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Tetrahedron: *Asymmetry* 17 (2006) 347–354

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Solid-state reshaping of nanostructured crystals: supramolecular chirality of layered materials derived from polyethylenoxa-pillared zirconium phosphate

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Received 17 November 2005; accepted 16 January 2006
Available online 20 February 2006

Dedicated to Ernest L. Eliel

Abstract—The pillaring of γ-zirconium phosphate with either dissymmetric or non-dissymmetric polyethylenoxa diphosphonates leads to organic–inorganic nanostructures, in which the coiling of organic columns is the source of supramolecular chirality and chiral memory.

1. Introduction

We are currently involved in the building of 3D architectures, based on layered zirconium phosphate (ZrP).[1] In previous papers, we and others have described the mechanism of the topotactic phosphonate/phosphate exchange reaction that takes place at the surface of the inorganic layers.[2] With this method we are able to nanostructure the interlayer space of ZrP microcrystals by the covalent bonding of various phosphonates to the inorganic lamellae.[3]

In general, the modification of any crystalline structure once it has formed is quite a difficult task and has only been achieved in very limited cases. However, in a previous paper, we reported on the flash porosity modification of layered zirconium phosphate derivatives containing polyethylenoxa diphosphonate pillars.[4] Simple reaction of these solid, insoluble, nanostructured microcrystalline materials with methylamine in water dispersion produced a spectacular increase of interlayer distance and hence a strong increment of porosity. This behaviour was attributed to hydrogen bonding among the superficial phosphates of the inorganic layers and the oxygen atoms of the organic polyethylenoxa columns, which was broken by the intercalation of the amine and its subsequent acid–base reaction with the phosphates. Powder X-ray diffraction (XRD) of the methylamine-intercalated materials showed interlayer distances, which were compatible with the coiled conformation of the polyethylenoxa columns (Fig. 1) as also supported by IR data.

It occurred to us that the helicity attained by polyethylenglycol derivatives, a well known fact in solutions, but also strongly evidenced in our layered materials, could be further supported by the appropriate building of ZrP materials containing dissymmetric components. Moreover, the adequate selection and handling of the latter, together with the easily variable porosity of the ZrP derivatives could lead to interesting experiments concerning the nanoscale tuning of supramolecular chirality in the solid state.

One of the oldest fields of chemistry is the study of chiroptical properties of substances. Some time ago, Brewster suggested that these important physical properties should be strongly affected in single molecules by their conformational behaviour.[5] Fifteen years ago, we published what we believe is still one of the most clear-cut cases in the literature concerning the problem in solution, namely *cis*-3-hydroxythiane (*S*)-oxide **1** (Fig. 2).[6] The subtle balance between intra- and intermolecular hydrogen bondings made the diaxial conformer prevail in dilute samples in dichloromethane, whereas at high

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doi:10.1016/j.tetasy.2006.01.014

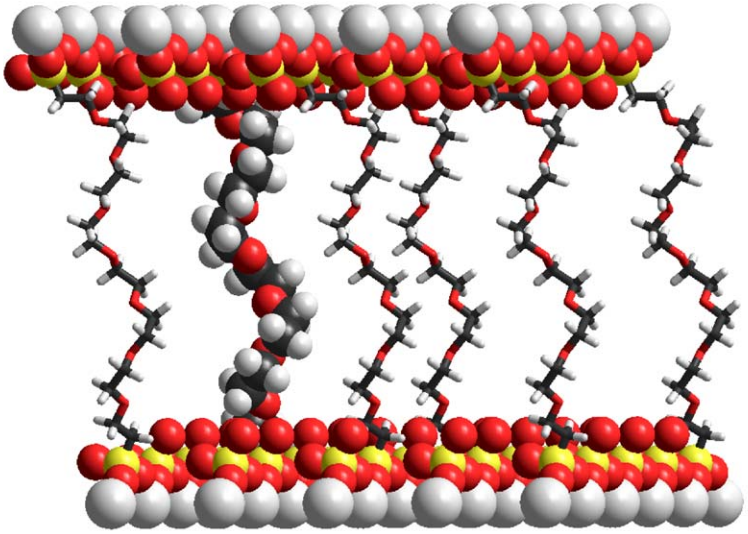


Figure 1. Molecular model of the arrangement of the organic columns resulting from the topotactic exchange (25%) of hexaethylenglycol diphosphonate into γ-ZrP. Interlayer distance was taken from X-ray powder diffraction data of the material intercalated with methylamine (internal layer phosphates and intercalated ammonium ions are not shown).

