785–3799.
Beneš, L., Melánová, K., Svoboda, J., Zima, V., 2012. Intercalation chemistry of layered vanadyl phosphate: a review. J. Incl. Phenom. Macrocycl. Chem. 73, 33–53.
Berends, H.-M., Homburg, T., Kunz, I., Kurz, P., 2011. K10 montmorillonite supported manganese catalysts for the oxidation of water to dioxygen. Appl. Clay Sci. 53, 174–180.
Bergaya, F., Lagaly, G., 2006. General introduction: Clays, Clay Minerals and Clay Science, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier Ltd, Amsterdam, pp. 1–18.
Bergaya, F., Lagaly, G., Beneke, K., 2006a. History of clay science: a young discipline, in: Bergaya, Faiza, Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier Ltd, Amsterdam, pp. 1163–1181.
Bergaya, F., Theng, B.K.G., Lagaly, G., 2006b. Handbook of clay science. Vol. 1, Developments in Clay Science. Elsevier Ltd, Amsterdam
Birjega, R., Matei, A., Mitu, B., Ionita, M.D., Filipescu, M., Stokker-Cheregi, F., Luculescu, C., Dinescu, M., Zavoianu, R., Pavel, O.D., Corobea, M.C., 2013. Layered double hydroxides/polymer thin films grown by matrix assisted pulsed laser evaporation. Thin Solid Films 543, 63–68.
Biswick, T., Jones, W., Pacuła, A., Serwicka, E., 2006. Synthesis, characterisation and anion exchange properties of copper, magnesium, zinc and nickel hydroxy nitrates. J. Solid State Chem. 179, 49–55.
Blumstein, A., 1965. Polymerization of adsorbed monolayers. I. Preparation of the clay–polymer complex. J. Polym. Sci. Part A 3, 2653–2664.
Brack, A., 2006. Clay minerals and the origin of life, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier Ltd, Amsterdam, pp. 379–391.
Bradley, W.F., 1945. Molecular associations between montmorillonite and some polyfunctional organic liquids. J. Am. Chem. Soc. 67, 975–981.
Burkett, S.L., Press, A., Mann, S., 1997. of Layered Inorganic-Organic Nanocomposites Based on 2 : 1 Trioctahedral Phyllosilicates 4756, 1071–1073.
Cao, G., Hong, H.G., Mallouk, T.E., 1992. Layered metal phosphates and phosphonates: from crystals to monolayers. Acc. Chem. Res. 25, 420–427.
Carrado, K. A., Forman, J.E., Botto, R.E., Winans, R.E., 1993. Incorporation of phthalocyanines by cationic and anionic clays via ion exchange and direct synthesis. Chem. Mater. 5, 472–478.
Carrado, K. A., Xu, L., Csencsits, R., Muntean, J. V., 2001. Use of Organo- and Alkoxysilanes in the Synthesis of Grafted and Pristine Clays. Chem. Mater. 13, 3766–3773.
Carreterro, M.I., Gomes, C., Tateo, F., 2006. Clays and human health, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Amsterdam, pp. 717–741.
Chen, B., Evans, J.R.G., Greenwell, H.C., Boulet, P., Coveney, P. V, Bowden, A. a, Whiting, A., 2008. A critical appraisal of polymer-clay nanocomposites. Chem. Soc. Rev. 37, 568–94.
Choi, S.-J., Oh, J.-M., Choy, J.-H., 2008. Anticancer drug-layered hydroxide nanohybrids as potent cancer chemotherapy agents. J. Phys. Chem. Solids 69, 1528–1532.
Choudhury, A., Neeraj, S., Natarajan, S., Rao, C.N.R., 2002. Transformations of two-dimensional layered zinc phosphates to three-dimensional and one-dimensional structures. J. Mater. Chem. 12, 1044–1052.

Choy, J., Choi, S., Oh, J., Park, T., 2007. Clay minerals and layered double hydroxides for novel biological applications. Appl. Clay Sci. 36, 122–132.
Choy, J.H., Kwak, S.Y., Park, J.S., Jeong, Y.J., Portier, J., 1999. Intercalative nanohybrids of nucleoside monophosphates and DNA in layered metal hydroxide. J. Am. Chem. Soc. 121, 1399–1400.
Ciesla, C.-S., Werner, M., 2012. Nanocomposite Materials. ObservatoryNANO Briefing 30, 1-4.
Clearfield, A., 1988. Role of Ion Exchange in Solid-state Chemistry. Chem. Rev. 88, 125–148.
Clearfield, A., 2012. The Early History and Growth of Metal Phosphonate Chemistry, in: Metal Phosphonate Chemistry: From Synthesis to Applications. pp. 1–44.
Clement, R., Gamier, O., Jegoudez, J., 1986. Coordination Chemistry of the Lamellar MPS3 Materials: Metal-Ligand Cleavage as the Source of an Unusual "Cation-Transfer" Intercalation Process. Inorg. Chem. 25, 1404–1409.
Coiai, S., Scatto, M., Conzatti, L., Azzurri, F., Andreotti, L., Salmini, E., Stagnaro, P., Zanolin, A., Cicogna, F., Passaglia, E., 2011. Optimization of organo-layered double hydroxide dispersion in LDPE-based nanocomposites. Polym. Adv. Technol. 22, 2285–2294.
Cooper, M.A., Hawthorne, F.C., 1996. The crystal structure of shigaite. Can. Mineral. 34, 91–97.
Coradin, T., Cedex, O., Lacroix, P.G., 1996. From Intercalation to Aggregation : Nonlinear Optical Properties of Stilbazolium Chromophores - MPS3 Layered Hybrid Materials. Chem. Mater. 8, 2153–2158.
Cunha, A. F., Wu, Y.-J., Santos, J.C., Rodrigues, A. E., 2013. Sorption enhanced steam reforming of ethanol on hydrotalcite-like compounds impregnated with active copper. Chem. Eng. Res. Des. 91, 581–592.
Da Silva, M.L.N., Marangoni, R., Cursino, A.C.T., Schreiner, W.H., Wypych, F., 2012. Colorful and transparent poly(vinyl alcohol) composite films filled with layered zinc hydroxide salts, intercalated with anionic orange azo dyes (methyl orange and orange II). Mater. Chem. Phys. 134, 392–398.
Darder, M., Ruiz-Hitzky, E., 2005. Caramel–clay nanocomposites. J. Mater. Chem. 15, 3913-3918.
Darder, M., Aranda, P., 2010. Applied Clay Science Multifunctional materials based on graphene-like / sepiolite nanocomposites. Appl. Clay Sci. 47, 203–211.
Darder, M., Colilla, M., Ruiz-Hitzky, E., 2005. Chitosan-clay nanocomposites: application as electrochemical sensors. Appl. Clay Sci. 28, 199–208.
Darder, M., Aranda, P., Ruiz-Hitzky, E., 2007. Bionanocomposites: A new concept of ecological, bioinspired, and functional hybrid materials. Adv. Mater. 19, 1309–1319.
De Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R., 2008. Organoclays: Properties, preparation and applications. Appl. Clay Sci. 42, 8–24.
De, S., Dey, A., De, S.K., 2007. Electrical transport and optical properties of vanadyl phosphate—polyaniline nanocomposites. J. Phys. Chem. Solids 68, 66–72.
Deemie, R.W., Rao, M., Knight, D.A., 1999. An organometallic sol–gel route to layered zinc phenylphosphonate and encapsulation studies with η6-(C6H6)Cr(CO)3. J. Organomet. Chem. 585, 162–166.
Delahaye, É., Eyele-Mezui, S., Diop, M., Leuvrey, C., Rabu, P., Rogez, G., 2010. Rational synthesis of chiral layered magnets by functionalization of metal simple hydroxides with chiral and non-chiral Ni(II) Schiff base complexes. Dalton Trans. 39, 10577–10580.

