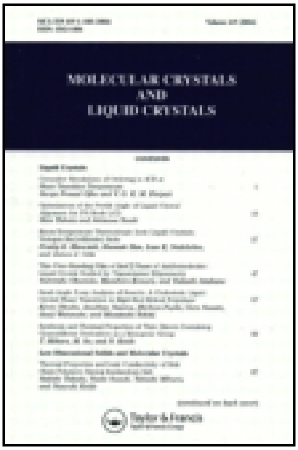

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

How Do Molecules Behave in Supramolecular Assemblies: Formation of Stable Thionine Lamellar Arrays in the Interlayer of α-Tin and α-Zirconium Phosphate: Intercalation, Metachromatia, and Exciton Coupling

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Version of record first published: 04 Oct 2006

To cite this article: Fernando Souto, Enrique Rodríguez, Georges Siegel, Antonio Jimenez, Lolita Rodríguez, Pascual Olivera, Josefa Mérida, Francisco Pérez & Manuel Alcantara (1998): How Do Molecules Behave in Supramolecular Assemblies: Formation of Stable Thionine Lamellar Arrays in the Interlayer of α-Tin and α-Zirconium

Phosphate: Intercalation, Metachromatia, and Exciton Coupling, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 409-416

To link to this article: http://dx.doi.org/10.1080/10587259808042418

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 409–416
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How Do Molecules Behave in Supramolecular Assemblies?
Formation of Stable Thionine Lamellar Arrays in the Interlayer of α-Tin and α-Zirconium Phosphate: Intercalation, Metachromatia, and Exciton Coupling

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This paper reports the formation of monomolecular lamellar arrays of thionine (TH) and methylene blue (MB) by self-assembly in the interlayer of metal phosphates formulated as $M(IV)(HPO_4)_2 \bullet H_2O$, with M = Sn and Zr (α–SnP and α–ZrP). We apply the molecular exciton model to the interpretation of the electronic reflectance spectra of the intercalation compounds and find that metachromatia upon sorption and intercalation is understandable with exciton theory. We describe how delaminated α–SnP and α–ZrP are useful as template layers for self-assembly of amphiphilic dyes in well-ordered monolayers. Starting with well-characterized template layers, it is possible to quantify the self-assembly steps and infer how the order of the active sites in the template layers extends to the molecular aggregates. We find that the dye layers achieve a high orientational order and that the organization of active sites in the template layers is an essential factor. The agreement between observed and calculated exciton displacement terms proves the possibility of deducing ultra-structure characteristics of nanocomposite materials by simple absorption measurements.

Keywords: thionine; intercalation; zirconium phosphate, tin phosphate

INTRODUCTION

The promise to tune the properties of molecular systems—by controlling the structural design, disposition, and density of key molecules within organized assemblies—is an important driving force in current chemical research.[1] Stable multi-molecular superstructures, consisting of self-assembled arrays of well-ordered monolayers (supramolecular assemblies),[2] hold the potential to create new materials with novel functions, determined by the collective behavior of the molecules, not by their individual properties. Self-assembly of organic molecules at template surfaces is an example of a powerful method that can produce functional thin films by deliberate manipulation of component molecules.[3]

In principle, the restricted geometry of the intracrystalline interlayer space in clay minerals[4] and layered phosphates[5] is suitable for the controlled growth of molecular aggregates with near crystalline characteristics. However, recent reviews suggest that while we can derive the structures of condensed phases from the characteristics of the isolated molecular building blocks, relating the structure and function of supra-molecular assemblies is still difficult.[6] One key question is how do molecules behave in ordered aggregates as compared with their behavior as isolated molecules? Supramolecular chemistry turns naturally to spectroscopic probes to interpret the behavior of molecules in ordered superstructures. To this end are pertinent studies on the sorption and intercalation chemistry of thiazine dyes in smectite minerals,[7] layered phosphates,[8] and other restricted cavity materials such as the zeolites.[9]

Here we report the formation of stable lamellar assemblies of thionine (TH) and methylene blue (MB) upon intercalation in layered tetravalent metal phosphates (α–SnP and α–ZrP). We apply the molecular exciton model[10] to the interpretation of the electronic spectra of the intercalates and find that it is possible to deduce details about the molecular ultrastructure of nanocomposite materials by simple electronic absorption measurements.[11] Since the exciton model also supplies mechanistic information on the migration of excitation energy in molecular aggregates, this approach provides also fundamental insights on the potential photochemical applications of these new materials. Layered phosphates, expanded or pillared with amphiphilic organic chromophores, pigments or dyes, can be cast into thin films apt for applications that range from guest-induced photochemistry within a shape selective matrix to molecular devices with nonlinear optical properties and chemical sensors.