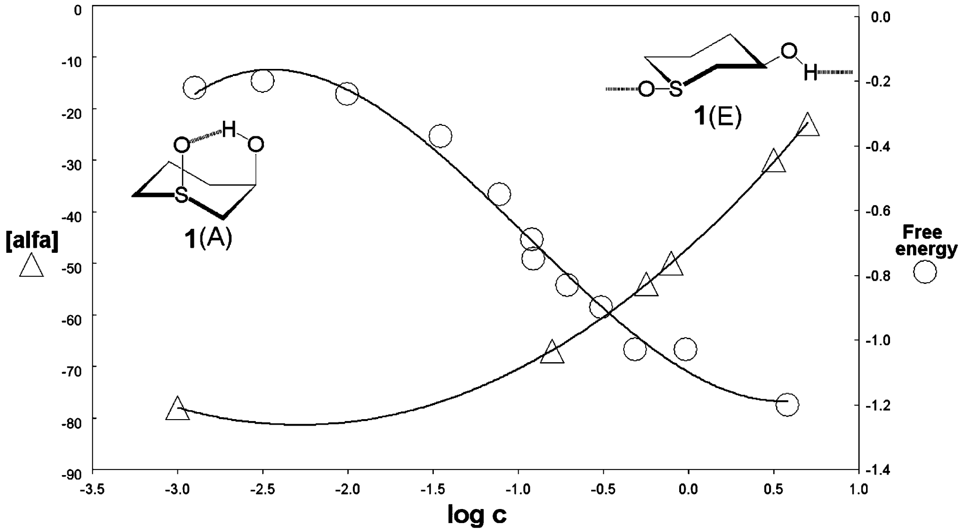


Figure 2. Plot of $[\alpha]_D^{25}$ (triangles) of compound **1** and ΔG° of the 1(A) ↔ 1(E) equilibrium (circles) versus logarithm of its concentration in CD_2Cl_2.

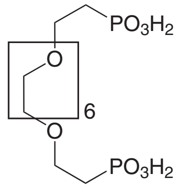
concentrations it was the diequatorial conformation, which dominated. These large conformational changes produced quite sizable variations in the specific rotation of an enantioenriched sample of **1**, an evidence that spectacularly illustrates Brewster's statement.

Despite the vast progress made in the understanding of specific rotation and the advancement of empirical and theoretical predictive techniques, there are certain areas, namely the solid state, where questions still remain.[7] It is true that self-assembly of even achiral molecules might lead to chiral crystals.[8] Yet, as we mentioned before, modification of a crystalline structure is not easy once it is formed. Layered ZrP containing non-chiral or chiral polyethylenoxaphosphonates in the interlayer space and its simple reaction with non-chiral or chiral amines might constitute an excellent material workbench on which to test Brewster's assertion in the solid sate, in a parallel way as shown with compound **1** in solutions. To the best of our knowledge, there is no report on the creation or modification of chirality in the solid state using a bottom-up approach as simple as the one described in the sequel.

2. Results and discussion

To this effect, besides the simple, non-dissymmetric polyethylenoxa diphosphonates prepared in previous work **2** (Scheme 1), we synthesized the dissymmetric mono-**4** and diphosphonate **3** indicated in Scheme 1 bearing one and two stereocentres, respectively.

The synthesis is straightforward starting from, enantiomerically pure (*R*)-glycidol. Its Michael-type addition to diethyl vinylphosphonate yielded (*R*)-diethyl(oxyran-2-



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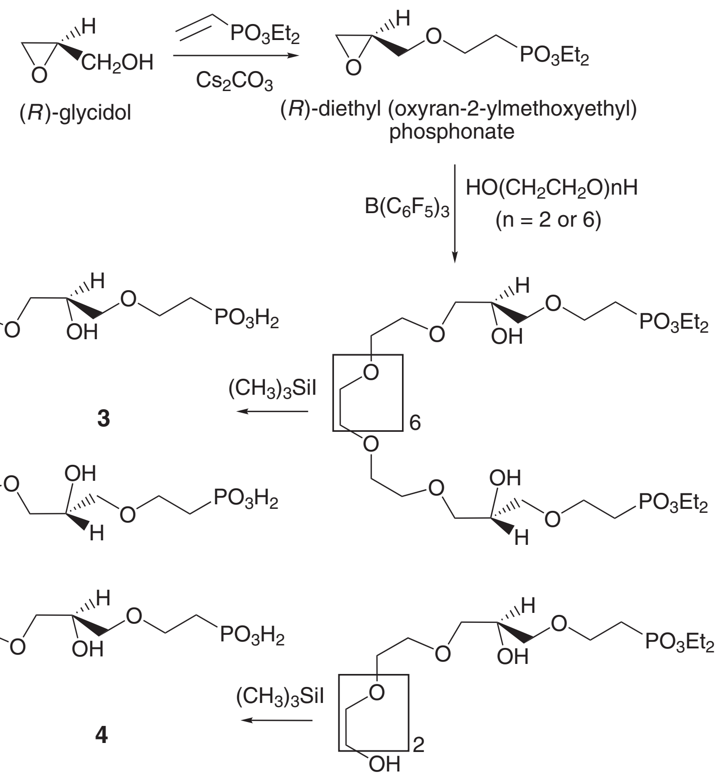


