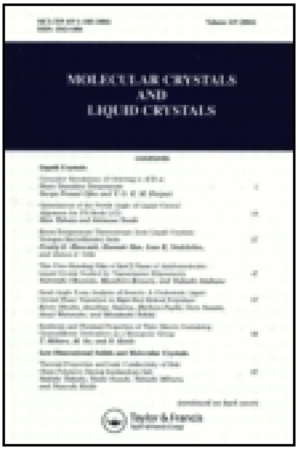

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Preparation and spectroscopic characterisation of intercalation compounds of α-zirconium phosphate with Rhodamine B

Gian Gaetano Aloisi [a], Umberto Costantino [a], Fausto Elisei [a], Morena Nocchetti [a] & Claudia Sulli [a]

[a] Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 06123, Perugia, ITALY

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Preparation and spectroscopic characterisation of intercalation compounds of α-zirconium phosphate with Rhodamine B

GIAN GAETANO ALOISI, UMBERTO COSTANTINO, FAUSTO ELISEI,
MORENA NOCCHETTI and CLAUDIA SULLI.
Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 06123
Perugia, ITALY

The addition of increasing volumes of 10^{-2} M Rhodamine chloride solution to colloidal dispersions of α-zirconium phosphate exfoliated with n-propylamine induces flocculation of the layered compound, accompanied by ion exchange of the dye for the propylammonium cation, to give two intercalation compounds containing 0.19 and 0.66 mol of Rhodamine per mol of Zr, and having interlayer distances of 1.9 and 2.47 nm, respectively. Excitation and emission spectra of the intercalation compounds showed a relevant blue-shift (15 nm) of the typical emission maximum of solid Rhodamine B, centred at 690 nm.The accommodation of guest molecules in the layered host is also discussed, on the basis of experimental data and computer simulation.

Keywords: layered α-zirconium phosphate; dye intercalation; Rhodamine B; fluorescence.

INTRODUCTION

The insertion of dye molecules into inorganic host materials such as gel-glasses, zeolites and layered compounds has recently received increasing attention to gain, a fundamental knowledge of how these large molecules organise themselves in a microenvironment and how this organisation modifies the photochemical and photophysical properties of the dyes. Furthermore, the composites obtained have potential application in optical data storage, sensing devices and molecular recognition[1]. Zirconium phosphates and phosphonates with layered structures of α- and γ-type are very suitable inorganic and inorgano-organic hosts for the intercalation of a large variety of polar molecules[2]. The intercalation of $[Ru(bipy)_3]^{2+}$, aminophenyl and pyridinium-substituted porphyrins[3], and crystalviolet[4] has already been studied.

In the present communication we report the intercalation, *via* ion exchange, of Rhodamine B cation (Rhod) in α-zirconium phosphate and the photochemical and photophysical characterisation of the compounds thereby obtained.

EXPERIMENTAL

Tetraethylrhodamine chloride (Rhodamine B) and zirconium oxychloride were Fluka and Merck products respectively. All other chemicals were from C. Erba, ACS grade. A batch of α-$Zr(HPO_4)_2 \cdot H_2O$ (hereafter α-ZrP, interlayer distance 0.76 nm, ion exchange capacity (IEC) 6.6 mmol H^+/g) was prepared according to the HF procedure[2]. Intercalation compounds with ethanol and with 1-propanol were prepared from α-$Zr(HPO_4)(NaPO_4) \cdot 5H_2O$ (interlayer distance 1.18 nm) as described in ref. [5]. X-ray powder diffraction patterns (XRPD) were recorded with a computer controlled Philips 1710 diffractometer, using the Cu-K_α radiation (40 KV; 30 mA). Coupled thermogravimetric (TGA) and differential (DTA) analysis were carried out with a Stanton-Redcroft 781 Thermoanalyser at 5°/min heating rate, under air flow. Excitation and emission spectra corrected for the instrumental response were carried out by using a spectrofluorimeter Spex Fluorolog F112 in a front-face geometry.