The Phosphate Template Layers

The preparation and characterization methods of the layered phosphates used in the self-assembly experiments follow well-known literature procedures.[12] Briefly, the initial base materials were highly crystalline α–ZrP and α–SnP prepared by standard methods (α–ZrP: $\alpha\text{–Zr(HPO}_4)_2 \bullet H_2O$, interlayer distance $d_{00l} = 7.58$ Å, surface area $\leq 5\ m^2g^{-1}$. α–SnP: $\alpha\text{–Sn(HPO}_4)_2 \bullet H_2O$, $d_{00l} = 7.76$ Å, surface area = $11.2\ m^2g^{-1}$). Although the crystallinity of α–SnP is extremely sensitive to details of the preparative procedure, this phosphate is virtually isostructural with α–ZrP. Thus, a single description of the phosphate layers will be sufficient for our purposes.

The layered structure of α–ZrP shows remarkable analogy with that of smectite clays, e.g., montmorillonite.[4] In both cases, the micro crystals arise from packing of individual layers, each layer formed by concatenation of silica or phosphate tetrahedra with alumina or zirconia octahedra through the vertices or the corners. However, the structure of α–ZrP differs from that of smectite in that the P groups bridge the metal atoms. The tips of the P tetrahedra are alternating above and below the metal atom planes, with three O of each P group joined to three different Zr atoms. The fourth O carries a proton and points away from the layer. This arrangement creates an array of six-sided cavities of zeolitic type where the water molecules reside.

A simplified structure for the metal phosphate layers is essential to what it follows, Figure 1. The free P–OH groups on each side of a layer have an equilateral triangular distribution. The distance between adjacent P–OHs in a given layer is 5.25 Å, α–ZrP and 5.02 Å, α–SnP. Adjacent layers are shifted relative to each others so that projection of the free P–OH groups of two facing sides in an intermediate plane provides a combined honey comb structure for the active sites.

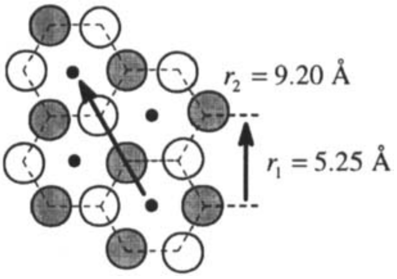

FIGURE 1 Layer structure of α–ZrP

The central cavities of the projected hexagons are interlayer pockets, capped by a free P–OH group on the other side of each layer, where polar organic molecules can be posted as slanted pillars. The intercenter distances between adjacent hexagons define the distance between adjacent molecular centers in the intercalation compounds (α–ZrP: $r_1 = 5.25$ Å, $r_2 = 9.20$ Å. α–SnP: $r_1 = 5.02$ Å, $r_2 = 8.69$ Å). Thus, the metal phosphate layers are ideal as templates to form well-ordered lamellar arrays of organic chromophores.

Intercalation Chemistry[13]

Direct reaction of aqueous dye solutions with M(IV)P suspensions failed to provide intercalation compounds after contacting at 25°C for 3 days. Preswelling with *n*-propylamine at 50% of the exchange capacity[5] (n-C_3H_7–NH_3^+/α–ZrP) gave excellent results for the intercalation of TH and MB in α–ZrP. For intercalation in α–SnP, we preferred preswelling with $(CH_3)_4N^+$ ions since use of phases pre-swelled with n-C_3H_7–NH_2 generally leads to amorphous intercalation compounds. The method[14] simply involves exchange of interlayer n-C_3H_7–NH_3^+ by $(CH_3)_4N^+$ ions to form stable colloidal suspensions of $(CH_3)_4N^+$/α–SnP. TH and MB intercalated readily in α–SnP upon contact of aqueous dye solutions with this material.