Scheme 1.

ylmethoxyethyl)phosphonate. The $B(C_6F_5)_3$-catalyzed oxyran aperture with the appropriate amount of di- and hexaethylenglycol and subsequent treatment with $(CH_3)_3SiI$, rendered the mono-**4** and diphosphonic **3** acids, respectively, with correspondingly $[\alpha]_D^{25}$ values of +0.7 (*c* 0.074, methanol) and +1.1 (*c* 0.634, methanol). Although we were unable to measure the enantiomeric purity of these compounds by the usual techniques (GC, HPLC, NMR), the extremely high $[\alpha]_D^{25}$ values observed in the experiments explained below should validate our results, notwithstanding the enantiomeric richness of the phosphonic acids.

Following previously reported procedures,[2] we intercalated pure γ-ZrP with (+)-1-phenethylamine to prepare a test material [γ-ZrP-PEA(+)] with which we devised a method used throughout this work to measure optical rotation of the solid samples. The basal spacing of native γ-ZrP (1.2 nm) was increased to 2.1 nm by (+)-PEA intercalation as measured by XRD. Thermogravimetric and elemental analyses gave a formula of $ZrPO_4(H_2PO_4)(C_8H_{11}N)\cdot 1.9H_2O$. All these data and simple molecular modelling suggest that as is usual in amine intercalation of γ-ZrP, a double layer of (+)-PEA molecules was formed between the inorganic lamellae.

Optical rotation measurements were performed at 25 °C in a 0.1 dm quartz cuvette, from suspensions of 5 mg of each solid material in 10 mL of 1:1 water–acetone mixture, over a certain time span in order to average the observed oscillations in the measured α due to light dispersion by the suspended particles.[9] After 10 min sonication, the suspension was placed in the quartz cell and measured six times every 30 s after an initial delay of 15 min. Oscillations were higher for shorter delays and optical rotation drastically diminished for longer ones due to solid deposition.

Under these conditions, γ-ZrP-PEA(+) gave to our surprise a polarimeter reading of $\alpha = +2.7 \pm 0.3$, which corresponds to a huge $[\alpha]_D^{25} = +54{,}000 \pm 6000$, more than 3 orders of magnitude higher than the specific rotation of pure (+)-PEA in solutions.

It should be noted that the structure of every lamellae of γ-ZrP as determined by Clearfield et al. (Rietveld refinement of XRD pattern[10]) is intrinsically dissymmetric.

However, considered in bulk, γ-ZrP prepared in the absence of any chiral influence must not display any optical activity inasmuch as either racemic mixtures or *meso* forms do not. Despite this, we did check that samples of plain γ-ZrP or intercalated with (±)-PEA showed negligible specific rotation. De-intercalation of (+)-PEA by HCl treatment of γ-ZrP-PEA(+) rendered a sample of γ-ZrP, which did not retain any measurable specific rotation. Therefore, the source of the large specific rotation as measured should be the supramolecular ordered arrangement of the (+)-PEA molecules within the inorganic layers. Herein, it should be realized that the whole structure, intercalated amine and inorganic layers, must contribute to the observed rotation since the intercalation of the enantiomerically pure amines breaks the symmetry of the racemic- or *meso*-type inorganic supramolecular structure. Therefore, intercalation of the opposite (−)-PEA enantiomer should not necessarily give the opposite result as that obtained with γ-ZrP-PEA(+) because this intercalate and its γ-ZrP-PEA(−) counterpart are diastereomeric (not enantiomeric) in supramolecular nature. As a matter of fact, we repeated, under identical conditions, specific rotation measurements with the γ-ZrP-PEA(−) intercalate [it gave the very same XRD pattern and same formula by TGA and elemental analysis as γ-ZrP-PEA(+)], which led to a disappointing and negligible polarimeter reading ($\alpha = 0.0 \pm 0.05$). It remains to be seen whether these specific rotation values are the product of a matching [γ-ZrP-PEA(+)] or perfect mismatching [γ-ZrP-PEA(−)] phenomenon between the chirality of the ordered amine and the symmetry-breaking of the inorganic salt. We are certain that the observed phenomenon does not strictly lie within what may be named induction of supramolecular chirality because the chiral amine did not chemically alter the inorganic scaffold. However, the layered nanoarrangement of superficial phosphates in ZrP certainly served as a frame to orderly attach small chiral guests, whose chiroptical properties were thus supramolecularly amplified or cancelled.

