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Supramolecular Jacks: Control of Interlayer Interactions in Layered Vanadyl Phosphonates on the Angstrom Length Scale

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The desire to control chemical interactions on molecular length scales has led to the design of architectures with complexities extending beyond the molecule. The complementary binding sites offered by supramolecules enable guests and hosts to be juxtaposed within a well-defined structure to engender a wide variety of function based on noncovalent intermolecular interactions.[1] A goal of recent years is to impart the control offered by supramolecular architectures to the intracrystalline environments of extended arrays.[2] Molecular subunits may be arranged into ordered geometries by exploiting covalent and noncovalent interactions to form bilipid vesicles,[3] Langmuir−Blodgett films,[4] and self-assembled monolayers[5] and multilayers.[6] In these structures, the functional subunits are typically placed in static and well-defined geometries. Yet the design of new supramolecular materials may be advanced when the subunit preorganization can be adjusted variably on the molecular length scale. The ability to tune the interaction of functional subunits within the supramolecular architecture provides a way to design materials in which structure/function properties may be triggered; such fundamental design strategies are useful to the development of schemes for sensor,[7] photonics,[8] and electronics[9] applications.

Our interest in exploring approaches to develop materials with tunable properties led us to consider the environments of layered vanadyl phosphonate host structures. A pendent organic group in the interlayer region is provided by the host template and an intergallery guest may be introduced by coordinating Lewis bases at the vanadium center of the layer. We report here the synthesis and photophysical properties of two naphthalene-modified layered vanadyl phosphonates (LVPs) of the $V(O)O_3PR\cdot H_2O\cdot R'OH$ structural type, where the naphthalene chromophore may be introduced as the R or R′ functionality. When R′ = naphthalene, the positioning of the aromatic rings is controlled by varying the length of the alkylphosphonate pendent, R, to induce or prevent the formation of excimers. In the congener material, the cofacial alignment of neighboring aromatic rings is adjusted with the alcohol co-solvate. These results show that the dimensionally limited environments of layered phosphonates offer a supramolecular architecture in which the interaction of functional subunits may be controlled with precision on the angstrom-length scale.

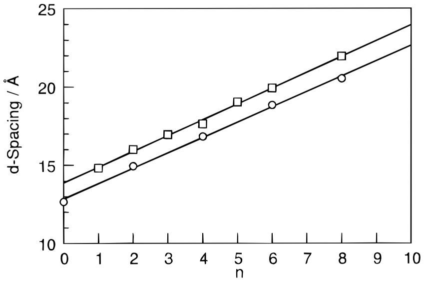

Figure 1. Plots of the *d*-spacing for (□) $V(O)O_3PR\cdot H_2O\cdot C_{10}H_7CH_2OH$ as a function of the number of carbon atoms in alkyl pendent (slope = 1.01 Å/CH_2 and intercept = 13.9 Å) and for (○) $V(O)O_3PC_{10}H_7\cdot H_2O\cdot R'OH$ as a function of the number of carbon atoms in the intercalated alcohol chain (0.98 Å/CH_2 and an intercept of 12.8 Å).

The $V(O)O_3PR\cdot H_2O\cdot R'OH$ layers are composed of distorted vanadium octahedra and phosphate tetrahedra.[10] Each vanadium octahedron shares three equatorial oxygen atoms with three different phosphonates. The fourth equatorial position is occupied by a strongly coordinated water of crystallization. The two axial positions are occupied by a vanadyl oxygen and a substitutionally labile alcohol. Jacobson and Johnson showed,[10,11] in their benchmark work on these systems, that benzyl alcohol can be removed thermally, resulting in an isotactic collapse of the interlayer spacing; other alcohols can subsequently be reintroduced to the layers.[11b] This methodology was exploited to introduce the naphthalene chromophore within $V(O)O_3PR$ interlayers. Benzyl alcohol (BzOH) was removed thermally from $V(O)O_3PR\cdot H_2O\cdot BzOH$ and replaced with 2-naphthalenemethanol (Aldrich) by stirring the alcohol-free $V(O)O_3PR\cdot H_2O$ (R = methyl, ethyl, butyl, pentyl, hexyl, and octyl) powder in a 1.0 M toluene solution of 2-naphthalenemethanol for 48 h to yield $V(O)O_3PR\cdot H_2O\cdot C_{10}H_7CH_2OH$. The single, narrow, and strong low-angle peak and accompanying higher order reflections in the powder X-ray diffraction patterns of these materials indicate that they consist of a single phase and are well-ordered layers along the *c*-dimension.

Figure 1a shows a plot of the interlayer spacing of $V(O)O_3PR\cdot H_2O\cdot C_{10}H_7CH_2OH$ as a function of the number of alkyl carbons in the pendent phosphonate spacer. Least-squares fitting gives a line with a slope of 1.01 Å/CH_2 and an intercept of 13.9 Å. The anchoring of the alkylphosphonate pendent to the layer via a perpendicular P−C bond engenders a 56° tilt angle for an *all-trans*-poly(methylene) chain. For interdigitated chains, the layer spacing should increase at 1.05 Å/CH_2 whereas a bilayer arrangement would show an interlayer expansion of 2.10 Å/CH_2.[11b,12] The results of Figure 1a clearly indicate that the pendent poly(methylene) units of adjacent layers interdigitate, as has previously been observed for these layered materials.[11b]

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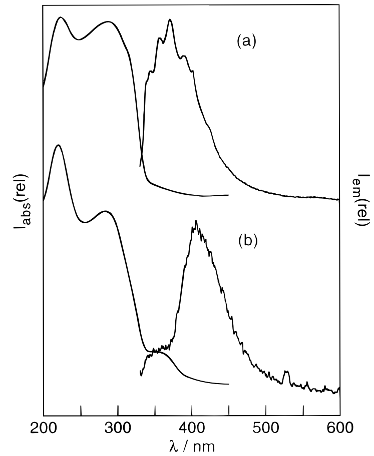

Figure 2. UV−visible diffuse reflectance and luminescence spectra of $V(O)O_3PR{\cdot}H_2O{\cdot}C_{10}H_7CH_2OH$ for (a) R = methyl and (b) R = ethyl.

