properties are carefully controlled (*16*), and the function of membrane proteins is modulated by these parameters (*17*). Often the growth temperatures are just above the temperatures for the onset of phase separations (*18*) and therefore may be close to lipid critical temperatures. The experiments show how proximity to a critical point allows the local lipid composition to adjust to the presence of an electric field (*19*). Electric fields are of course only one source of local intermolecular forces that play roles in lipid-protein interactions. Lipid mixtures near critical points should be responsive to many of these forces.

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20. We are indebted to J. Brauman and J. Seelig for helpful discussions. This work was supported by the National Science Foundation (NSF DMB 90-05556) and the Deutsche Forschungsgemeinschaft (K1 834/1-1).

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Stilbazolium-MPS_3 Nanocomposites with Large Second-Order Optical Nonlinearity and Permanent Magnetization

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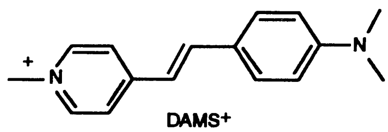
Intercalated layered materials comprising an organic dye and inorganic MPS_3 [where M is either the manganese ion (Mn^{2+}) or the cadmium ion (Cd^{2+})] phases have been prepared. The intercalation process induces a spontaneous poling, giving rise to an efficiency of 750 times that of urea in second-harmonic generation for the cadmium derivative. In addition, the manganese derivative displays a permanent magnetization below 40 kelvin. Thus, these materials exhibit both a large optical nonlinearity and magnetic ordering.

Since the observation that a single crystal of quartz could frequency-double the output of a ruby laser (*1*), the search for nonlinear optical (NLO) materials has been motivated by the potential applications in many areas of optoelectronics. Although most of the currently available materials are inorganic, molecular or organic materials that exhibit a second-order NLO response that, in some cases, is several orders of magnitude higher than that of inorganic compounds have the potential to supplant inorganic crystals (*2*). However, one of the main bottlenecks to the development of new optical materials is the compulsory noncentrosymmetric environment of the chromophores if the molecular hyperpolarizability (β) is to contribute to an observable bulk nonlinear susceptibility (χ^2) (*3*). Various strategies have been reported for the engineering of molecules into acentric arrangements in single crystals (*4*) or for the poled polymer approach (*5*), in which the polarizable chromophores are oriented by a strong electric field at temperatures above the glass transition of the films.

The fact that such promising materials are not yet readily available is closely related to problems in their alignment stability over time. Hence, there is a need for alternative routes to stabilize permanently the polar order of the chromophores. Several attempts have already been performed to incorporate chromophores into organic (*6–8*) and inorganic (*9–12*) hosts to generate spontaneous poling. Efficiencies of several times that of urea were achieved even when neither the pure host nor the pure guest could frequency-double. This method could be particularly important in the case of ionic or non-dipolar guests [for example, octupolar chromophores (*13*)], as poling fields require neutral species as well as a nonzero dipole moment.

One of the largest classes of organics with large second-order polarizabilities consists in donor-acceptor–substituted stilbenes. Among them, the 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium cation ($DAMS^+$) has been reported to exhibit one of the largest known frequency-doubling capacities (*14*).



$DAMS^+$

We found that $DAMS^+$ could be successfully intercalated by an ion-exchange process (*15–17*) into several MPS_3 (or $M_2P_2S_6$, where M = Mn^{2+} or Cd^{2+}) phases (*18*). These are a class of lamellar materials made up of M^{2+} cations and $P_2S_6^{4-}$ anions first described by Klingen and colleagues (*19*) and exhibit a great variety of properties, including magnetism (*17, 20, 21*) and metallic behavior (*22*). The intercalates were initially found to give a small second-harmonic generating (SHG) response on the order of that of urea, but these results were not conclusive: DAMS chromophores can be 10^3 times more efficient than urea (*14*), and so the poor SHG signals recorded might have originated from grain surface effects only. Also, these intercalates were not well crystallized, which could also explain low SHG efficiency.