We then moved on to γ-ZrP 25% pillared with achiral diphosphonate **2** (Scheme 1), derived from hexaethylenglycol. As in the previous work,[2] we named this material H25. Plain H25 and its intercalate with $MeNH_2$ (H25-MA) showed negligible optical rotation in the usual measurement conditions. In contrast, pillared H25 intercalated with optically pure (+)- or (−)-PEA [H25-PEA(+), H25-PEA(−)][11] displayed positive average values of $\alpha = 0.15 \pm 0.03$ and 0.80 ± 0.1, respectively, corresponding to $[\alpha]_D^{25} = +3000 \pm 600$ for H25-PEA(+) and $[\alpha]_D^{25} = +16,000 \pm 2000$ for H25-PEA(−), ca. 2–3 orders of magnitude higher than the specific rotation of the pure enantiomers of PEA and very different values to those observed for γ-ZrP-PEA(+) and γ-ZrP-PEA(−) (vide supra). Again the supramolecular edifice 'amplifies' the chiroptical properties of the amine but the pillaring of achiral diphosphonate **2** now introduces additional factors affecting the specific rotation, which are specially relevant if one compares γ-ZrP-PEA(−) ($\alpha = 0.0 \pm 0.05$) with H25-PEA(−) ($\alpha = 0.80 \pm 0.1$).

We then smoothly replaced (+)- or (−)-PEA by hexylamine HA, resulting in new materials labelled as H25-PEA(+) $\Longleftrightarrow$ HA and H25-PEA(−) $\Longleftrightarrow$ HA.[12] Long-term acquisition of the ^{1}H NMR spectra of these phases dissolved (destroyed) in HF/DMSO-d_6 showed no discernible aromatic signals meaning that the residual PEA, if any, should be under 2% molar after its replacement reaction with HA. H25-PEA(+) $\Longleftrightarrow$ HA showed $\alpha = 0.17 \pm 0.04$, corresponding to $[\alpha]_D^{25} = +3400 \pm 800$, whereas H25-PEA(−) $\Longleftrightarrow$ HA displayed $\alpha = -0.02 \pm 0.04$, corresponding to $[\alpha]_D^{25} = -400 \pm 800$. Since all the starting enantiomerically pure PEA was replaced by the non-dissymmetric, optically inactive hexylamine (as shown by solution NMR spectra) and the rigidity and stability of the inorganic layers make highly improbable the induction of homochirality into their internal phosphates, *the only source of optical activity should be the highly ordered supramolecular assembly of the organic polyethylenoxa columns*, strongly suggesting that PEA enantiomers induced in them, some distortion in the statistical distribution of *P* and *M* helicity of the starting material that was maintained when the achiral amine replaced the chiral one. It should be noted that as in the first set of experiments, the symmetry of the racemic- or *meso*-type inorganic supramolecular structure of H25 should be broken down by the chiral amine intercalation. Consequently, the conjectured homohelicity of the organic pillars induced by the chiral amines, which appears to remain after they are smoothly exchanged by hexylamine, makes the couple H25-PEA(+) $\Longleftrightarrow$ HA and H25-PEA(−) $\Longleftrightarrow$ HA to be also diastereomeric. This explains the non-mirror image α values displayed by these materials.

Therefore, the presented evidence, in our belief, documents eloquent cases of asymmetric induction of supramolecular chirality. While this phenomenon has been widely studied in polymeric structures[13] and achieved in inorganic metal-coordinated systems[14] and in organic hydrogen bonded networks,[15] it has not yet been tried in laminar, hybrid organic–inorganic pillared materials. Besides, the fact that chirality was retained in the presence of the achiral hexylamine might make these materials an entry point to the intriguing possibility of creating porous, layered composites with a chiral memory.