Delahaye, É., Eyele-Mezui, S., Bardeau, J.-F., Leuvrey, C., Mager, L., Rabu, P., Rogez, G., 2009. New layered organic-inorganic magnets incorporating azo dyes. J. Mater. Chem. 19, 6106-6115.

Delhoyo, C., 2007. Layered double hydroxides and human health: An overview. Appl. Clay Sci. 36, 103–121.

Delmas, C., Fouassier, C., Hagenmuller, P., 1980. Structural classification and properties of the layered oxides. Phys. B+C 99B, 81–85.

Demessence, A., Yassar, A., Rogez, G., Miozzo, L., De Brion, S., Rabu, P., 2010. Synthesis, optical and magnetic properties of hybrid α,α′-oligothiophenecarboxylates/transition metal hydroxide multilayered compounds. J. Mater. Chem. 20, 9401–9414.

Desigaux, L., Belkacem, M. Ben, Richard, P., Cellier, J., Léone, P., Cario, L., Leroux, F., Taviot-Guého, C., Pitard, B., 2006. Self-assembly and characterization of layered double hydroxide/DNA hybrids. Nano Lett. 6, 199–204.

Dimotakis, E.D., Pinnavaia, T.J., 1990. New Route to Layered Double Hydroxides Intercalated by Organic Anions: Precursors to Polyoxometalate-Pillared Derivatives. Inorg. Chem. 29, 2393–2394.

Drillon, M., Panissod, P., 1998. Long-range ferromagnetism in hybrid compounds: The role of dipolar interactions. J. Magn. Magn. Mater. 188, 93–99.

Emodi, B.S., 1949. The adsorption of dyestuff by montmorillonite. Clay Miner. 0, 76–79.

Eyele-Mezui, S., Delahaye, E., Rogez, G., Rabu, P., 2012. Functional Hybrid Materials Based on Layered Simple Hydroxide Hosts and Dicarboxylate Schiff Base Metal Complex Guests. Eur. J. Inorg. Chem. 2012, 5225–5238.

Filonenko, V.P., Sundberg, M., Werner, P.-E., Zibrov, I.P., 2004. Structure of a high-pressure phase of vanadium pentoxide, beta-V2O5. Acta Crystallogr. B. 60, 375–81.

Fonseca, M. da, Silva, C., Airoldi, C., 1999. Aminated phyllosilicates synthesized via a sol-gel process. Langmuir 5048–5055.

Fonseca, M. da, Silva, C., Barone, J., Airoldi, C., 2000. Layered hybrid nickel phyllosilicates and reactivity of the gallery space. J. Mater. Chem. 10, 789–795.

Fonseca, M. da, Silva Filho, C., Machado Junior, R.S., Arakaki, L.N., Espinola, J.G., Airoldi, C., 2004. Zinc phyllosilicates containing amino pendant groups. J. Solid State Chem. 177, 2316–2322.

Forano, C., Hibino, T., Leroux, F., Taviot-Guého, C., 2006. Layered double hydroxides, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier Ltd, Amsterdam, pp. 1021–1095.

Forster, P.M., Tafoya, M.M., Cheetham, A.K., 2004. Synthesis and characterization of Co7(OH)12(C2H4S2O6)(H2O)2—a single crystal structural study of a ferrimagnetic layered cobalt hydroxide. J. Phys. Chem. Solids 65, 11–16.

Frink, K., Wang, R., Colon, J., Clearfield, A., 1991. Intercalation of ammonia into zinc and cobalt phenylphosphonates. Inorg. Chem. 30, 1438–1441.

Fu, R., Xiang, S., Zhang, H., Zhang, J., Wu, X., 2005. Syntheses, Characterization, and Magnetic Properties of Four New Layered Transition-Metal Hydroxyl - Carboxylate - Phosphonates : [M(CH(OH)(CO2)(PO3H))(H2O)2](M= Mn, Fe, Co, Zn). Cryst. Growth Des. 5, 1795–1799.

Fujii, K., Hayashi, S., Kodama, H., 2003. Synthesis of an Alkylammonium/Magnesium Phyllosilicate Hybrid Nanocomposite Consisting of a Smectite-Like Layer and Organosiloxane Layers. Chem. Mater. 15, 1189–1197.

Fujita, W., Awaga, K., 1996. Magnetic Properties of Cu2(OH)3(alkanecarboxylate) Compounds : Drastic Modification with Extension of the Alkyl Chain. Inorg. Chem. 35, 1915–1917.

