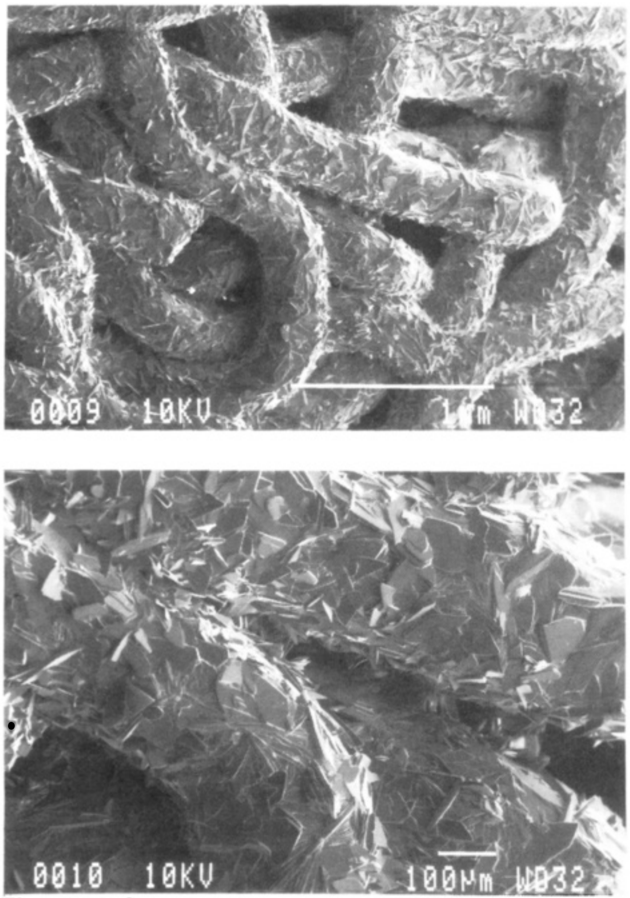

Figure 3. Scanning electron micrographs of electrolytically deposited brushite coatings on titanium mesh.

metal surfaces that will promote bone fixation to metallic prostheses.

Acknowledgment. This work was made possible through financial support from the Whitaker Foundation.

Registry No. Brushite, 14567-92-1; 316L stainless steel, 11134-23-9.

Highly Organized Molecular Assemblies of Porphyrin Guest Molecules in Mica-Type Silicates: Influence of Guest–Host Interactions on Molecular Organization

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The need for materials with well-defined molecular architectures that can be manipulated into technologically useful forms such as thin films is well recognized.[1] Toward this goal we have been using intercalation of layered solids as an alternative to the Langmuir–Blodgett technique for manipulating molecular and polymeric guest species into well-defined multilayered thin-film structures.[2] The technique provides an opportunity to control the thickness and molecular organization of guest species by fine-tuning the guest–host molecular interactions.[3]

Table I. UV–Visible Absorptions in the Soret Region of CuTMPyP in Solution and Intercalated Form[a]

solvt or host	band posn, nm	solvt or host	band posn, nm
H_2O	422	hectorite	446
1 N HCl	422	fluorohectorite	413

[a] The spectra of intercalated samples were recorded in suspension at maximum loading (i.e., 0.175 and 0.475 mmol of porphyrin/g of hectorite and fluorohectorite, respectively).

In the present work we report the synthesis of well-organized assemblies of the Cu-metalated form of tetrakis(1-methyl-4-pyridyl)porphyrin (CuTMPyP) in the galleries of Na hectorite and Li fluorohectorite. The molecular orientation of the gallery molecules is dictated by the surface area available per exchange site, which in turn depends on the layer charge density (isomorphous substitution) of the host lattice.

Although intercalation of naturally occurring macrocycles and synthetic porphyrins in the galleries of layered silicates has been studied before, none of the studies focused on the effect of the inorganic host on the organization of the guest molecules.[4-6] In addition, the use of the Cu-metalated form in this study provides an excellent probe for distinguishing possible molecular orientations by ESR spectroscopy.