Finally, we prepared γ-ZrP phases topotactically exchanged with 25% of the chiral di- and monophosphonates **3** and **4** in the usual manner and the resulting solids, named H*25 (H* from chiral hexaethylenglycol-derived diphosphonate) and DM*25 (DM* from chiral diethylenglycol-derived monophosphonate), respectively, were characterized by the standard techniques. It should be noted that while H*25 is a pillared material similar to H25 (vide supra), DM*25 is not because the organic chain bears a single phosphonic group and cannot thus attach to consecutive layers. Figure 3 shows the outstanding variation of $[\alpha]_D^{25}$ (and interlayer distance) when H*25 was intercalated with simple alkylamines of increasing length. It may be seen that whilst the basal spacing increases continuously with amine length, optical rotation shows a different evolution that passed through a maximum estimated to occur at the intercala-

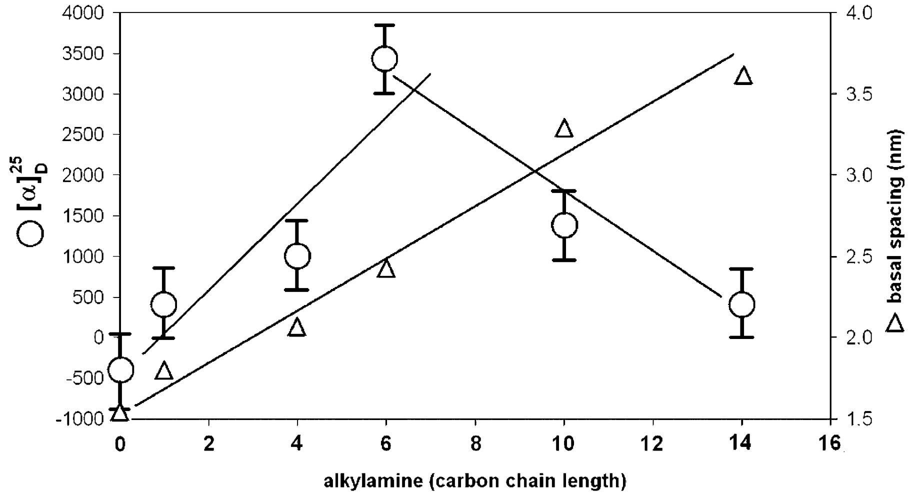
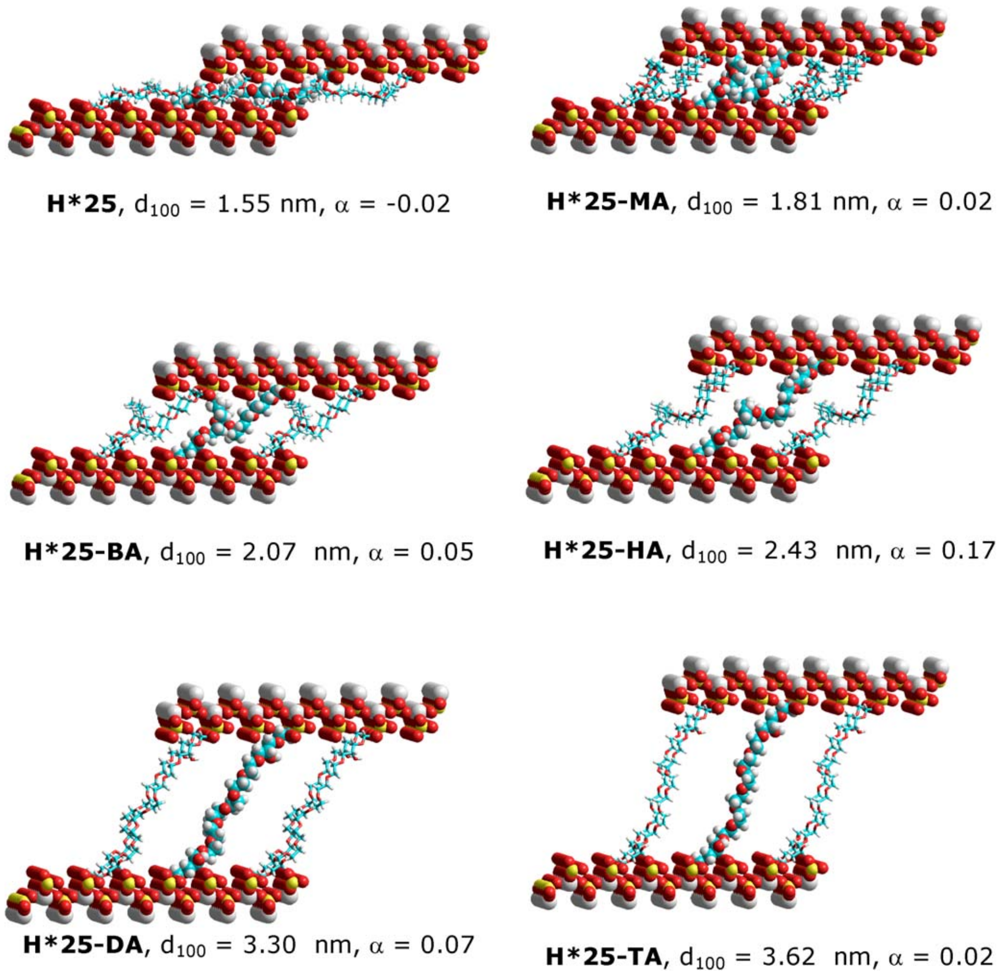