Fukushima, Y., Inagaki, S., 1987. Synthesis of an Intercalated Compound of Montmorillonite and 6-Polyamide. J. Incl. Phenom. 5, 473–482.
Fukushima, Y., Tani, M., 1995. An Organic/lnorganic Hybrid Layered Polymer: Methacrylate-Magnesium(Nickel) Phyllosilicate. J. Chem. Soc. Chem. Commun. 241–242.
Fukushima, Y., Okada, A., Kawasumi, M., Kurauchi, T., Kamigaito, O., 1988. Swelling behaviour of montmorillonite by poly-6-amide. Clay Miner. 23, 27–34.
Gallégo, J.-C., Jaber, M., Miehé-Brendlé, J., Marichal, C., 2008. Synthesis of new lamellar inorganic–organic talc-like hybrids. New J. Chem. 32, 407.
Gao, M., Yao, W., Yao, H., Yu, S., 2009. Synthesis of Unique Ultrathin Lamellar Mesostructured CoSe 2-Amine (Protonated) Nanobelts in a Binary Solution. J. Am. Chem. Soc. 131, 7486–7487.
Geim, A.K., Grigorieva, I.. V., 2013. Van der Waals heterostructures. Nature 499, 419–425.
Gérardin, C., Kostadinova, D., Coq, B., Tichit, D., 2008. LDH Nanocomposites with Different Guest Entities as Precursors of Supported Ni Catalysts. Chem. Mater. 20, 2086–2094.
Ghose, S., 1964. The crystal structure of hydrozincite, Zn5(OH)6(CO3)2. Acta Crystallogr. 17, 1051–1057.
Giannelis, E.P., 1996. Polymer Layered Silicate Nanocomposites. Adv. Mater. 8, 29–35.
Gieseking, J.E., 1939. The mechanism of cation exchange in the montmorillonite-beidellite-nontronite type of clay minerals. Soil Sci. 47, 1–13.
Gilman, J.W., 1999. Flammability and thermal stability studies of polymer layered-silicate clay / nanocomposites 31–49.
Guerra, E.M., Ciuffi, K.J., Oliveira, H.P., 2006. V2O5 xerogel–poly(ethylene oxide) hybrid material: Synthesis, characterization, and electrochemical properties. J. Solid State Chem. 179, 3814–3823.
Guerrero, G., Mutin, P., Vioux, A., 2000. Mixed nonhydrolytic/hydrolytic sol-gel routes to novel metal oxide/phosphonate hybrids. Chem. Mater. 12, 1268–1272.
Hang, P.T., Brindley, G.W., 1970. Methylene blue adsorption by clay minerals. Determination of surface areas and cation exchange capacities. Clays Clay Miner. 18, 203–212.
He, J., Wei, M., Li, B., Kang, Y., Evans, D.G., Duan, X., 2006. Preparation of Layered Double Hydroxides, in: Duan, X., Evans, D.G. (Eds.), Layered Double Hydroxides. Springer Berlin / Heidelberg, Berlin, pp. 89–119.
Hendricks, S.B., 1941. Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to Van Der Waals forces. J. Phys. Chem. 45, 65–81.
Hoffmann, R.W., Brindley, G.W., 1960. Clay-Organic studies 2. Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite. Geochim. Cosmochim. Acta 20, 15–29.
Hoffmann, R.W., Brindley, G.W., 1961. Clay-Organic studies 5. Adsorption of ethylene glycol and glycerol by montmorillonite. Am. Mineral. 46, 450–452.
Holmström, S.C., Patil, A.J., Butler, M., Mann, S., 2007. Influence of polymer co-intercalation on guest release from aminopropyl-functionalized magnesium phyllosilicate mesolamellar nanocomposites. J. Mater. Chem. 17, 3894.
Hussein, M.Z. Bin, Yahaya, A.H., Ping, L.M., 2004a. Dye-interleaved nanocomposite: Evan's Blue in the lamella of Mg–Al-layered double hydroxide. Dyes Pigments 63, 135–140.

Hussein, M.Z. Bin, Yahaya, A.H., Shamsul, M., Salleh, H.M., Yap, T., Kiu, J., 2004b. Acid fuchsin-interleaved Mg–Al-layered double hydroxide for the formation of an organic–inorganic hybrid nanocomposite. Mater. Lett. 58, 329–332.
Illaik, A., Taviot-Guého, C., Verney, V., Leroux, F., Pascal, B., 2008. Unusual Polystyrene Nanocomposite Structure Using Emulsifier-Modified Layered Double Hydroxide as Nanofiller. Chem. Mater. 20, 4854–4860.
Jaber, M., Miehé-Brendlé, J., 2008. Synthesis, characterization and applications of 2:1 phyllosilicates and organophyllosilicates: Contribution of fluoride to study the octahedral sheet. Microporous Mesoporous Mater. 107, 121–127.
Jaber, M., Miéhé-Brendlé, J., Delmotte, L., Le Dred, R., 2003. New range of Al–Mg organoclays with tailored hydrophobicity: incorporation of fluoride as a local probe to study the octahedral character. Microporous Mesoporous Mater. 65, 155–163.
Jaber, M., Miéhé-Brendlé, J., Delmotte, L., Le Dred, R., 2005. Formation of organoclays by a one step synthesis. Solid State Sci. 7, 610–615.
Jaber, M., Miehé-Brendlé, J., Roux, M., Dentzer, J., Le Dred, R., Guth, J.-L., 2002. A new Al,Mg-organoclay. New J. Chem. 26, 1597–1600.
Jaynes, W.E.I., Vance, G.E., 1999. Sorption of benzene, toluene, ethylbenzene and xylene (BTEX) compounds by hectorite clays exchanged with romatic organic cations 47, 358–365.
Jordan, J.W., 1949. Organophilic Bentonites. I. Swelling in Organic Liquids. J. Phys. Colloid Chem. 53, 294–306.
Judeinstein, P., Sanchez, C., 1996. Hybrid organic-inorganic materials : a land of multidisciplinarity. J. Mater. Chem. 6, 511–525.
Kanatzidis, M.G., Wu, C.G., Marcy, H.O., Kannewurf, C.R., 1989. Conductive-polymer bronzes. Intercalated polyaniline in vanadium oxide xerogels. J. Am. Chem. Soc. 111, 4139–4141.
Karmaoui, M., Ferreira, R.S., 2006. Lanthanide-based lamellar nanohybrids: Synthesis, structural characterization, and optical properties. Chem. Mater. 18, 4493–4499.
Karmaoui, M., Mafra, L., 2007. Photoluminescent rare-earth based biphenolate lamellar nanostructures. J. Phys. Chem. C 111, 2539–2544.
Karmaoui, M., Sá Ferreira, R. A., Carlos, L.D., Pinna, N., 2007. Lanthanide-based lamellar nanohybrids: The case of erbium. Mater. Sci. Eng. C 27, 1368–1371.
Khan, S., Liu, C., Jang, E., Akhtar, K., Han, H., 2011. Encapsulation of organic UV ray absorbents into layered double hydroxide for photochemical properties. Mater. Lett. 65, 2923–2926.
Kim, Y., Atherton, S.J., Brigham, E.S., Mallouk, T.E., 1993. Sensitized Layered Metal Oxide Semiconductor Particles for Photochemical Hydrogen Evolution from Nonsacrificial Electron Donors. J. Phys. Chem. 97, 11802–11810.
Kojima, N., Okubo, M., Shimizu, H., Enomoto, M., 2007. Control of magnetism by isomerization of intercalated molecules in organic–inorganic hybrid systems. Coord. Chem. Rev. 251, 2665–2673.
Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., Kamigaito, O., 1993. Mechanical properties of Nylon 6-clay hybrid. J. Mater. Res. 8, 1185–1189.
Komarneni, S., Breval, E., 1986. Synthesis and Characterization of a 12.6 A calcium silicate hydrate. Cem. Concr. Res. 16, 580–586.
Kozak, M., Domka, L., 2004. Adsorption of the quaternary ammonium salts on montmorillonite. J. Phys. Chem. Solids 65, 441–445.
Kraus, K.A., Phillips, H.O., 1956. Adsorption on inorganic materials. I. Cation exchange properties of zirconium phosphate. J. Am. Chem. Soc. 78, 694.

