



The use of lanthanide luminescence as a reporter in the solid state: Desymmetrization of the prochiral layers of γ -zirconium phosphate/phosphonate and circularly polarized luminescence

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Dedicated to the late Christian Claessens, Professor of Organic Chemistry at Universidad Autónoma de Madrid.

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ABSTRACT

Solid-state CPL measurements were performed for the first time on hybrid, laminar materials based on γ -ZrP pillared with organic diphosphonates. *Ad hoc* optically pure diphosphonates were synthesized and the luminescence properties of their complexation with Tb(III) were verified in solution. CD and CPL measurements showed that the bistriazolylpyridine chromophores bonded to the metal provided an effective chiral environment that produced significant signals. In the case of the γ -ZrP-derived materials, experimental evidence and simple molecular modeling hinted to the occurrence of supramolecular chirality in the particles, induced by the intrinsic dissymmetry of the organic diphosphonates or by the intercalation of chiral species such as 1-phenethylamine. Chirality at the supramolecular level was revealed in the solid state by the CPL signals measured from reporter Tb(III) ions intercalated in the hybrid matrix.

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1. Introduction

The structure and chemistry of layered materials is fascinating. One excellent example is that of zirconium phosphate and its gamma allotropic form (γ -ZrP). The molecular formula of this salt [$\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)$] and its laminar structure (Fig. 1) is constituted by two kinds of phosphate groups. Those at the surface of both faces of a layer are bonded to only two Zr metal atoms and are amenable of topotactic exchange reactions with other phosphorus functions such as organic phosphonates. The phosphates interior to the lamellae are no less important. They are responsible for preserving the structure of the layers when reactions occur at their surface. Furthermore, these internal phosphates are bonded to four different Zr atoms and are thus stereogenic centers. The structure of the lamellae of γ -ZrP is therefore intrinsically dissymmetric [1]. Yet, as it happens in racemic mixtures or *meso* forms, no in-bulk optical activity is expected unless any additional stereocen-

ters of fixed configuration are introduced. In previous work, we have shown that the simple intercalation of an optically pure molecule, such as (+)-1-phenethylamine [(+)-PEA], produces a material showing an optical rotation three orders of magnitude larger than the parent amine in solution [2].

The pillaring of γ -ZrP with either symmetric or dissymmetric diphosphonates has led to interesting stereochemical observations. For instance, the topotactic reaction of γ -ZrP with **1** (Scheme 1) produced a pillared material whose interlaminar distance could be greatly varied in the solid-water interface by simple acid–base reactions. At the maximum basal separation, the ethylenopolyoxa columns are in the usual helicoid conformation. However, no optical rotation was observed because the amine used to cause the elongation was not dissymmetric and the P/M helicity was random. When the base employed to increase the interlayer separation was (+)-PEA a sizeable optical rotation was measured. Interestingly, when (+)-PEA was smoothly replaced with hexylamine, the material still exhibited optical rotation. This suggests that the homohelicity of the columns induced by the chiral (+)-PEA was retained when the latter was replaced by the symmetric hexylamine.