Figure 3. Plot of $[\alpha]^{25}_D$ and basal spacing (XRD) versus carbon chain length for material **H*25** (initial value of abscissa means no amine intercalation).

tion of ca. heptylamine ($([\alpha]^{25}_D)_{max} \cong +3500$. The very same experiment performed on the non-pillared DM*25 gave a different result in that $[\alpha]^{25}_D$ stabilized around a value of +6000 ± 1500 for amines with carbon chains of 6 links or higher.

Figure 4 provides a qualitative explanation to these observations. It contains a series of molecular models (Hyperchem 7.5), where one exchangeable phosphate in every other four (simulation of 25% topotactic exchange) was replaced by diphosphonate **3** in the facing


H*25, d_{100} = 1.55 nm, α = -0.02

H*25-MA, d_{100} = 1.81 nm, α = 0.02

H*25-BA, d_{100} = 2.07 nm, α = 0.05

H*25-HA, d_{100} = 2.43 nm, α = 0.17

H*25-DA, d_{100} = 3.30 nm, α = 0.07

H*25-TA, d_{100} = 3.62 nm, α = 0.02

Figure 4. Molecular modelling of **H*25** at the interlayer distances measured by XRD corresponding to the intercalation of alkylamines (MA, methyl-; BA, butyl-; HA, hexyl-; DA, decyl-; TA, tetradecyl-). Intercalated amines have been omitted for the sake of clarity.

sides of reasonable portions of two consecutive, rigid layers of γ-ZrP. The layers were fixed at every experimental distance measured by XRD and displaced one another in their two parallel axes to allow for the best possible arrangement of the organic chains, which were energy minimized by Hyperchem molecular mechanics MM+.

The models suggest that at the initial and final interlayer separations sustained by amine intercalation, the chains are compressed or strongly elongated, respectively. At these stages, experimental $[\alpha]_D^{25}$ values remained low. However, in the model with the basal spacing corresponding to hexylamine intercalation, calculations predict that the organic chain may adopt a helicoidal conformation. Interestingly, at this interlayer distance the highest value of $[\alpha]_D^{25}$ was measured. The behaviour of H*25 with amine intercalation and the models of Figure 4 supply further, strong, evidence that the specific rotation is highly influenced by the supramolecular architecture and stems from the helicity of the polyethylenoxa chains as it presumably occurred in H25 (vide supra). In the latter, the supramolecular chirality was created by the momentary concourse of external dissymmetric species [enantiomerically pure PEA] whereas in H*25 the dissymmetry is already within the organic chain due to its two stereocentres. Yet, very importantly, the supramolecular chirality was not clearly manifested in H*25 until the appropriate conformation of the chains was attained at the right interlayer distance, following Brewster's principle in the solid state.

The behaviour of **DM*25** reinforces our reasoning, because its $[\alpha]_D^{25}$ increased for the intercalation of short amines, but did not decrease once it reached a certain value. In this non-pillared material, the chains are not attached to the consecutive layers and separation of the latter by amine intercalation cannot force chain elongation. Once layer compression at short basal spacing is relieved by amine intercalation, the chains are released to adopt free conformations, maximizing coiling and hence supramolecular chirality that should not change much by further increments of interlayer distance.

3. Conclusion

In conclusion, one of the most difficult tasks in solid-state chemistry, that is to modify the structure and properties of crystalline materials once they are formed, has easily been achieved by means of very mild processes in our layered γ-ZrP materials. The topotactic reactions of this inorganic phase allow for the smooth covalent inclusion of appropriate organic moieties whose conformation, and hence the structure of the entire 3D architecture were a posteriori modified. The body of evidence presented herein reveals that beyond simple shape or porosity changes, important properties of solid, nanostructured materials such as supramolecular chirality, can be developed or tuned in the solid state by the use of smooth processes. It is our belief that this work is a very important step to what was achieved in our previous paper about enantiomerically enriched *cis*-3-hydroxythiane (*S*)-oxide **1** (Fig. 1) where conformational changes, induced by relatively small concentration variations, modified bulk physical properties of the compound in a solution. This paper demonstrates for the first time ever that conformational changes in solids, produced by soft solid-state chemistry and amplified by an appropriate supramolecular layered structure, are paramount in the definition of the bulk physical properties of layered organic–inorganic solid materials. This is an example of a new line of reasoning in the chemistry of solids, which should help develop new areas of research.