Kuhlenbeck, H., Shaikhutdinov, S., Freund, H.-J., 2013. Well-ordered transition metal oxide layers in model catalysis-a series of case studies. Chem. Rev. 113, 3986–4034.
Kurmoo, M., Kumagai, H., Hughes, S.M., Kepert, C.J., 2003. Reversible guest exchange and ferrimagnetism (T(C) = 60.5 K) in a porous cobalt(II)-hydroxide layer structure pillared with trans-1,4-cyclohexanedicarboxylate. Inorg. Chem. 42, 6709–6722.
Kuroda, K., Shimojima, A., Kawahara, K., Wakabayashi, R., Tamura, Y., Asakura, Y., Kitahara, M., 2014. Utilization of Alkoxysilyl Groups for the Creation of Structurally Controlled Siloxane-Based Nanomaterials. Chem. Mater. 26, 211–220.
Kuwahara, T., Tagaya, H., Kadokawa, J., 2001. Intercalation of organic dyes in the layered host lattice V2O5. Inorg. Chem. Commun. 4, 63–65.
Kuźniarska-Biernacka, I., Pereira, C., Carvalho, A.P., Pires, J., Freire, C., 2011. Epoxidation of olefins catalyzed by manganese(III) salen complexes grafted to porous heterostructured clays. Appl. Clay Sci. 53, 195–203.
Kwolek, T., Hodorowicz, M., Stadnicka, K., Czapkiewicz, J., 2003. Adsorption isotherms of homologous alkyldimethylbenzylammonium bromides on sodium montmorillonite. J. Colloid Interface Sci. 264, 14–19.
Kyotani, T., Sonobe, N., Tomita, A., 1988. Formation of highly oriented graphite from polyacrylonitrile by using a two-dimensionak space betwee montmorillonite lamellae. Nature 331, 331–333.
Lagadic, I., Lacroix, P.G., Clément, R., 2012. Layered MPS3 (M = Mn, Cd) Thin Films as Host Matrixes for Nonlinear Optical Material Processing. Chem. Mater. 3, 2004–2012.
Lagadic, I.L., 2006. Schiff base chelate-functionalized organoclays. Microporous Mesoporous Mater. 95, 226–233.
Lagadic, I.L., Mitchell, M.K., Payne, B.D., 2001. Highly effective adsorption of heavy metal ions by a thiol-functionalized magnesium phyllosilicate clay. Environ. Sci. Technol. 35, 984–990.
Lagaly, G., 1999. Introduction: from clay mineral-polymer interactions to clay mineral-polymer nanocomposites. Appl. Clay Sci. 15, 1–9.
Lagaly, G., 2001. Pesticide–clay interactions and formulations. Appl. Clay Sci. 18, 205–209.
Lagaly, G., Ogawa, M., Dékany, I., 2006. Clay mineral organic interactions, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Amsterdam, pp. 309–377.
Laget, V., Hornick, C., Rabu, P., Drillon, M., Ziessel, R., 1998. Molecular magnets hybrid organic–inorganic layered compounds with very long-range ferromagnetism. Coord. Chem. Rev. 178-180, 1533–1553.
LeBaron, P.C., Wang, Z., Pinnavaia, T.J., 1999. Polymer-layered silicate nanocomposites: an overview. Appl. Clay Sci. 15, 11–29.
Lee, D.S., Kim, T.-H., Park, C.-H., Chung, C.-Y., Lim, Y.S., Seo, W.-S., Park, H.-H., 2013. Crystal structure, properties and nanostructuring of a new layered chalcogenide semiconductor, Bi2MnTe4. CrystEngComm 15, 5532-5538.
Leroux, F., Taviot-Guého, C., 2005. Fine tuning between organic and inorganic host structure: new trends in layered double hydroxide hybrid assemblies. J. Mater. Chem. 15, 3628-3642.
Leroux, F., Gachon, J., Besse, J.-P., 2004. Biopolymer immobilization during the crystalline growth of layered double hydroxide. J. Solid State Chem. 177, 245–250.
Leroux, F., Illaik, A., Verney, V., 2009. A comprehensive study of an unusual jammed nanocomposite structure using hybrid layered double hydroxide filler. J. Colloid Interface Sci. 332, 327–35.
Li, F., Duan, X., 2006. Applications of Layered Double Hydroxides, in: Duan, X., Evans, D.G. (Eds.), Layered Double Hydroxides. Berlin, pp. 193–223.

Lin, Z., Bu, X., Feng, P., 2010. Two new layered bimetallic sulfides: Solvothermal synthesis, crystal structure, optical and magnetic properties. Microporous Mesoporous Mater. 132, 328–334.
Livage, J., 1991. Vanadium pentoxide gels. Chem. Mater. 3, 578–593.
MacEwan, D.M.C., 1946. Halloysite-organic complexes. Nature 157, 159–160.
MacEwan, D.M.C., 1948. Complexes of clays with organic compounds. I. Complex formation between montmorillonite and halloysite and certain organic liquids. Trans. Faraday Soc. 44, 349–367.
Maier, E., Fischereder, A., Haas, W., Mauthner, G., Albering, J., Rath, T., Hofer, F., List, E.J.W., Trimmel, G., 2011. Metal sulfide–polymer nanocomposite thin films prepared by a direct formation route for photovoltaic applications. Thin Solid Films 519, 4201–4206.
Malaman, B., Bagtache, R., Abdmeziem, K., 2010. Synthesis and structure of Cu3PO4[1,2,4-triazole]2OH with a hybrid layered structure: A new organically templated copper (II) hydroxyphosphate. Solid State Sci. 12, 1178–1182.
Mane, A.T., Pinna, N., 2006. Lanthanide-Based Lamellar Nanohybrids: Synthesis, Structural Characterization, and Optical Properties. Chem. Mater. 18, 4493–4499.
Mann, S., Burkett, S., Davis, S., 1997. Sol-gel synthesis of organized matter. Chem. Mater. 4756, 2300–2310.
Marangoni, R., Taviot-Guého, C., Illaik, A., Wypych, F., Leroux, F., 2008. Organic inorganic dye filler for polymer: blue-coloured layered double hydroxides into polystyrene. J. Colloid Interface Sci. 326, 366–73.
Martínez-Ortiz, M.D.J., Tichit, D., Gonzalez, P., Coq, B., 2003. The “one-pot” synthesis of 4-methyl-2-pentanone (methyl isobutyl ketone) from acetone over PdCu catalysts prepared from layered double hydroxides. J. Mol. Catal. A Chem. 201, 199–210.
Melo, M. A., Oliveira, F.J.V.E., Airoldi, C., 2008. Novel talc-like nickel phyllosilicates functionalized with ethanolamine and diethanolamine. Appl. Clay Sci. 42, 130–136.
Mercier, L., Detellier, C., 1995. Preparation, characterization, and applications as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite. Environ. Sci. Technol. 29, 1318–1323.
Merlin, F., Lombois, H., Joly, S., Lequeux, N., Halary, J.-L., Van Damme, H., 2002. Cement-polymer and clay-polymer nano- and meso-composites: spotting the difference. J. Mater. Chem. 12, 3308–3315.
Messersmith, P.B., Giannelis, E.P., 1993. Polymer-Layered Silicate Nanocomposites: In Situ Intercalative Polymerization of c-Caprolactone in Layered Silicates. Chem. Mater. 5, 1064–1066.
Messersmith, P.B., Giannelis, E., 1995. Synthesis and Barrier Properties of Poly (e-Caprolactone)-Layered Silicate Nanocomposites. J. Polym. Sci. Part A Polym. Chem. 33, 1047–1057.
Meyn, M., Beneke, K., Lagaly, C., 1993. Anion-Exchange Reactions of Hydroxy Double Salts. Inorg. Chem. 32, 1209–1215.
Miao, Y.-E., Zhu, H., Chen, D., Wang, R., Tjiu, W.W., Liu, T., 2012. Electrospun fibers of layered double hydroxide/biopolymer nanocomposites as effective drug delivery systems. Mater. Chem. Phys. 134, 623–630.
Minet, J., Abramson, S., Bresson, B., 2004. New layered calcium organosilicate hybrids with covalently linked organic functionalities. Chem. Mater. 16, 3955–3962.
Minet, J., Abramson, S., Bresson, B., Franceschini, A., Van Damme, H., Lequeux, N., 2006. Organic calcium silicate hydrate hybrids: a new approach to cement based nanocomposites. J. Mater. Chem. 16, 1379.