RESULTS AND DISCUSSION

Figure 1a shows the structural formula and the approximate dimensions of Rhodamine B, a quinonic dye of the family of the pyronines. Figure 1b shows the structure of the host that arises from the packing of layers composed of metal atoms bridged by tetrahedral phosphate groups lying alternately above and below the mean plane containing the metal atoms. The "free area" around each phosphate group is 0.24 nm^2.

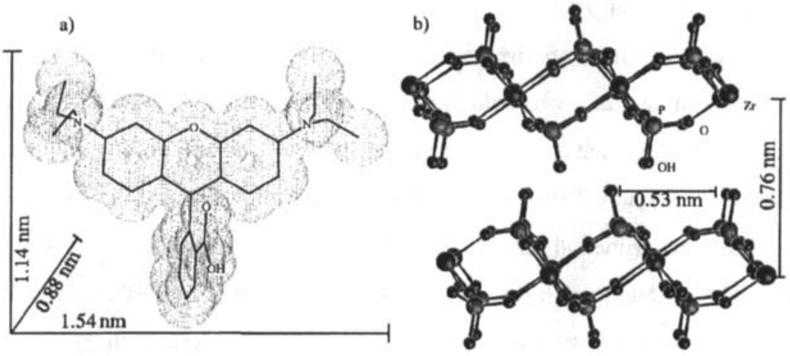

FIGURE 1 a) Structure of Rhod; approximate Van der Waals dimensions are indicated and b) sequence of two layers of α-ZrP.

The intercalation of Rhod requires a marked increase of the interlayer distance, the H^+/Rhod ion exchange process, and the diffusion of the counterion towards the inner part of the crystallites. Due to the large size of the guest, preliminary attempts at Rhod intercalation showed that the process is extremely slow, even though α-ZrP preswelled with ethanol or propanol was used as host. Higher rates could be expected if the zirconium phosphate microcrystals were exfoliated in single layers, or packets of few layers, so that all the ionogenic groups are easily accessible to the incoming counterions. Moreover, hydrophobic interactions between the dye cations present on the surface of the layers could induce the recomposition of the layered microcrystals to give intercalation compounds. α-ZrP microcrystals, half titrated with n-propylamine under vigorous stirring, spontaneously exfoliate to give a colloidal dispersion of lamellae[6]. Exfoliation occurs also when the host is titrated up to 25% of its ion exchange capacity and it was convenient to use these latter dispersions that contain a lower amount of propylammonium. Portions of 16.6 ml of 0.1 M propylamine were added to a series of flasks containing 1 g of α-ZrP dispersed in 80 ml of distilled water, to obtain the exfoliation of the microcrystals. Volumes of 10^{-2} M Rhod solution, corresponding to an amount of dye equal to 12.5, 25, 50, and 100% of the IEC were then added, at 70°C, to the colloidal dispersions thereby obtained. After three days of equilibration, the flocculated samples were centrifuged and washed until the washing water was colourless. XRPD patterns and TG curves of these samples, conditioned at room temperature and 75% relative humidity, are shown in Figures 2 (a) and 2 (b) respectively. It may be noted that the samples are, within the experimental errors, free from propylammonium ions probably removed by exchange with Rhod and by prolonged heating at 70°C. It seems that Rhod uptake occurs in two steps: the first gives rise to a phase with an interlayer distance (d_l) of 1.9 nm containing 0.19 mol of Rhod per mol of Zr; in the second step, as the Rhod content increase, this phase is transformed into another phase with an interlayer distance of 2.47 nm and a composition of 0.66 mol Rhod per mol of Zr. In both these phases the thermal decomposition of Rhod starts at temperatures higher than 350°C. It is not easy to foresee the arrangement of Rhod within the interlayer region. However, considerations based on the dye dimension and the structure of the host, and some computer simulations lead one to suppose that the 1.9 nm-phase contains a monolayer of Rhod species with their major axis tilted by 45° to the layer plane, while in the 2.47 nm-phase the Rhod species are accommodated as a monofilm with the axis almost perpendicular to the layer plane. Note that in non-polar solvents Rhod gives rise to two kinds of dimers, the J-dimer, with oblique geometry and the H-dimer with a sandwich type structure[7]. These two situations resemble those hypothesised in the intercalates.