Following our first results (*18*), we targeted an optimized intercalation process in one step by direct reaction at 130°C of MPS_3 powder with an ethanolic solution of DAMS iodide in the presence of pyridinium chloride (*23*). The role of pyridinium chloride is to generate in situ an intermediate pyridinium intercalate that undergoes rapid exchange with the DAMS species. Eventually, we synthesized two compounds of formula $Cd_{0.86}PS_3(DAMS)_{0.28}$ and $Mn_{0.86}PS_3(DAMS)_{0.28}$,

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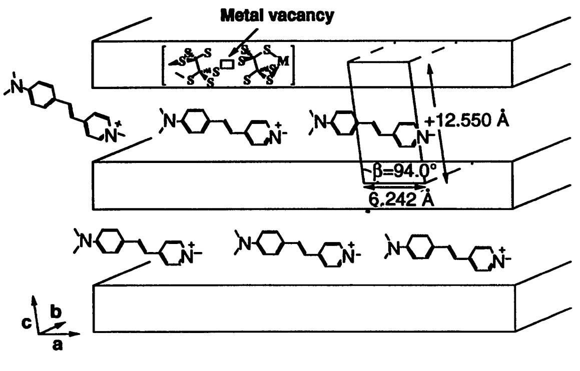

Fig. 1. Model for spontaneous poling achieved by the intercalation process. The dimensions of the unit cell are given after intercalation. The stereochemistry of the "$-(P_2S_6)^{4-} - M^{2+} - (P_2S_6)^{4-} - M^{2+} -$" linkage that builds up the lamellar structure is sketched with the appearance of metal vacancies that arise during intercalation.

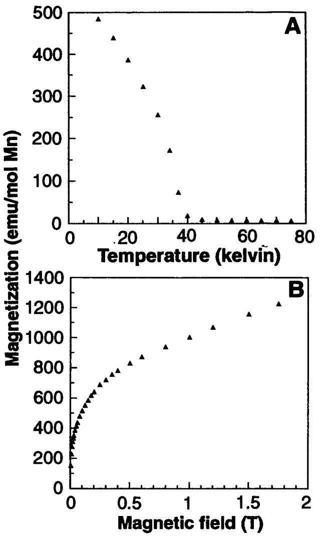

Fig. 2. Magnetic properties of the $Mn_{0.86}PS_3$-$(DAMS)_{0.28}$ intercalate (expressed per mole of manganese): (**A**) temperature dependence of the magnetization (applied field of 300 G) and (**B**) magnetization versus applied magnetic field *H*.

which were characterized by standard methods including infrared spectroscopy, x-ray diffraction, and elemental analysis (*24*). On the basis of this characterization, these new intercalates might be thought of as similar to the earlier materials (*18*), although they are much better crystallized and do not contain any residual solvent. However, these apparently minor changes have a dramatic influence on the NLO properties.

The SHG properties were recorded by the Kurtz powder technique (*25*), with a 1.34-μm laser radiation to ensure transparency of the samples at the doubled frequency. The wavelength of the maximum absorption of the intercalates is 0.58 μm. The manganese derivative exhibits an efficiency 300 times that of urea, and the cadmium derivative reaches 750 times the efficiency of urea, which is among the largest powder efficiencies reported for stilbazolium-based chromophores. The measurements have been reproduced several times, with the use of samples selected from different batches. The high intensity of SHG excludes the possibility of only surface effects contributing to the measurement and indicates that the chromophores are spontaneously well aligned between the MPS_3 slabs. The schematic structural model in Fig. 1 takes into account the fact that the DAMS species are oriented "edge on" (basal spacing of 12.4 Å) and closely packed (to account for the host/guest ratio). Intercalation does not cause significant dilution of the chromophores; for example, there is one DAMS species in 525 $Å^3$ of the tosylate salt (*14*) compared to one DAMS in 740 $Å^3$ of the present intercalates.

Two factors can favor or enforce dipole ordering: (i) The pyridinium groups of the DAMS molecules bear the positive charge, so they may tend to penetrate first and drive the insertion stereochemistry. Substituted aromatics exhibit a tendency toward group-oriented insertion (*26*). However, this argument is not sufficient to account for the fact that dipole alignment must be kept over many adjacent guest layers. (ii) The MPS_3 host lattice [space group *C*2/*m* (*19*)] is centrosymmetric and therefore should not a priori enforce a noncentrosymmetrical arrangement on the guest species. However, we have shown that the host lattice is substantially modified once intercalated [superstructures have been seen (*21*)], so that its role in the chromophore poling will have to be reconsidered.

