Functionalization of the internal surfaces of layered cadmium thiophosphate with cationic surfactants: adsolubilization of uncharged organic molecules

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Ion-exchange intercalation of the cationic surfactant cetyl trimethylammonium in layered CdPS$_3$ leads to the formation of an intercalated bilayer within the galleries, thereby converting the internal surface of the layers from hydrophilic to hydrophobic. Several uncharged organic 'guest' molecules were found to be solubilized in the intercalated bilayer 'host'.

The self-organization of long chain amphiphilic molecules introduced by intercalation within the galleries of layered solids provides a novel route to the construction of organic–inorganic supramolecular assemblies.[1–3] The unique feature of these materials is that the essentially hydrophilic internal surface of the inorganic solid is converted to a hydrophobic surface, thus the material can act as a 'host' for non-polar as well as poorly water-soluble species,[4] in much the same way as a surfactant micelle can solubilize these species in aqueous media.[5]

The layered divalent metal thiophosphates MPS$_3$, where M = Mn, Fe or Cd, undergo an unusual ion-exchange intercalation reaction in which hydrated cationic 'guest' species from aqueous solution insert into the interlamellar space with an equivalent loss of the divalent metal ion from the layers.[6–10] Several inorganic, organic and organometallic cationic species have been intercalated in these systems by the above method and shown to exhibit a variety of interesting properties.[11,12] These systems also undergo solvent exchange reactions wherein the water of hydration of the interlamellar ion can be replaced by other solvating species, like poly(ethylene oxide), crown ethers, *etc.*, through ion–dipole interactions.[13–15] The types of guest species that can be intercalated by the above two methods are, however, restricted to cationic species or molecules that can solvate the intercalated cations. Here, we report the functionalization of the internal surface of one of the members of this family of layered solids, namely cadmium thiophosphate (CdPS$_3$), by intercalation with a surfactant cation, cetyl trimethylammonium (CTA).[16] We demonstrate that by functionalizing the internal surface of CdPS$_3$, several uncharged as well as poorly water-soluble organic species can be inserted into the interlamellar region.

Cadmium thiophosphate, CdPS$_3$, was prepared from the elements following the procedure reported in the literature.[17] Cadmium metal powder, phosphorous and sulfur in stoichiometric amounts were sealed in quartz ampoules at 10^{-6} Torr and heated at 650 °C for two weeks. CdPS$_3$ was treated with a 4 M aqueous solution of potassium chloride in the presence of 0.1 M EDTA and 1 M K$_2$CO$_3$–KHCO$_3$ as buffer, to give Cd$_{0.83}$PS$_3$K$_{0.34}$(H$_2$O), in which hydrated K$^+$ ions reside in the interlamellar region. The compound has a lattice spacing of 9.4 Å, corresponding to a lattice expansion of 2.8 Å as compared to pristine host CdPS$_3$.[6]

Two different methods were employed to confine neutral organic guest molecules within the galleries of CdPS$_3$. In the first, referred to as the "solubilization" method, the organic guest molecules (G) are first solubilized in methanol–water using the surfactant CTAB. On addition of Cd$_{0.83}$PS$_3$K$_{0.34}$(H$_2$O) the hydrated K$^+$ ions in the galleries exchange with the CTA ions. The cationic surfactant carries the guest molecule with it during the ion-exchange process, leading to the formation of Cd$_{0.83}$PS$_3$CTA$_{0.34}$(G)$_y$ [Fig. 1(a)]. In the second method, the interlamellar K$^+$ ions in Cd$_{0.83}$PS$_3$K$_{0.34}$(H$_2$O) are exchanged with CTA ions by reacting with a 0.05 M aqueous solution of CTAB, to give Cd$_{0.83}$PS$_3$(CTA)$_{0.34}$. The compound has a lattice expansion of 26.5 Å, with the alkyl chains of the intercalated surfactant adopting a tilted bilayer structure.[16] This compound was then treated with methanol–hexane solutions of different organic guest molecules [Fig. 1(b)]. The guest molecules are 'adsolubilized' in the intercalated surfactant bilayer ("adsolubilization" method).

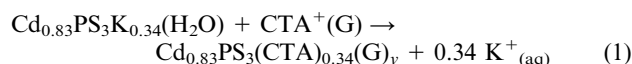The overall reaction in the "solubilization" method can be represented as:

$$Cd_{0.83}PS_3K_{0.34}(H_2O) + CTA^+(G) \rightarrow$$
$$Cd_{0.83}PS_3(CTA)_{0.34}(G)_y + 0.34\ K^+_{(aq)} \qquad (1)$$

Fig. 2 shows the powder X-ray diffraction patterns of crystals of Cd$_{0.83}$PS$_3$(CTA)$_{0.34}$(G)$_y$ for four different organic guest molecules; n-decanol, nitrobenzene, benzyl alcohol and 2-napthol. The nitrobenzene-intercalated compound shows a lattice spacing of 37.5 Å and the 2-napthol intercalate shows a lattice spacing of 36.5 Å. A list of organic guest molecules that have been intercalated into CdPS$_3$ along with their lattice spacings are given in Table 1. Stoichiometries were determined by elemental analysis. The values indicated in Table 1 are for the maximum concentration of the intercalated guest molecule. For smaller 'guests' like phenol, aniline and benzyl alcohol, a range of compositions are possible, with the maximum as shown in Table 1. The interlayer lattice spacing, however,
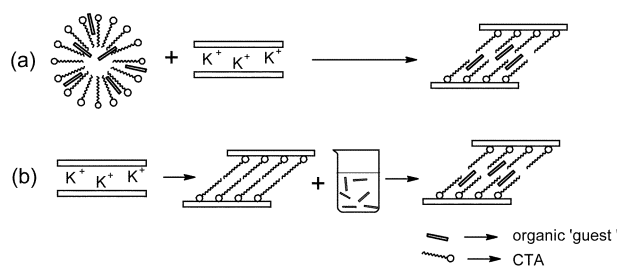