The Dye Uptake Isotherms

Intercalation reactions of aqueous dye solutions with colloidal phosphate suspensions were sistematically explored using classical batch methods.[8]

Thionine acetate

The uptake curve of TH$^+$ AcO$^-$ on $(CH_3)_4N^+$/α–SnP is of the Langmuir type according to the Giles' classification.[15] The initial slope is very steep and a plateau of 3.25mmol TH per g of equivalent pyrophosphate is reached at low dye concentrations (~ 10 mM, see Figure 2). This is indicative of a high affinity of TH towards α–SnP. Analysis of the materials isolated at the isotherm points indicated the existence of two intercalation stages, with different mechanisms. Table I lists the composition of the material at the maximum dye uptake. Nearly 1 mol TH intercalates per formula of α–SnP, i.e., the maximum capacity of 2 mol –NH_2 groups is achieved. This corresponds to the amount of P–OH and P–O$^-$ groups present in $(CH_3)_4N^+$/α–SnP and suggest a very specific interaction between the P–O and –NH_2 groups.

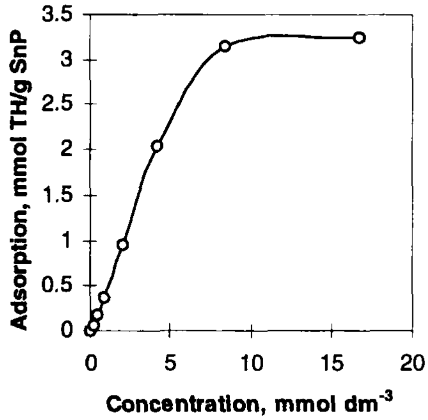

FIGURE 2 Adsorption Isotherm of Thionine on α–SnP

XRD patterns obtained for the isolated materials showed single phases independent of the intercalation stage. In the first stage, with loadings < 0.30 mol TH/mol α–SnP, the interlayer distances were slightly higher than the original $(CH_3)_4N^+$/α–SnP (16.5 Å). During the second stage, with higher dye loadings, the interlayer distances increased to a maximum of 18.3 Å. The observed basal spacings and compositions are consistent with the following process. Initially, the template layers orient TH$^+$ in the interlayer space so as to cause the minimum expansion of the layers. At this stage, TH$^+$ is held in holes between hydrated $(CH_3)_4N^+$ forming a solid solution. The free space available, 10.0 – 11.8 Å,[16] is smaller than the van der Waals length of TH$^+$along its longitudinal axis (15 Å). Evidently, the aromatic rings lie flatter until the phosphate layers are densely covered. As the loading rises, the rings begin increasingly to slip over one another and stand more erect. The layers expand until they achieve a final arrangement in which TH$^+$ has an inclination θ = 38° measured with respect to the normal to the phosphate plane (Table II).

TABLE I Chemical composition, interlayer distances, and exciton splittings for the intercalation compounds at the highest dye loadings

Sample	Empirical Formulation	d_{00l}* (Å)	λ_{max} (nm)	
			H band†	*J* band‡
1	$Zr(TH)_{0.91}H_{1.09}(PO_4)_2 \cdot 2.11\ H_2O$	17.73	493	626
2	$Sn(TH)_{0.92}H_{1.08}(PO_4)_2 \cdot 1.10\ H_2O$	18.31	461	625
3	$Zr(MB)_{0.54}H_{1.46}(PO_4)_2 \cdot 1.81\ H_2O$	18.70	560	742
4	$Sn(MB)_{0.50}H_{1.50}(PO_4)_2 \cdot 1.00\ H_2O$	19.20	535	700

*Interlayer distances determined by XRD as the average value of the *00l* reflections.
†Blue shifted (hyprochromic) bands observed in the intercalates by diffuse reflectance.
‡Red shifted (Jelly) shoulder or minor bands resolved by derivative spectroscopy.