The ability of the ancillary phosphonate chains to mechanically jack the LVP layers apart with 1 Å resolution directly affects the spectroscopy of the naphthyl alcohol cosolvate.

Figure 2 shows the absorption and emission spectra of the solids with methyl and ethyl phosphonate spacers. For R = methyl, an intense and structured absorption manifold is observed, which is characteristic of the naphthalene chromophore ($\lambda_{max}(^1B_b) = 220$ nm, $\lambda_{max}(^1L_a) = 280$ nm[13]). The absorption profile is complemented by the highly structured fluorescence band of naphthalene at $\lambda_{max} = 370$ nm. Two prominent changes are observed in the absorption and emission profiles when the length of the phosphonate pendent is increased by the addition of a methylene unit. As shown in Figure 2b, the luminescence spectrum of the solid is that of naphthalene excimers and not individual monomers.[14] Excimer luminescence results from the overlap of the π systems of a ground and electronically excited naphthalene, which is a thermodynamically favorable interaction when one of the species is electronically excited.[15] Interestingly the absorption spectrum indicates that this cofacial arrangement of the naphthalenes is not formed upon excitation but is preorganized within the interlayer region. The 360-nm absorption on the low-energy tail of the $^1(\pi \rightarrow \pi^*)$ transition is a signature of juxtaposed naphthalene rings with overlapping π systems in the ground state.[16] The overlap of the low-energy tail of the dimer absorption band and the high-energy tail of the excimer emission band is consistent with the excimer emission originating from a preorganized dimer ground state. These results suggest that the interdigitation of the naphthalene rings in the layered material with R = Et establishes a high degree of interlayer order, with naphthalene rings cofacially organized and overlapping. This order is presumably present for the methylphosphonate LVP too, but the deeper interdigitation of the naphthalene rings eliminates absorption and emission spectral features that are characteristic of cofacially disposed, overlapping rings.

As longer and longer alkyl pendents sequentially jack the layers apart, the dimer absorption band gives way to the absorption band of the isolated naphthalene chromophores, as shown in Figure 1a. These observations reflect the passing of neighboring naphthalenes from "out of registry," when the spacer is methyl through an "in registry" alignment for an ethyl spacer to "out of registry" again on the other side. Yet the presence of excimer emission for spacers greater than butyl indicates that the well-defined order present in the interlayer region of $V(O)O_3PR{\cdot}H_2O{\cdot}C_{10}H_7CH_2OH$ for R = methyl and ethyl is disrupted for R ≥ butyl. In view of the large interlayer spacing for materials with R ≥ butyl, the observation of excimer emission is explained by the interaction of naphthalene rings appended to the same side of the same layer. In the less congested environment of noninterdigitated pendents, rotation of the naphthyl moiety about the methylene of the $V-O-CH_2-C_{10}H_7$ linkage can result in an overall translation of adjacent naphthalene rings by nearly 3 Å thereby allowing the excimer to form.

The motion of the naphthalene rings afforded by the free rotation an alkyl tether is eliminated by appending the naphthalene group directly to the inorganic framework of the LVP. We prepared $V(O)O_3PC_{10}H_7{\cdot}H_2O{\cdot}R'OH$ (R = methyl, ethyl, butyl, hexyl, and octyl) according to previously described methods,[11b] where the alcohol cointercalant now provides the function of mechanically jacking the layers apart. As shown in Figure 1b, a slope of 0.98 Å per methylene unit reveals that this material also assumes an interdigitated arrangement of primary alcohols from adjacent layers. Molecular modeling calculations[17] show that the single-bond spacing of the naphthalene from the layer engenders a cofacial alignment of the aromatic rings only when alcohol is absent. This is supported by the observation of excimer emission ($\lambda_{em,max} = \sim 410$ nm) for the alcohol-free material, $[V(O)O_3PC_{10}H_7{\cdot}H_2O]$. Substitution of the water by ethanol or alcohols of longer chain length[18] leads to the prompt disappearance of the excimer emission, which is replaced by fluorescence of the naphthalene monomer. In these systems, the interlayer spacing is too large to permit the overlap of the aromatic rings of naphthalene.

The structural motif of layered vanadyl phosphonates permits the intermolecular interaction of functionalized pendents to be controlled on the angstrom length scale. The intralayer phosphorus−phosphorus distance is sufficiently large in this class of materials to accommodate interdigitation of pendents from adjacent layers. By exploiting of the additional alcohol binding site, interactions of the pendent functional phosphonate groups can be "dialed in" as a function of the intercalating alcohol's chain length, or alternatively, interlayer guest−guest interactions can be incrementally adjusted by using an ancillary phosphonate pendent to adjust the interlayer spacing. This approach complements the recent studies of Mallouk[19] in which photoactive active sites of different interlayers interact across the inorganic phosphate host layers. For the results described here, the interaction of active sites may be incrementally tuned in a well-defined structural arrangement within the same interlayer. Our approach is not confined to the design of optical materials inasmuch as the vanadyl phosphonates may be modified with other functional groups. For instance, the introduction of metal binding sites, paramagnetic centers, and unsaturated olefins provides a framework for materials design of ion channels, thin layer magnets, or conductors, respectively. In each case, the possibility exists for the response of the material to be turned on or off by simply using the ancillary spacer to jack the functional groups into and out of alignment.

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