Miyata, S., 1983. Anion-Exchange Properties of Hydrotalcite-Like Compounds. Clays Clay Miner. 31, 305–311.
Moscofian, A.S.O., Airoldi, C., 2008. Synthesized layered inorganic-organic magnesium organosilicate containing a disulfide moiety as a promising sorbent for cations removal. J. Hazard. Mater. 160, 63–69.
Mrlino, S., Bonaccorsi, E., Armbruster, T., 1999. Tobermorites : Their real structure and order-disorder (OD) character. Am. Mineral. 84, 1613–1621.
Mutin, P.H., Guerrero, G., Vioux, A., 2005. Hybrid materials from organophosphorus coupling molecules. J. Mater. Chem. 15, 3761–3768.
Nejati, K., Davary, S., Saati, M., 2013. Study of 2,4-dichlorophenoxyacetic acid (2,4-D) removal by Cu-Fe-layered double hydroxide from aqueous solution. Appl. Surf. Sci. 280, 67–73.
Nennemann, A., Mishael, Y., Nir, S., Rubin, B., Polubesova, T., Bergaya, F., van Damme, H., Lagaly, G., 2001. Clay-based formulations of metolachlor with reduced leaching. Appl. Clay Sci. 18, 265–275.
Newman, S.P., Jones, W., 1999. Comparative Study of Some Layered Hydroxide Salts Containing Exchangeable Interlayer Anions. J. Solid State Chem. 148, 26–40.
Nicoleau, L., Gädt, T., Chitu, L., Maier, G., Paris, O., 2013. Oriented aggregation of calcium silicate hydrate platelets by the use of comb-like copolymers. Soft Matter 9, 4864.
Nicolosi, V., Chhowalla, M., Kanatzidis, M.G., Strano, M.S., Coleman, J.N., 2013. Liquid Exfoliation of Layered Materials. Science (80-.). 340, 1226419–1226419.
Ogawa, M., Asai, S., 2000. Hydrothermal Synthesis of Layered Double Hydroxide - Deoxycholate Intercalation. Chem. Mater. 12, 3253–3255.
Ohtomo, A., Kawasaki, M., Ohkubo, I., Koinuma, H., Yasuda, T., Segawa, Y., 1999. Structure and optical properties of ZnO/Mg[0.2]Zn[0.8]O superlattices. Appl. Phys. Lett. 75, 980–982.
Ohtsuka, K., 1997. Preparation and Properties of Two-Dimensional Microporous Pillared Interlayered Solids. Chem. Mater. 9, 2039–2050.
Okada, T., Ide, Y., Ogawa, M., 2012. Organic-inorganic hybrids based on ultrathin oxide layers: designed nanostructures for molecular recognition. Chem. Asian J. 7, 1980–92.
Okano, K., Uemoto, M., Kagami, J., Miura, K., Aketo, T., Toda, M., Honda, K., Ohtake, H., 2013. Novel technique for phosphorus recovery from aqueous solutions using amorphous calcium silicate hydrates (A-CSHs). Water Res. 47, 2251–9.
Oriakhi, C., Farr, I. V, Lerner, M.M., 1996. Incorporation of poly(acrylic acid), poly(vinylsulfonate) and poly(styrenesulfonate) within layered double hydroxideswithin layered double hydroxides. J. Mater. Chem. 6, 103–107.
Osada, M., Sasaki, T., 2009. Exfoliated oxide nanosheets: new solution to nanoelectronics. J. Mater. Chem. 19, 2503.
Osada, M., Sasaki, T., 2012. Two-dimensional dielectric nanosheets: novel nanoelectronics from nanocrystal building blocks. Adv. Mater. 24, 210–28.
Otero, R., Fernández, J.M., González, M. A., Pavlovic, I., Ulibarri, M. a., 2013. Pesticides adsorption–desorption on Mg–Al mixed oxides. Kinetic modeling, competing factors and recyclability. Chem. Eng. J. 221, 214–221.
Patakfalvi, R., Oszkó, A., Dékány, I., 2003. Synthesis and characterization of silver nanoparticle/kaolinite composites. Colloids Surfaces A Physicochem. Eng. Asp. 220, 45–54.
Patel, V., Mahajan, Y., 2012. Polymer nanocomposites drive opportunities in the automotive sector [WWW Document]. Nanowerk.