The uptake isotherm of TH^+ on α–ZrP follows closely the previous case. Thionine exhibits also a high affinity towards α–ZrP but the curve (not shown) reaches its plateau at higher dye concentrations, ~20 mM. Analysis of the materials isolated showed that here the intercalation is a single exchange process. Despite the similarities, the XRD patterns exhibit remarkable differences. At low loadings, two phases coexist, the original phosphate with a reflection at 14.67 Å and a new intercalated phase at 17.73 Å. This reflection increases with loading, while that of the original phosphate decreases. Loadings greater than 0.5 mol per formula show a single phase with this basal spacing. In contrast to the Sn intercalates, in the case of Zr diffusion of the dye begins at the edges of the crystals and proceeds with an advancing phase boundary towards the inside of the interlayer space. Tables I and II list the interlayer distances d_{00l} and free interlayer heights Δ, as well as the final inclination angles, θ, of dye molecules in the interlayer space.[17]

Methylene blue

The uptake of MB by α–ZrP and α–SnP shows a similar behavior. However, detailed analysis of the intercalation compounds indicated significant differences. First, the formulae of the intercalation compounds separated at the maximum MB uptake have much lower loadings than the TH complexes (Table I). Secondly, the intercalation of MB in Zr occurs by stages in a process similar to that of TH in Sn. At low MB loadings, the XRD patterns show a single phase with d_{00l} = 14.7 Å. This corresponds to a solid solution of MB in the phosphate precursor. At intermediate loadings, two phases coexist: the original with a reflection at 14.75 Å and a new phase at 18.32 Å. Greater loadings than 0.45 mmol MB/mol α–ZrP result in a single phase with a reflection line between 18.22 and 18.76 Å.

TABLE II Free heights, inclination angles, intermolecular distances, and interaction energies for the TH and MB intercalation compounds.

Sample[a]	Δ_{obs},[b] Å	θ_{obs}[c]	θ^x_{calc}[d]	θ^y_{calc}[e]	θ_{calc}[f]	Δ_{calc}[g]	$\bar{r}$,[h] Å	ε_{obs},[i] eV	ε_{calc},[j] eV
1	11.4	40.4	32.0	24.6	39.6	11.6	7.90[k]	0.438	0.465
2	11.8	38.1	30.1	22.8	37.1	12.0	7.47[k]	0.612	0.638
3	12.4	46.5	26.2	41.0	47.4	12.2	7.95[l]	0.347	0.340
4	12.7	45.1	24.7	37.9	44.3	12.9	7.53[l]	0.450	0.466

[a] Sample numbers correspond to the composition in Table I.

[b] Free height of the phosphate interlayer in the intercalates estimated as the difference between the interlayer distance (Table I) and the thickness of the phosphate layers.[16],[17]

[c] Inclination angles of the longitudinal axis of dye molecules with respect to the normal to the phosphate layers calculated from the XRD free height and the van der Waals length of the hydrogen bonded dye, 15 Å for TH and 18 Å for MB.

[d] Lateral inclination with respect to the surface normal of the dye plane in the x-axis direction to attain effective interaction of both amino groups with suitable triangular cavities in opposing phosphate layers. The angle is calculated from the van der Waals length of the respective dye and the intercenter distance in the normal plane between active centers in one phosphate layer and the corresponding active center in the opposite layer, 7.53 Å for α-ZrP and 7.95 Å for α-SnP.

[e] Tilt angle of the dye plane in the y-axis direction so that both amino groups are keyed into suitable cavities. This is a shift in the y-axis direction with respect to the surface normal of 5.30 Å for α-ZrP and 5.02 Å for α-SnP, in the case of TH, and twice those values in the case of MB.

[f] Overall inclination angle of the longitudinal axis of dye molecules with respect to the surface normal calculated from θ^x and θ^y.

[g] Free height of the phosphate interlayer in the intercalates derived from the calculated inclinations and the van der Waals lengths of the dyes. The error between observed and calculated values is < 2%.

[h] Calculated mean distance between adjacent molecular centers within the TH and MB intercalates, see note *k* below.

[i] Experimental interaction energy calculated from the pronounced blue shift observed in the electronic absorption spectra of the intercalates, $\varepsilon_{obs} = \Delta\nu = \nu_{int} - \nu_{mon}$, where the subscripts refer to the respective monomers and the intercalates.