Natural hectorite and synthetic fluorohectorite belong to the general family of mica-type layered silicates. Their lattice structure consists of two tetrahedral sheets fused to an edge-shared octahedral sheet.[7] The stacking of these layers leads to the formation of interlayers or "galleries" normally occupied by hydrated cations that balance the charge deficiency generated by the isomorphous substitution in the tetrahedral or octahedral sheets. The strong intraplanar and weak interplanar binding forces that arise from the two-dimensional structure allow the introduction (intercalation) of guest species into the galleries of the host lattice by simple ion exchange. CuTMPyP was chosen as a model compound because of the presence of permanent charge on the pyridyl substituents and its resistance to demetalation in acidic media.

Addition of stoichiometric amounts of CuTMPyP from an aqueous solution to a suspension of either hectorite or fluorohectorite (0.175 and 0.475 mmol of porphyrin/g of silicate, respectively) results in almost complete adsorption of the porphyrin molecules within a few minutes. X-ray diffraction patterns of fluorohectorite and hectorite intercalated products show that crystallographically well-ordered structures are obtained with (001) harmonics corresponding to a primary repeat unit (*d* spacing) of 20.1 and 14.0 Å for fluorohectorite and hectorite, respectively. The difference of 4.4 Å from the corresponding 9.6 Å for the silicate framework for hectorite is in accord with the expected size of the porphyrin ring lying parallel to the silicate layers. In contrast, the observed 10.5-Å difference for fluorohectorite is consistent with either a bilayer of porphyrin molecules or an inclined arrangement of the porphyrin plane with respect to the silicate layers. The latter arrangement has been observed for alkylammonium

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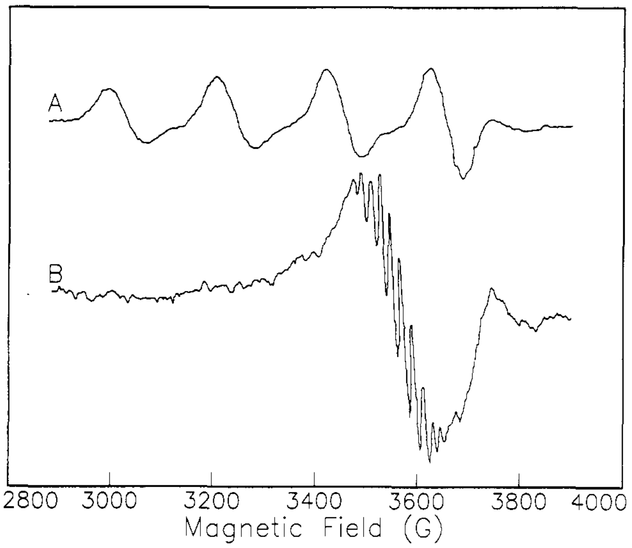

Figure 1. ESR spectra of oriented films of CuTMPyP–hectorite with the silicate layers positioned perpendicular (A) and parallel (B) to the magnetic field.

intercalates in highly charge layered silicates,[8] when the area per exchange site is insufficient to accommodate the long hydrocarbon chains.

The electronic absorption spectra of CuTMPyP in solution and in the intercalated form are summarized in Table I. Aqueous solutions of the metalated porphyrin exhibit a Soret band a 422 nm. The Soret band remains unchanged when the porphyrin is dissolved in 1 N HCl, demonstrating the stability of the metal complex in an acidic environment. However, intercalation in hectorite causes the Soret band to shift to longer wavelengths (446 nm). In contrast, the fluorohectorite intercalate exhibits an absorption at 413 nm. The bathochromic shift observed for the hectorite intercalate is, most likely, due to the twist of the pyridyl substituents imposed by the host template upon intercalation. The latter leads to an increased resonance interaction between the pyridyl substituents and the porphyrin macrocycle (the substituents being nearly coplanar with the ring) similar to that observed upon protonation of the free base.[9]