Patil, A.J., Mann, S., 2008. Self-assembly of bio–inorganic nanohybrids using organoclay building blocks. J. Mater. Chem. 18, 4605.
Patil, A.J., Muthusamy, E., Mann, S., 2004. Synthesis and self-assembly of organoclay-wrapped biomolecules. Angew. Chem. Int. Ed. Engl. 43, 4928–33.
Patil, A.J., Muthusamy, E., Mann, S., 2005. Fabrication of functional protein–organoclay lamellar nanocomposites by biomolecule-induced assembly of exfoliated aminopropyl-functionalized magnesium phyllosilicates. J. Mater. Chem. 15, 3838.
Patil, A.J., Li, M., Dujardin, E., Mann, S., 2007. Novel bioinorganic nanostructures based on mesolamellar intercalation or single-molecule wrapping of DNA using organoclay building blocks. Nano Lett. 7, 2660–2665.
Paul, D.R., Robeson, L.M., 2008. Polymer nanotechnology: Nanocomposites. Polymer 49, 3187–3204.
Pavlovic, I., Barriga, C., Hermosín, M.C., Cornejo, J., Ulibarri, M. a., 2005. Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. Appl. Clay Sci. 30, 125–133.
Petrov, K., Markov, L., Rachev, P., 1987. Thermal decomposition of mixed magnesium(II)-cobalt(II) hydroxide nitrate crystals to MgxCo3-xO4 (0<x<1) spinels. React. Solids 3, 67–74.
Petrov, K., Lyubchova, a., Markov, L., 1989. Synthesis and thermal decomposition of magnesium hydroxide nitrates. Polyhedron 8, 1061–1067.
Pinna, N., 2007. The "benzyl alcohol route": an elegant approach towards organic-inorganic hybrid nanomaterials. J. Mater. Chem. 17, 2769–2774.
Pinna, N., Garnweitner, G., Beato, P., Niederberger, M., Antonietti, M., 2005. Synthesis of yttria-based crystalline and lamellar nanostructures and their formation mechanism. Small 1, 112–21.
Podsiadlo, P., Kaushik, A.K., Arruda, E.M., Waas, A.M., Shim, B.S., Xu, J., Nandivada, H., Pumplin, B.G., Lahann, J., Ramamoorthy, A., Kotov, N.A., 2007. Ultrastrong and stiff layered polymer nanocomposites. Science 318, 80–83.
Ponnamperuma, C., Shimoyama, A., Friebele, E., 1982. Clay and the origin of life. Orig. Life 12, 9–40.
Posati, T., Benfenati, V., Sagnella, A., Pistone, A., Nocchetti, M., Donnadio, A., Ruani, G., Zamboni, R., Muccini, M., 2014. Innovative multifunctional silk fibroin and hydrotalcite nanocomposites: a synergic effect of the components. Biomacromolecules 15, 158–68.
Pradhan, B., Srivastava, S.K., Bhowmick, A.K., Saxena, A., 2012. Effect of bilayered stearate ion-modified Mg-Al layered double hydroxide on the thermal and mechanical properties of silicone rubber nanocomposites. Polym. Int. 61, 458–465.
Prasad, A.V., Biying, A.O., Ling, W.Y., Stubbs, L.P., Zhu, Y., 2013. Synthesis and new application of green and recyclable cyclic poly(L-lactide)-clay hybrid. J. Polym. Sci. Part A Polym. Chem. 51, 4167–4174.
Rabu, P., Angelov, S., Legoll, P., M, B., Drillon, M., 1993. Ferromagnetism in Triangular Cobalt (II) Layers : Comparison of Co(OH)2 and Co2(N03)(0H)3. Inorg. Chem. 32, 2463–2468.
Radisavljevic, B., Radenovic, a, Brivio, J., Giacometti, V., Kis, A, 2011. Single-layer MoS2 transistors. Nat. Nanotechnol. 6, 147–50.
Ray, S. S., Okamoto, M., 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci. 28, 1539–1641.
Ray, S. S., Okamoto, M., 2003. Biodegradable Polylactide and Its Nanocomposites: Opening a New Dimension for Plastics and Composites. Macromol. Rapid Commun. 24, 815–840.

Richard-Plouet, M., Vilminot, S., Guillot M., 2004. Synthetic transition metal phylosilicates and organic-inorganic related phases 1073–1082.
Richard-Plouet, M., Vilminot, S., Guillot, M., Kurmoo, M., 2002. Canted antiferromagnetism in an organo-modified layered nickel phyllosilicate. Chem. Mater. 14, 3829–3836.
Richardson, I.G., 2008. The calcium silicate hydrates. Cem. Concr. Res. 38, 137–158.
Rogez, G., Massobrio, C., Rabu, P., Drillon, M., 2011. Layered hydroxide hybrid nanostructures: a route to multifunctionality. Chem. Soc. Rev. 40, 1031–58.
Rojas, R., Ulibarri, M.Á., Barriga, C., Rives, V., 2010. Chromate intercalation in Ni–Zn layered hydroxide salts. Appl. Clay Sci. 49, 176–181.
Roland-Swanson, C., Besse, J., Leroux, F., 2004. Polymerization of sulfopropyl methacrylate, a surface active monomer, within layered double hydroxide. Chem. Mater. 16, 5512–5517.
Rueff, J., Nierengarten, J.-F., Pierre, G., Demessence, A., Cregut, O., Drillon, M., Rabu, P., 2004. Influence of Magnetic Ordering on the Luminescence in a Layered Organic - Inorganic OPV - Ni (II) Compound. Chem. Mater. 16, 2933–2937.
Ruiz-Hitzky, E., Van Meerbeek, A., 2006. Clay mineral- and organoclay-polymer nanocomposite, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, Amsterdam.
Ruiz-Hitzky, E., Ariga, K., Lvov, Y.M., 2007. Bio-inorganic Hybrid Nanomaterials, Strategies, Syntheses, Characterization and Applications. Wiley-VCH, Weinheim.
Ruiz-Hitzky, E., Aranda, P., Darder, M., Rytwo, G., 2010. Hybrid materials based on clays for environmental and biomedical applications. J. Mater. Chem. 20, 9306-9321.
Ruiz-Hitzky, E., Darder, M., Fernandes, F.M., Zatile, E., Palomares, F.J., Aranda, P., 2011. Supported Graphene from Natural Resources: Easy Preparation and Applications. Adv. Mater. 23, 5250–5255.
Ruiz-Hitzky, E., Darder, M., Fernandes, F.M., Wicklein, B., Alcântara, A.C.S., Aranda, P., 2013. Fibrous clays based bionanocomposites. Prog. Polym. Sci. 38, 1392–1414.
Rytwo, G., 2008. Clay Minerals as an Ancient Nanotechnology : Historical Uses of Clay Organic Interactions, and Future Possible Perspectives. Macla 9, 15–17.
Rytwo, G., Gonen, Y., Afuta, S., Dultz, S., 2005. Interactions of pendimethalin with organo-montmorillonite complexes. Appl. Clay Sci. 28, 67–77.
Sá Ferreira, R.A., Karmaoui, M., Nobre, S.S., Carlos, L.D., Pinna, N., 2006. Optical properties of lanthanide-doped lamellar nanohybrids. Chemphyschem 7, 2215–2222.
Saikia, D., Saikia, P.K., Gogoi, P.K., Das, M.R., Sengupta, P., Shelke, M.V., 2011. Synthesis and characterization of CdS/PVA nanocomposite thin films from a complexing agent free system. Mater. Chem. Phys. 131, 223–229.
Sanchez, C., In, M., 1992. Molecular design of alkoxide precursors for the synthesis of hybrid organic-inorganic gels. J. Non. Cryst. Solids 147 & 148, 1–12.
Sanchez, C., Ribot, F., 1994. Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry. New J. Chem. 18, 1007–1047.
Sanchez, C., Julián, B., Belleville, P., Popall, M., 2005. Applications of hybrid organic–inorganic nanocomposites. J. Mater. Chem. 15, 3559–3592.
Sanchez, C., Belleville, P., Popalld, M., Nicole, L., 2011. Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market. Chem. Soc. Rev. 40, 696–753.
Sanchez del Rio, M., Doménech, A., Doménech-Carbo, M.T., Vazquez de Agredos Pascual, M.L., Suarez, M., Garcıa-Romero, E., 2011. The Maya Blue Pigment, in: Galàn, E., Singer, A. (Eds.), Developments in Palygorskite-Sepiolite Research. Elsevier B.V., Oxford, pp. 453–481.