4. Experimental

4.1. General

All reagents were purchased from Aldrich and used without further purification. Liquid ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 and 75 MHz, respectively), in the indicated solvents. Liquid ^{31}P NMR spectra of the solid materials were recorded in HF/DMSO-d_6 on Bruker AMX-300 (121 MHz). All chemical shifts are reported in parts per million referenced to residual protonated solvent. MAS and CP-MAS ^{31}P NMR were recorded on Bruker AV400 WB. Interlayer distances were measured by X-ray powder diffraction on a Phillips PW1710 diffractometer at room temperature. Elemental analyses were performed on a Perkin Elmer II 2400 CHN analyzer. Optical rotation measurements were performed in a Perkin Elmer 241 MC polarimeter from suspensions of 5 mg of material in 10 mL of water–acetone 1:1 mixture (see text). Thermogravimetric analyses were performed in a Mettler Toledo TGA/SDTA 851^e analyzer with a heating rate of 5 °C/min.

4.2. Topotactic exchange with compounds 2 and 3 and amine intercalation of γ-ZrP

This was performed as previously described.[2] The exchange of intercalated amines was performed using the following method: A suspension of H25-PEA (200 mg) in 43.8 mL of 1 M aqueous hexylammonium hydrochloride (43.8 mL) was stirred for 24 h at room temperature. The solid was then centrifuged, washed with water (3 × 20 mL) and ethanol (20 mL), dried at 100 °C for 6 h and conditioned over satd $BaCl_2$.

4.3. Diethyl[2-(oxyran-2-ylmethoxy)ethyl]phosphonate

Diethyl-vinylphosphonate (5.3 g, 32.1 mmol), Cs_2CO_3-(2.0 g, 6.4 mmol) and glycidol (2.4 g, 32.1 mmol) were mixed and heated at 50 °C for 5 h. After cooling, the reaction mixture was dissolved in 30 mL of water, extracted three times with CH_2Cl_2, dried over $MgSO_4$ and evaporated in vacuum. The crude product was purified by flash column chromatography (10% ethanol/ethylacetate) to afford 6.3 g (83%). $[\alpha]_D = +5$ (*c* 2.08, chloroform). ^1H NMR ($CDCl_3$) δ (ppm): 1.17 (t, 6H);

2.01 (dt, 2H); 2.46 (t, 1H); 2.64 (t, 1H); 2.99 (m, 1H); 3.61 (q, 1H); 3.61 (m, 1H); 3.95 (m, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.2 (d, $J = 5.6$ Hz), 26.9 (d, $J = 139.1$ Hz), 44.1, 50.6, 61.5, 65.2, 71.5. MS (FAB) *m*/*z*: 239.1 ($[M+1]^+$).

4.4. Compound 2 (Scheme 1)

To a stirred solution of diethyl[2-(oxyran-2-ylmethoxy)ethyl]phosphonate (1 g, 4.2 mmol) in dry CH_2Cl_2, $B(C_6F_5)_3$ (0.13 g, 0.25 mmol) and hexaethyleneglycol (2.1 mmol) were added and the reaction mixture refluxed overnight. The solvent was then evaporated and the crude mixture purified by column chromatography (20% methanol/ethylacetate) to afford an oily product, which was dissolved in CH_2Cl_2 under argon. Iodotrimethylsilane (200 μL) was then added at 0 °C via a syringe. The mixture was then maintained at 0–10 °C for 8 h and the solvent was evaporated in vacuo. The brownish residue was stirred with water (3 mL) at room temperature, washed with toluene (3 × 2 mL) and the solvent removed in the rotary evaporator yielding 0.3 g (25%) of **2**. $[\alpha]_D = +0.7$ (*c* 0.0743, methanol). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.0 (dt, 4H); 3.5 (m, 36H); 3.9 (m, 2H); 4.7 (br s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 32.8 (d, $J = 132.6$ Hz); 65.6 (d, $J = 6.3$ Hz); 73.9, 74.6, 74.8, 74.9, 76.6, 76.9 (d, $J = 6.3$ Hz), 77.3. Anal. Calcd for $C_{22}H_{48}O_{17}P_2$: C, 40.87; H, 7.48. Found: C, 40.85; H, 7.51. MS (FAB) *m*/*z*: 647.3 ($[M+1]^+$).