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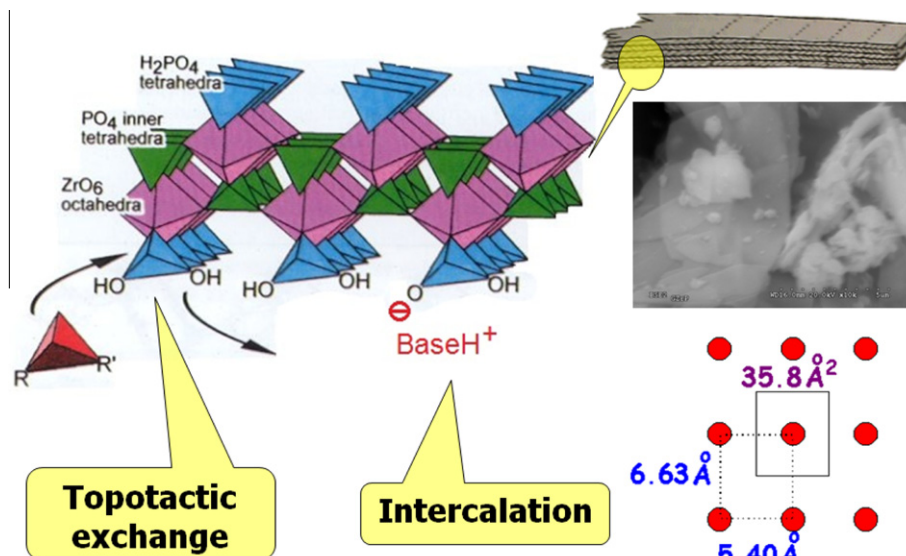
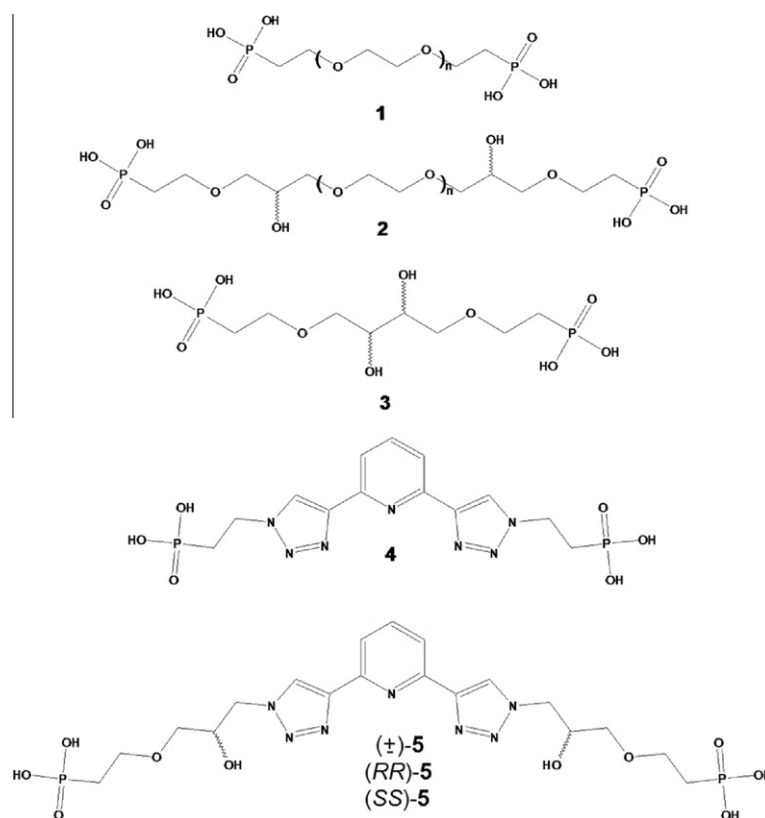


Fig. 1. SEM image of γ -ZrP and polyhedral model of a portion of one layer of it, sketching the topotactic exchange and intercalation processes; the scheme at the bottom-right shows the available area around every surface phosphate.



Scheme 1.

When γ -ZrP was submitted to the topotactic exchange with optically pure **2** (Scheme 1) and the resulting material intercalated with linear, symmetric alkylamines of increasing length, the measured optical rotation passed through a maximum value that occurred at an interlayer distance where molecular modeling suggested the expression of helicity by the columns is maximum [3].

Last but not least, we have observed thermodynamic and kinetic chiral recognition phenomena in materials pillared with

optically pure columns derived from tartaric acid (**3** in Scheme 1) [4].

To summarize, plenty of evidence shows that laminar γ -ZrP can be developed into a powerful dissymmetric matrix displaying a variety of properties. On the other hand, we have also shown that appropriate γ -ZrP matrices are able to produce the sensitized emission of lanthanides by the well-known *antenna effect*. For instance, the material bearing diphosphonate **1** (Scheme 1) and intercalated with 2,2'-bipyridyl gave rise to strong Eu(III) and

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