Scaffaro, R., Botta, L., Frache, a., Bellucci, F., 2013. Thermo-oxidative ageing of an organo-modified clay and effects on the properties of PA6 based nanocomposites. Thermochim. Acta 552, 37–45.
Schoonheydt, R.A., Pinnavaia, T., Lagaly, G., Gangas, N., 1999. Pillared clays and pillared layered solids. Pure Appl. Chem. 71, 2367–2371.
Shi, Y., Yang, H., Zhao, X., Cao, T., Chen, J., Zhu, W., Yu, Y., Hou, Z., 2012. Au–Pd nanoparticles on layered double hydroxide: Highly active catalyst for aerobic oxidation of alcohols in aqueous phase. Catal. Commun. 18, 142–146.
Si, S., Taubert, A., Mantion, A., Rogez, G., Rabu, P., 2012. Peptide-intercalated layered metal hydroxides: effect of peptide chain length and side chain functionality on structural, optical and magnetic properties. Chem. Sci. 3, 1945-1957.
Stähler, R., Bensch, W., 2001. The Hydrothermal Synthesis, Crystal Structures and Thermal Stability of the Novel One- and Two-Dimensional Thioantimonate (III) Compounds [Co(tren)]Sb2S4 and [Ni(tren)] Sb2S4R. Eur. J. Inorg. Chem. 3073–3078.
Stähler, R., Näther, C., Bensch, W., 2003. Solvothermal syntheses, crystal structures, and thermal stability of two new thioantimonates(III) using complex transition metal cations as structure directing agents: the layered compound [Ni(dien)2]Sb4S7·H2O and the three-dimensional compound [Ni(dien)2. J. Solid State Chem. 174, 264–275.
Stählin, W., Oswald, H.R., 1970. The crystal structure of zinc hydroxide nitrate, Zn5(OH)8(NO3)2.2H2O. Acta Crystallogr. B 26, 860–863.
Stephenson, H.H., 1927. A note on the thixotropy of clays. J. Am. Ceram. Soc. 10, 924.
Sun, Y., Jiang, S., Bi, W., Wu, C., Xie, Y., 2011. Highly ordered lamellar V2O3-based hybrid nanorods towards superior aqueous lithium-ion battery performance. J. Power Sources 196, 8644–8650.
Tagaya, H., Saito, K., Kuwahara, T., Kadokawa, J., Chiba, K., 1993. Intercalation of layered compounds into layered titanobiate KTiNbO5. Catal. Today 16, 463–470.
Takada, K., Sakurai, H., Takayama-Muromachi, E., 2003. Superconductivity in two-dimensional CoO 2 layers 422, 53–55.
Takehira, K., Shishido, T., 2007. Preparation of supported metal catalysts starting from hydrotalcites as the precursors and their improvements by adopting "memory effect". Catal. Surv. from Asia 11, 1–30.
Takei, T., Kobayashi, Y., Hata, H., Yonesaki, Y., Kumada, N., Kinomura, N., Mallouk, T.E., Pennsyl, T., State, V., Uni, V., Park, U. V, Pennsyl, V., 2006. Anodic Electrodeposition of Highly Oriented Zirconium Phosphate and Polyaniline-Intercalated Zirconium Phosphate Films. J. Am. Chem. Soc. 128, 16634–16640.
Tang, Z., Kotov, N. a, Magonov, S., Ozturk, B., 2003. Nanostructured artificial nacre. Nat. Mater. 2, 413–418.
Taylor, D., 1989. A calcian analcime-bytownite intergrowth in basalt, from Skye, Scotland, and calcian analcime relationships. Mineral. Mag. 53, 382–385.
Terasaki, I., Sasago, Y., Uchinokura, K., 1997. Large thermoelectric power in NaCo2O4 single crystals. Phys. Rev. B 56, 685–687.
Thies, H.R., 1925. Relation between Dye Adsorption of Clays and Their Behavior in Rubber Compounds. Ind. Eng. Chem. 523, 1165–1169.
Thomas, J.J., Jennings, H.M., Allen, A.J., 2010. Relationships between Composition and Density of Tobermorite, Jennite, and Nanoscale CaO−SiO2−H2O. J. Phys. Chem. C 114, 7594–7601.
Tichit, D., Gérardin, C., Durand, R., Coq, B., 2006. Layered double hydroxides: precursors for multifunctional catalysts. Top. Catal. 39, 89–96.

Tichit, D., Ortiz, M.D.J.M., Francová, D., Gérardin, C., Coq, B., Durand, R., Prinetto, F., Ghiotti, G., 2007. Design of nanostructured multifunctional Pd-based catalysts from layered double hydroxides precursors. Appl. Catal. A Gen. 318, 170–177.

Tjong, S.C., 2006. Structural and mechanical properties of polymer nanocomposites. Mater. Sci. Eng. R Reports 53, 73–197.

Tronto, J., Leroux, F., Dubois, M., Taviot-Guého, C., Valim, J.B., 2006. Hybrid organic–inorganic materials: Layered hydroxy double salts intercalated with substituted thiophene monomers. J. Phys. Chem. Solids 67, 978–982.

Tronto, J., Sanchez, K.C., Crepaldi, E.L., Naal, Z., Klein, S.I., Valim, J.B., 2004a. Synthesis, characterization and electrochemical study of layered double hydroxides intercalated with 2-thiophenecarboxylate anions. J. Phys. Chem. Solids 65, 493–498.

Tronto, J., Reis, M.J. Dos, Silvério, F., Balbo, V.R., Marchetti, J.M., Valim, J.B., 2004b. In vitro release of citrate anions intercalated in magnesium aluminium layered double hydroxides. J. Phys. Chem. Solids 65, 475–480.