Further interest arises from the opportunity to observe in the $Mn_{0.86}PS_3(DAMS)_{0.28}$ composite both strong NLO properties and a spontaneous magnetization (below 40 K). Intercalation is known to exert a dramatic influence on the magnetic properties of the MPS_3 (M = Mn or Fe) compounds (*17*, *20*, *21*). Whereas pristine $MnPS_3$ orders antiferromagnetically below 78 K, many intercalates become (ferri) magnets below a Curie temperature that can be as high as 92 K (*20*). This modification arises because the intralayer metallic vacancies, created during intercalation, undergo ordering and destroy the balance between the antiferromagnetically coupled spins (*21*).

The temperature dependence of the magnetization of $Mn_{0.86}PS_3(DAMS)_{0.28}$ (measured with a Metronique Ingénierie superconducting quantum interference detector in a field of 300 G) is shown in Fig. 2A. The magnetization sharply increases below 40 K, indicating the occurrence of a magnetic transition. The dependence of the magnetization versus applied magnetic field has been measured at 20 K, and the results are shown in Fig. 2B. As the field strength increases, the magnetization first rapidly increases and then tends to saturate in a behavior typical of a bulk magnet. The saturation value [around 1000 electromagnetic units (emu) per mole of Mn] is only a fraction (≈4%) of the value for NgβS that would be reached if all manganese spins were parallel (24,000 emu). These results are consistent with the general magnetic behavior of the MPS_3 family, and $Mn_{0.86}PS_3(DAMS)_{0.28}$ appears to be a new material that possesses both strong spontaneous NLO properties and spontaneous magnetization up to a high temperature ($T_c \approx 40$ K) (*27*).

Intercalation provides an alternative to sol-gel methods (*28*), at least in certain circumstances, for the synthesis of hybrid organic-inorganic nanocomposites, providing the advantage of a better crystallinity that can be important when cooperative interactions are required. We did not record any significant decay of the NLO signal over a period of several months, which is a crucial point in the search for suitable SHG materials. However, to be appropriate in optical devices, such materials must be available as single crystals or thin films. It is too early to predict whether this goal will be achieved, but efforts are in progress to process the MPS_3 intercalates as thin films and to take advantage of the aqueous chemistry of the MPS_3 phases (*16*) and of their ability to insert polymers such as polyethyleneoxide (*29*).

The emergence of molecular electronics and photonics as multidisciplinary frontiers of science and technology should greatly benefit from the advances in nonlinear optics, molecular ferromagnets, or molecular metals. Therefore, molecular materials that merge magnetic and NLO properties might inspire considerable interest.

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23. MPS_3 powder (100 mg) was soaked in an ethanolic solution (10 ml) containing DAMS iodide (250 mg) and pyridinium chloride (100 mg). The reaction was carried out in a pyrex ampoule that was sealed under vacuum and heated around 130°C overnight.
24. Elemental analysis for the cadmium intercalate found: C, 18.34; H, 1.91; N, 2.66; S, 33.17; P, 10.30; and Cd, 31.96. Required for $Cd_{0.86}PS_3(DAMS)_{0.28}$: C, 18.50; H, 1.84; N, 2.70; S, 33.07; P, 10.65; and Cd, 33.24. Elemental analysis for the manganese intercalate found: C, 21.67; H, 2.22; N, 3.17; S, 38.98; P, 12.84; and Mn, 19.20. Required for $Mn_{0.86}PS_3(DAMS)_{0.28}$: C, 22.29; H, 2.22; N, 3.25; S, 39.84; P, 12.83; and Mn, 19.57. The intercalation of cationic species is accompanied by the creation of interlayer metal vacancies to maintain the electrical neutrality. The unit cell of the intercalates is closely related to the cell of the pure host lattice. The "in plane" **a** and **b** parameters are quasi-identical, and the **c** parameter is enlarged because of the bulk of the guest species. The parameters for $Cd_{0.86}PS_3(DAMS)_{0.28}$ are $a = 6.242$ Å, $b = 10.768$ Å, $c = 12.550$ Å, and $\beta = 94.0°$; versus $a = 6.218$ Å, $b = 10.763$ Å, $c = 6.867$ Å, and $\beta = 107.6°$ for pure $CdPS_3$.
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Paleoindians in Beringia: Evidence from Arctic Alaska