Further evidence for the orientation of the porphyrin intercalates was provided, in part, by anisotropic electron spin resonance spectroscopy of oriented film samples. ESR spectra were recorded for different sample orientations corresponding to the magnetic field direction oriented parallel and perpendicular to the plane of the silicate sheets. The resulting spectra provide experimental values of the g factor and the hyperfine coupling constant A. Figure 1 shows the spectra recorded at room temperature with the magnetic field oriented parallel and perpendicular for the hectorite intercalate. When the magnetic field is oriented parallel to the silicate layers, the electron spin is quantized parallel to the host layers, and only the g perpendicular is observed ($g_{\perp} = 2.098$). The g parallel ($g_{\parallel}$) component is observed when the magnetic field is perpendicular to the host layers ($g_{\parallel} = 2.245$, $A = 0.0208\ \mathrm{cm}^{-1}$). The hyperfine structure of the spectrum is due to the four nitrogen atoms ($I = 1$) of the tetrapyrrolic ring ($B_{\mathrm{N}} = 0.0014\ \mathrm{cm}^{-1}$). Because $g_{\parallel}$ and $g_{\perp}$ are observed for the perpendicular and parallel orientations, respectively, it can be concluded that the molecular plane of the tetragonal complex is parallel to the silicate layers.[10] The ESR spectra for random powder samples indicate the Cu^{2+} ions also possess a tetragonal symmetry with both components present in the spectrum ($g_{\parallel} = 2.153$, $A = 0.0205\ \mathrm{cm}^{-1}$, $g_{\perp} = 2.059$, $B = 0.0091\ \mathrm{cm}^{-1}$, $B_{\mathrm{N}} = 0.0014\ \mathrm{cm}^{-1}$). There is no apparent change when the spectrum is recorded at 77 K.

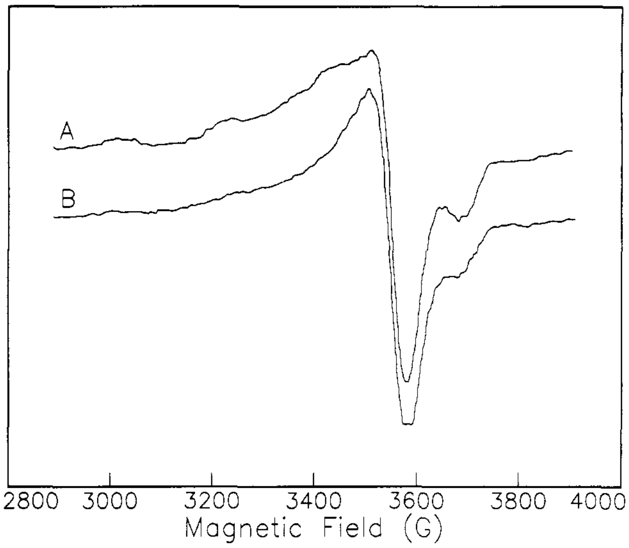

Figure 2. ESR spectra of oriented films of CuTMPyP–fluorohectorite with the silicate layers positioned parallel (A) and perpendicular (B) to the magnetic field.

In contrast, the ESR spectrum of the fluorohectorite intercalate is orientation independent, though anisotropic ($g_{\parallel} = 2.24$, $A = 0.0208\ \mathrm{cm}^{-1}$, $g_{\perp} = 2.111$, $B = 0.0093\ \mathrm{cm}^{-1}$; Figure 2). Both the parallel and perpendicular components are seen when the permanent magnetic field is oriented parallel or perpendicular to the silicate layers. The lack of orientation dependence indicates that the porphyrin molecules are oriented near 45° to the host layers so that the magnetic field "sees" the same molecular environment regardless of film orientation with respect to the magnetic field.[10] The observed orientation is in accord with the X-ray and UV–visible absorption data.

The preferred orientation depends on the arrangement that optimizes charge balance with the area needed to accomodate each guest molecule. For example, if the porphyrin molecules are taken to have a square shape, then the area needed to accommodate each molecule oriented parallel to the layers is approximately 300 Å^2. Since the area per unit charge in hectorite is 80 Å^2, the porphyrin molecules with a charge of 4+ should be able to spatially balance the host layer charge with the bulk of the molecular rings lying parallel to the silicate layers[4,11] (available area per molecule 320 Å^2).

In contrast, an inclined arrangement of the porphyrin molecules is predicted for fluorohectorite due to its higher charge density. Since the gallery area per unit charge is now only 27 Å^2, the porphyrin molecules are incapable of balancing the host layer charge when intercalated at the monolayer level.[11] Charge balance is accomplished by forcing the porphyrin molecules to attain a tilted configuration. On the basis of the molecular dimensions and the observed d spacing, we calculate the long axis of the porphyrin cross section to be inclined to the silicate layers with a tilt angle of 35°. This value represents only a lower bound, since it ignores "keying" of the guest molecules with the gallery "floor" and "ceiling".[10] When "keying" is taken

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into account a higher value is obtained, in good agreement with the ESR results. A tilted arrangement was recently proposed for porphyrin–fluorohectorite intercalates based on X-ray diffraction data but with a much smaller tilt angle (ϕ = 7°). Note, however, that the low-charge fluorohectorite used in the previous study possesses a charge intermediate to the natural hectorite and fluorohectorite used in the present study.