4.5. Compound 3 (Scheme 1)

The procedure was identical to that of compound **2** except that diethylenglycol was used (4.5 mmol). Overall yield was 30%. $[\alpha]_D = +1.1$ (*c* 0.634, methanol). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.98 (dt, 2H), 3.51 (m, 14H); 3.85 (m, 1H), 4.73 (br s, 4 OH). ^{13}C NMR ($CDCl_3$) δ (ppm): 32.8 (d, $J = 132.6$ Hz); 65.9, 66.3 (d, $J = 6.3$ Hz), 74.2, 75.1, 75.5, 76.9, 77.2, 77.6. Anal. Calcd for $C_9H_{21}O_8P$: C, 37.50; H, 7.34. Found: C, 37.53; H, 7.33. MS (FAB) *m*/*z* 289.1 ($[M+1]^+$).

4.5.1. Material H25 and PEA intercalation. Interlayer distance, 2.2 nm; amine content/Zr, 0.75; PEA exchanged with hexylamine [materials H25-PEA $\Longleftrightarrow$ HA]: interlayer distance, 2.1 nm; amine content/Zr, PEA <0.02; hexylamine 0.43.

4.5.2. Material H*25. Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}\cdot 2.2H_2O$: C, 8.2; H, 3.0. Found: C, 8.1; H, 3.1. MAS ^{31}P NMR δ, ppm (integral): −29.6 (100), −16.3 (77), 16.2 (25); TGA °C (weight loss): 25–150 °C (10.8%), 150–400 °C (11.5%), 400–600 °C (4.2%), 600–1100 °C (3.5%).

H*25 intercalate with methylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}(CH_5N)_{0.88}\cdot 2H_2O$: C, 10.6; H, 3.9; N, 3.1. Found: C, 10.6; H, 3.9; N, 2.9.

H*25 intercalate with butylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}(C_4H_{11}N)_{0.85}\cdot 2H_2O$: C, 16.7; H, 4.7; N, 2.7. Found: C, 16.8; H, 4.2; N, 2.8.

H*25 intercalate with hexylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}(C_6H_{15}N)_{0.84}\cdot 2H_2O$: C, 20.1; H, 5.2; N, 2.6. Found: C, 20.1; H, 4.7; N, 2.8.

H*25 intercalate with decylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}(C_{10}H_{23}N)_{0.85}\cdot 2H_2O$: C, 26.2; H, 6.1; N, 2.3. Found: C, 26.4; H, 5.9; N, 2.7.

H*25 intercalate with tetradecylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.76}(C_{22}H_{46}O_{17}P_2)_{0.12}(C_{14}H_{31}N)_{0.85}\cdot 2H_2O$: C, 31.5; H, 6.8; N, 2.2. Found: C, 31.2; H, 6.8; N, 2.2.

4.5.3. Material DM*25. Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.78}(C_9H_{19}O_8P)_{0.22}\cdot 2H_2O$: C, 6.7; H, 2.7. Found: C, 6.7; H, 2.7. MAS ^{31}P NMR δ, ppm (integral): −29.8 (100), −16.5 (79), 16.8 (23); TGA °C (weight loss): 25–150 °C (8.9%), 150–350 °C (5.0%), 350–600 °C (4.4%), 600–1100 °C (3.2%).

DM*25 intercalate with butylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.78}(C_9H_{19}O_8P)_{0.22}(C_4H_{11}N)_{0.80}\cdot 2H_2O$: C, 14.8; H, 4.5; N, 2.7. Found: C, 14.8; H, 4.2; N, 2.7.

DM*25 intercalate with hexylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.78}(C_9H_{19}O_8P)_{0.22}(C_6H_{15}N)_{0.80}\cdot 2H_2O$: C, 18.4; H, 5.0; N, 2.5. Found: C, 18.5; H, 4.8; N, 2.6.

DM*25 intercalate with decylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.78}(C_9H_{19}O_8P)_{0.22}(C_{10}H_{23}N)_{0.80}\cdot 2H_2O$: C, 24.6; H, 5.8; N, 2.3. Found: C, 24.6; H, 5.7; N, 2.1.

DM*25 intercalate with tetradecylamine: Anal. Calcd for $ZrPO_4(H_2PO_4)_{0.78}(C_9H_{19}O_8P)_{0.22}(C_{14}H_{31}N)_{0.80}\cdot 2H_2O$: C, 29.8; H, 6.6; N, 2.1. Found: C, 30.0; H, 6.5; N, 2.0.

Acknowledgements

This work was supported by MCYT of Spain under grants PB98-0103 and MAT2002-03243. We also thank FYSE-ERCROS S.A. (Aranjuez, Spain) for generous indirect funding.

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12. Molecular formula $ZrPO_4(H_2PO_4)_{0.76}(C_{16}H_{34}P_2O_{13})_{0.12}$-$(C_6H_{15}N)_{0.68}\cdot 2.4H_2O$ from elemental and TGA analyses. XRD interlayer distance 2.10 nm (conditioned over $BaCl_2$).
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