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Excavations at the Mesa site in arctic Alaska provide evidence for a Paleoindian occupation of Beringia, the region adjacent to the Bering Strait. Eleven carbon-14 dates on hearths associated with Paleoindian projectile points place humans at the site between 9,730 and 11,660 radiocarbon years before present (years B.P.). The presence of Paleoindians in Beringia at these times challenges the notion that Paleoindian cultures arose exclusively in mid-continental North America. The age span of Paleoindians at the Mesa site overlaps with dates from two other cultural complexes in interior Alaska. A hiatus in the record of human occupation occurs between 10,300 and 11,000 years B.P. Late Glacial climatic fluctuations may have made northern Alaska temporarily unfavorable for humans and spurred their southward dispersal.

Since the 16th century, the Bering Strait region has been viewed as the likely route for peopling of the New World from Asia (*1*). More than 60 years have elapsed since the 1926 discovery of Paleoindian fluted projectile points in undoubted association with extinct Pleistocene bison near Folsom, New Mexico (*2*), yet convincing evidence for a Paleoindian presence in Beringia has remained elusive (*3–5*). Although Paleoindian-like projectile points have been found in Alaska since the 1930s (6), most have come from undatable contexts (*4*). We report here on well-dated examples of lanceolate Paleoindian projectile points from Beringia. These were recovered from the Mesa site, a late Pleistocene–early Holocene hunting lookout located on the northern flanks of Alaska's Brooks Range (*7*) (Fig. 1).

The Mesa site has a commanding view from atop a weathered gabbro dike that rises 60 m above the Iteriak Creek valley. The view from the site, together with the predominance of point bases, the presence of impact-fractured points, the pattern of resharpening, and the large amount of flakes from point manufacture, all suggest that the site was used as a weapon-repair and game-spotting station. Artifacts come from the surface or from within a thin (<30 cm) layer of colluvium on top of the mesa. The most common tools are basally concave lanceolate projectile points, most of which are broken or resharpened (Fig. 2). These points display basal thinning although not true fluting. They have relatively thick lenticular to diamond-shaped cross sections and heavily ground proximal edges and bases. The Mesa points were finished by robust pressure flaking. Among the classic Paleoindian projectile point types from mid-continental North America, the Mesa points are most similar in technology to Agate Basin and Hell Gap points (*8*), but typically have basal concavities like Goshen and Plainview points (*9*).

Other tools in the assemblage include bifaces, spurred gravers, scrapers, and hammerstones (Fig. 2). These tools are all typical of Paleoindian assemblages. The core and blade technology reported from other early Alaskan sites (*10, 11*) is absent from this assemblage. Unlike many other sites in the region, the Mesa site was evidently not used by people of the ensuing Holocene cultural periods, despite the presence of their cultural remains in nearby sites along Iteriak Creek.

We discovered nine shallowly buried, unlined hearths on the mesa in association with artifact concentrations. Contemporaneity between the hearths and the Mesa points is demonstrated by occasional flakes and projectile point fragments that are associated with charcoal and possess pot-lid fractures, a pattern known to result from heating. Of the 11 accelerator mass spectrometry (AMS) ^{14}C dates on charcoal from the site, nine indicate occupation near 10,000 radiocarbon years before present (years B.P.), and two from a single hearth indicate occupation between 11,000 and 12,000 years B.P. (Table 1) (*12*). Apart from the Mesa site, only the Putu site 290 km to the east provides potential dating for a northern Paleoindian tradition (Fig. 1). At the Putu site, a single date of 11,470 ± 500 years B.P. may relate to a Paleoindian occupation containing both fluted and nonfluted lanceolate projectile points (*13*).

Our findings at the Mesa site have several implications. The Mesa Complex clearly demonstrates that Paleoindians once occupied Beringia, an occupation previously considered speculative by most prehistorians. The oldest date from the Mesa site, 11,660 ± 80 years B.P., seems to preclude the derivation of

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