[j] Interaction energy calculated with the following equation derived $\varepsilon_{calc} = 4.2\frac{M^2}{r^3}(3\cos^2\theta - 1)$ for simple lamellar arrays by Hochtrasser and Kasha.[18]

[k] The stoichiometry of the intercalates at high thionine loadings (Table I) requires that dye molecules distribute in the projected honey comb structure of the phosphate active sites as two collection of dipoles with different intercenter distances, r_1 and r_2. These are the intercenter distances between adjacent hexagons sharing an internal edge and that between opposed hexagons linked by and edge, respectively (Figure 1). The values we use in this case are a weighted average of 6 dipoles at $r_1 = 5.30$ Å and 12 dipoles at $r_2 = 9.20$ Å, for α–ZrP, and an average of 6 dipoles at $r_1 = 5.02$ Å and 12 dipoles at $r_2 = 8.69$ Å, for α–SnP.

[l] Lower dye loadings with MB permit a distribution of molecules in a single collection of dipoles separated by the distance between an active center in one layer and the corresponding center in the opposing layer.

Molecular Modeling

The near 1:1 stoichiometry of the intercalates at high TH loadings means that dye molecules occupy almost every binding site of the phosphate layers. Basal spacings and molecular model calculations have established that dye molecules are in the interlayer space tilted from the surface normal by angles that depend on the metal phosphate–dye combination (Table II). Both ends of the molecules must be in contact with opposing interlayer surfaces. The model starts with dye molecules in the up-right position and tries to fit them within the interlayer space. Taking into account the triangular arrangement of the P–O groups in the metal phosphate plane, we deduce that the amino groups are keyed into the triangular cavities of the phosphate sheets. To achieve this arrangement, the dye plane must tilt along its longitudinal axis in the x-axis direction an angle θ^x with respect to the surface normal. In addition, the dye plane must tilt in the y-axis direction, θ^y, until the other amino group is keyed into a suitable cavity in the opposing phosphate surface. The final arrangement is specially favored for TH because both amino groups are able to form hydrogen bonds with the oxygen atoms of the P–O triangles without major distortions of their valence angles and distances.

Electronic Absorption Spectra

Color changes upon contacting dye solutions with the colloidal phosphates were immediately evident. For instance, in the case of TH^+ and α–SnP/$(CH_3)_4N^+$, the color of the aqueous suspensions changed from blue to colorless, at low loadings, and from deep violet to light purple, at high loadings. Following partitioning by centrifugation, the upper natant fine suspensions and the heavier bottom materials were analyzed by electronic spectroscopy. Table I lists the maxima observed for the intercalates at the highest dye loadings. The blue shifts of the main absorption bands are evident (TH, M = 597 nm; MB, M = 664 nm). Exciton splittings calculated[11] for linear chain polymers with a co-planar inclined geometry (/ / / /) result in allowed transitions which are strongly red shifted with respect to the monomers. In fact, to observe a blue shift in a translational chain polymer, $\theta <$ arc sin $1/\sqrt{3}$ (~ 35.3°), smaller than any of the experimental inclinations (Table II). For a polymer with an oblique geometry (/ \ / \), the exciton model predicts a splitting into two bands of approximately equal intensities, far from observed. The electronic spectra of both upper natant suspensions (not described) and flocculated materials are only consistent with the formation of sandwiched multilayers of monomolecular dye lamellae within the interlayer of the metal phosphates. The large blue shifts observed are consistent only with a collection of regularly spaced dipoles with $\theta \ll$ arc cos $1/\sqrt{3}$ (~ 54.7°). For TH in α–SnP, the blue shift is over five times that of the dimer (D_H = 555 nm). The agreement between calculated and observed interaction energies, though not perfect, is remarkable considering the approximations made to derive the exciton theory.[18]

Acknowledgements

This work has been jointly supported by the Office of Naval Research (USA) and by the CYCIT (Spain). Illuminating discussions with Abraham Clearfield and Jorge Colón are acknowledged with appreciation.

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[16.] With an interlayer distance of 16.5 Å for $(CH_3)_4N^+/\alpha$–SnP and a layer thickness of 6.5 Å, the free space available is 10.0 Å.

[17.] A layer thickness of 6.30 Å is assumed for α–ZrP.

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