Umar, A., Hahn, Y.B., 2006. ZnO nanosheet networks and hexagonal nanodiscs grown on silicon substrate: growth mechanism and structural and optical properties. Nanotechnology 17, 2174–2180.

Usuki, A., Kojima, Y., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., Kamigaito, O., 1993. Synthesis of Nylon 6-clay hybrid. J. Mater. Res. 8, 1179–1184.

Vaia, R.A., Vasudevan, S., Krawiec, W., Scanlon, L.G., Giannelis, E.P., 1995. New polymer electrolyte nanocomposites: Melt intercalation of poly(ethylene oxide) in mica-type silicates. Adv. Mater. 7, 154–156.

Van Damme, H., Gmira, A., 2006. Cement hydrates, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier Ltd, Amsterdam, pp. 1113–1127.

Viani, A., Gualtieri, A., Artioli, G., 2002. The nature of disorder in montmorillonite by simulation of X-ray powder patterns. Am. Mineral. 87, 966–975.

Vieille, L., Taviot-Guého, C., Besse, J., Leroux, F., Pascal, B., 2003. Hydrocalumite and Its Polymer Derivatives. 2. Polymer Incorporation versus in Situ Polymerization of Styrene-4-sulfonate. Chem. Mater. 15, 4369–4376.

Vieille, L., Moujahid, E.M., Taviot-Guého, C., Cellier, J., Besse, J.-P., Leroux, F., 2004. In situ polymerization of interleaved monomers: a comparative study between hydrotalcite and hydrocalumite host structures. J. Phys. Chem. Solids 65, 385–393.

Villemin, D., Jaffrès, P., Nechab, B., Courivaud, F., 1997. Palladium complexes supported on hybrid organic-inorganic zirconium phosphite: selectivity in the Heck reaction. Tetrahedron Lett. 38, 6581–6584.

Vioux, A., Bideau, J. Le, Mutin, P., Leclercq, D., 2004. Hybrid organic-inorganic materials based on organophosphorus derivatives. Top. Curr. Chem. 232, 145–174.

Wang, G., Zhao, J., Li, X., Li, C., Yuan, W., 2009. Synthesis and characterization of electrically conductive and fluorescent poly(N-[5-(8-hydroxyquinoline)methyl]aniline)/V2O5 xerogel hybrids. Synth. Met. 159, 366–371.

Wang, P.-F., Cao, D.-K., Bao, S.-S., Jin, H.-J., Li, Y.-Z., Wang, T.-W., Zheng, L.-M., 2011. Co3(2-OOCC6H4PO4)2(H2O)3·H2O: a layered metal phosphonate showing reversible dehydration-rehydration behavior and ferrimagnetism. Dalt. Trans. 40, 1307–1312.

Wang, Q., Zhang, X., Wang, C.J., Zhu, J., Guo, Z., O'Hare, D., 2012. Polypropylene/layered double hydroxide nanocomposites. J. Mater. Chem. 22, 19113.

Weiss, A., 1963. Organic Derivatives of Mica-type Layer-Silicates. Angew. Chemie Int. Ed. English 2, 134–144.

Whilton, N.T., Vickers, P.J., Mann, S., 1997. Bioinorganic clays: synthesis and characterization of amino- and polyamino acid intercalated layered double hydroxides. J. Mater. Chem. 7, 1623–1629.
Wicklein, B., Darder, M., Aranda, P., Ruiz-Hitzky, E., 2010. Bio-organoclays based on phospholipids as immobilization hosts for biological species. Langmuir 26, 5217–5225.
Wu, C.-G., DeGroot, D.C., Marcy, H.O., Schindler, J.L., Kannewurf, C.R., Liu, Y.-J., Hirpo, W., Kanatzidis, M.G., 1996. Redox Intercalative Polymerization of Aniline in V2O5 Xerogel. The Postintercalative Intralamellar Polymer Growth in Polyaniline/Metal Oxide Nanocomposites Is Facilitated by Molecular Oxygen. Chem. Mater. 8, 1992–2004.
Wu, J., Zhu, Y.-J., Chen, F., Zhao, X.-Y., Zhao, J., Qi, C., 2013. Amorphous calcium silicate hydrate/block copolymer hybrid nanoparticles: synthesis and application as drug carriers. Dalton Trans. 42, 7032–7040.
Xu, M., Liang, T., Shi, M., Chen, H., 2013. Graphene-like two-dimensional materials. Chem. Rev. 113, 3766–3798.
Xu, Z., Mitzi, D.B., 2003. [CH(3)(CH(2))(11)NH(3)]SnI(3): a hybrid semiconductor with MoO(3)-type tin(II) iodide layers. Inorg. Chem. 42, 6589–6591.
Yan, D., Qin, S., Chen, L., Lu, J., Ma, J., Wei, M., Evans, D.G., Duan, X., 2010. Thin film of sulfonated zinc phthalocyanine/layered double hydroxide for achieving multiple quantum well structure and polarized luminescence. Chem. Commun. 46, 8654–8656.
Yang, B., Prosvirin, A. V, Guo, Y., Mao, J., 2008. Co[HO2C(CH2)3NH(CH2PO3H)2]2 : A New Canted Antiferromagnet. Inorg. Chem. 47, 1453–1459.
Yoshitake, S., Suzuki, T., Miyashita, Y., Aoki, D., Teramoto, Y., Nishio, Y., 2013. Nanoincorporation of layered double hydroxides into a miscible blend system of cellulose acetate with poly(acryloyl morpholine). Carbohydr. Polym. 93, 331–8.
Zeng, Z., Matuschek, D., Studer, A., Schwickert, C., Pöttgen, R., Eckert, H., 2013. Synthesis and characterization of inorganic-organic hybrid materials based on the intercalation of stable organic radicals into a fluoromica clay. Dalton Trans. 42, 8585–96.
Zhang, Y., Warren, C.J., Haushalter, R.C., Clearfield, A., Seo, D., Whangbo, M., 1998. Comparative Study of the Structural , Electronic , and Magnetic Properties of the Layered Ternary Vanadium Oxides CaV4O9 , Cs2V4O9 , and [H2N(CH2)4NH2]V4O9. Chem. Mater. 10, 1059–1064.
Zhao, M.-Q., Zhang, Q., Huang, J.-Q., Wei, F., 2012. Hierarchical Nanocomposites Derived from Nanocarbons and Layered Double Hydroxides-Properties, Synthesis, and Applications. Adv. Funct. Mater. 22, 675–694.
Zheng, N., Bu, X., Feng, P., 2005. Two-dimensional organization of [ZnGe3S9(H2O)]4- supertetrahedral clusters templated by a metal complex. Chem. Commun. 9, 2805–2807.
Zhou, C.H., 2011. An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis. Appl. Clay Sci. 53, 87–96.
Zou, Z., Ye, J., Sayama, K., Arakawa, H., 2001. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. Nature 414, 625–627.