Fig. 1 Schematic representation of the two methods employed to confine uncharged organic guest molecules in the interlamellar space of CdPS$_3$: (a) "solubilization" method; (b) "adsolubilization" method.
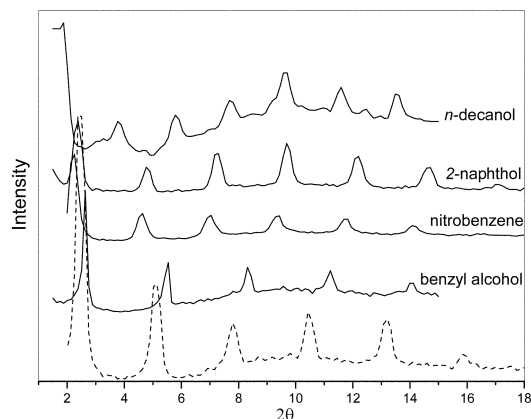
DOI: 10.1039/b211541g

Fig. 2 Powder X-ray diffraction patterns of intercalates obtained by reacting $Cd_{0.83}PS_3K_{0.34}(H_2O)$ with solutions of CTAB solubilized with the appropriate organic guest. The dashed line is the diffraction pattern of the host bilayer-intercalated phase, $Cd_{0.83}PS_3(CTA)_{0.34}$.

Table 1 Observed interlayer lattice spacing of organic guest-intercalated phases. The molar ratio of guest to intercalated surfactant is indicated for each case in the last column

Intercalated guest molecule	Log K_{OW}[18–20]	Lattice spacing/Å	'Guest'/CTA molar ratio
n-Dodecanol	5.13	51.0	2.35
Pyrene	4.77	34.5	0.27
n-Decanol	4.57	48.0	0.52
Azobenzene	3.82	36.5	0.12
2-Naphthol	2.82	36.5	0.84
4-Chlorophenol	2.39	36.0	1.31
Nitrobenzene	1.88	37.5	0.71
Phenol	1.46	36.0	1.09
4-Nitroaniline	1.39	32.0	7.50
Benzyl alcohol	1.10	32.5	0.66
Aniline	0.90	32.0	0.47

shows no change with the different guest to surfactant compositions.

Adsolubilization of organic guest molecules by the intercalated surfactant bilayer can be represented as:

$$Cd_{0.83}PS_3(CTA)_{0.34} + (G)_{hex} \rightarrow$$
$$Cd_{0.83}PS_3(CTA)_{0.34}(G)_y \quad (2)$$
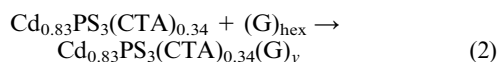
The powder X-ray diffraction patterns of the intercalated surfactant bilayer adsolubilized with aniline, 4-nitroaniline, nitrobenzene and azobenzene are shown in Fig. 3 along with that of the surfactant bilayer-intercalated host. The lattice spacings of the organic guest-adsolubilized phases are listed in Table 1. It will be noted that the intercalates of long chain aliphatic alcohols show similar lattice spacing, irrespective of the method by which they were prepared. The diffraction profiles, however, are sharper for the compounds prepared by the adsolubilization route, indicating that the integrity of the crystallites is better preserved.

We have shown that a variety of organic molecules of differing hydrophobicity, as characterized by their K_{OW} coefficients[18–20] (K_{OW} is the octanol–water partition coefficient), can be introduced into $CdPS_3$ functionalized by intercalation of CTA ions. The CTA ion being devoid of any functional group, the interaction of the organic guest molecules and the methylene chain of the intercalated host bilayer are
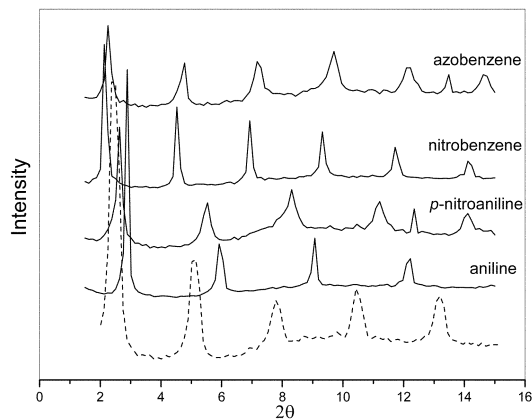

Fig. 3 Powder X-ray diffraction patterns of intercalates obtained by adsolubilization of organic guest molecules by the intercalated surfactant bilayer, $Cd_{0.83}PS_3(CTA)_{0.34}$.

purely dispersive in character. We observe that the interlayer spacing of the intercalated bilayer can either decrease, increase or remain the same on introduction of a neutral guest molecule. The increase in interlayer spacing may be understood as arising from the additional space required to accommodate the guest. In the case of smaller guest molecules, e.g., aniline, benzyl alcohol, etc., the guest molecules are probably accommodated by a change in the tilt angle of the methylene chains of the bilayer. This would lead to a decrease in the interlayer spacing. In the absence of guest molecules, the methylene chains of the bilayer are tilted away from the interlayer normal by an angle of $55°$.[16] As mentioned earlier, the host–guest chemistry of $CdPS_3$ was, until now, essentially limited to ion-exchange reactions. Here, we have shown that functionlization of the galleries of $CdPS_3$ by surfactant intercalation significantly alters this scenario.

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