Thus, intercalation of layered solids can be used to manipulate the structure of supermolecular assemblies. Specific guest–host interactions significantly influence the molecular organization (orientation and alignment) of guest molecules in the galleries of the layered template. By controlling these subtle interactions, one can mediate the architecture of a material at the molecular level. Experiments are in progress to evaluate the nonlinear optical and hole-burning properties of these new supermolecular assemblies.

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Registry No. CuTMPyP, 48242-70-2; hectorite, 12173-47-6; fluorohectorite, 68084-70-8.

Molecular Composites of Rigid-Rod Polymers in the Matrix of Flexible-Coil Polymers. Preparation of Thin-Film Nonlinear Optical Materials via Soluble Complexes

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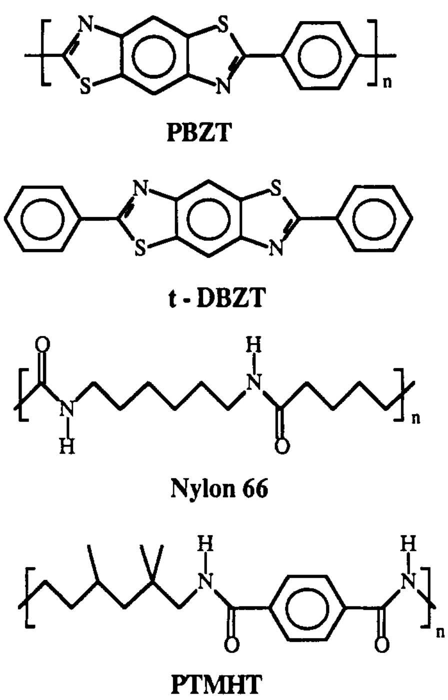
Molecular composites[1-8] are composite materials in which a high-strength, high-modulus, rigid-rod polymer is molecularly dispersed in the matrix of a flexible-chain polymer. One important aim of such a material system concept is to improve the mechanical properties, such as tensile strength and modulus, by a complementary blend of the structural and physical properties of the component polymers. Rod/coil molecular composites whose preparation, processing, phase behavior, and mechanical properties have been investigated include poly(p-phenylenebenzobisthiazole) (PBZT)/poly(2,5(6)-benzimidazole) (ABPBI),[1,2] 1,1-PBZT/poly(2,5(6)-benzothiazole) (ABPBT),[1,2] PBZT/poly(hexamethyleneadipamide) (nylon 66)[5,6] poly(p-phenyleneterephthalamide) (PPTA)/nylon 66, and PPTA/poly(caprolactam) (nylon 6).[4] These rod/coil composite materials are generally prepared from ternary solutions in strong concentrated protonic acids such as methanesulfonic acid (MSA).[1-8] The electroactive, linear optical, and nonlinear optical properties of rod/coil molecular composites have so far not been investigated.

Scheme I



Molecular composites that contain an electroactive or nonlinear optical component or components such as the conjugated rodlike PBZT and semiflexible coils ABPBI and ABPBT expand the range of organic solid-state materials and can be expected to exhibit a complementary blend of electroactive and optical properties. In this regard, although it would seem that the upper limits on the electroactive properties of molecular composites are set by those of the components, such a class of materials is nevertheless of theoretical and practical interest. For example, such composite materials are important model systems for the investigation of the effects of morphology and composition on electroactive and nonlinear optical properties. Also, in the case of third-order nonlinear optical (NLO) properties, there is precedence for enhanced NLO properties of composite materials (e.g., metal- or semiconductor-doped glasses and polymers) compared to the starting component materials.[9,10]

We report the preparation of thin films of rod/coil molecular composites of PBZT/nylon 66 (see Scheme I) and PBZT/poly(trimethylhexamethyleneterephthalamide) (PTMHT) using a novel approach of ternary solutions of the Lewis acid complexes of the polymers in organic solvents. We also demonstrate that the PBZT/nylon 66 and PBZT/PTMHT molecular composites have interesting nonlinear optical properties as will be reported in detail elsewhere.[11] We have previously reported that Lewis acid

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