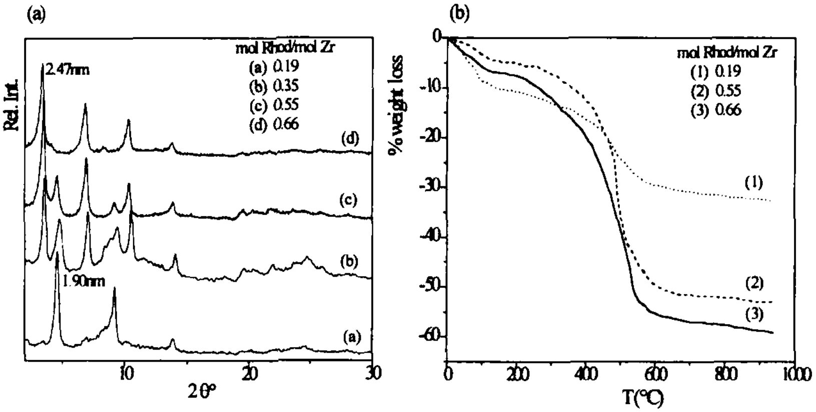

FIGURE 2 XRPD patterns (a) and TG curves (b) of samples of α-ZrP-Rhod intercalated having the indicated composition.

Fluorescence excitation and emission spectra were determined for samples where Rhod was intercalated, surface adsorbed or simply mixed with the α-zirconium phosphate. The results show that the photophysical properties of intercalated Rhod are different from those of the adsorbed and mixed dye and indicate that the observation of the Rhod fluorescence can be a suitable tool to study the intercalation process and to probe the nature of the interlayer microenvironment where the dye is located. Comparison was also made with the spectra obtained from ethanolic solution and a solid sample (powder) of Rhod which have emission spectra centred at 580 and 690 nm, respectively. When Rhod is simply mixed with α-ZrP its emission resembles that of the Rhod powder indicating that no relevant interaction is present between the two solids. Moreover the excitation spectrum of the mixture, having a maximum around 400 nm, is markedly different from that of the solution. Figure 3 shows the excitation and emission spectra of Rhod adsorbed on the surface (Figure 3*a*) and fully intercalated (d_l=2.47nm) in the structure of α-ZrP (Figure 3*b*). In the former sample the fluorescence properties resemble those of Rhod in ethanol, thus indicating small interactions between dye molecules. When Rhod is intercalated in the α-ZrP layers the emission maximum is shifted to 675 nm; the spectrum is close to that

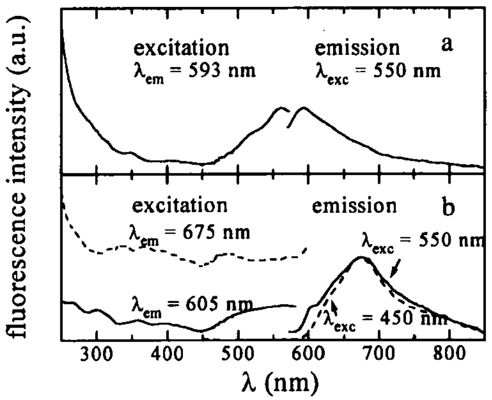

FIGURE 3 Normalised excitation and emission spectra of Rhod. B (a) adsorbed on the surface of α-ZrP and (b) fully intercalated in α-ZrP.

of the solid Rhod even though it is blue-shifted by 15 nm. Moreover, spectra of Figure 3b, in particular the shoulder at 605 nm and the corresponding excitation spectrum (solid lines), show also the presence of small amount of surface adsorbed dye. Is to be noted that intercalation compounds, having interlayer distance of 1.9 and 2.47 nm show emission spectra centred at ca. 675 nm with a shoulder at 605 nm. When the interlayer distance is larger, the shoulder is much less pronounced and the intensity of the long-wavelength site increases.

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