Toward New Multi-Property Materials

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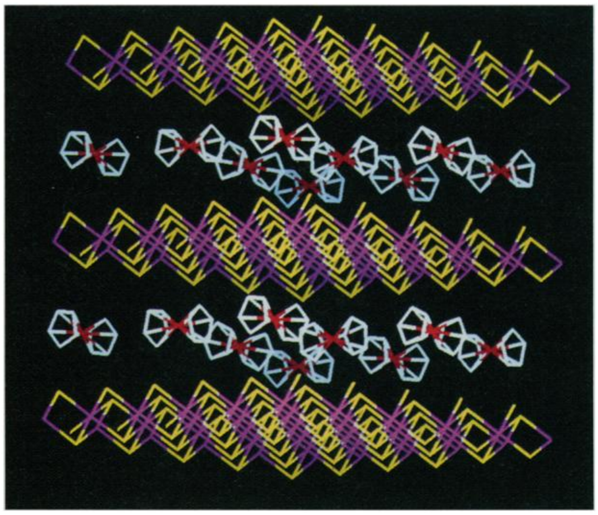
There is today a tremendous search for new materials that show various physical properties: conductivity, superconductivity, optical effects, magnetism, and so forth. Superconductivity, for example, is a good example of what can be achieved by both inorganic and organic chemistry. Organic superconductors were the focus of excitement in the early 1980s, but now the interest is in inorganic materials. But the question arises, by what chemical methods can we get the best improvement in whatever property we seek? On page 658 of this issue, Lacroix *et al.* (*1*) approach the issue with their report of progress in making materials that combine two useful properties: magnetization and second-harmonic generation.

For optical materials having quadratic (or second-order) nonlinear optical (NLO) properties (*2*), the story begins in the early 60s, when Franken *et al.* (*3*) observed the feeble second-harmonic generation from a quartz crystal illuminated by a ruby laser light, an inorganic material. Several efficient inorganic crystals emerged that are still used as NLO materials, such as potassium hydrogenophosphate (KDP), lithium niobate ($LiNbO_3$), or more recently, potassium phosphotitanate ($KTiOPO_4$). However, unlike inorganic materials where optical nonlinearities arise from the displacement or rearrangement of nuclear coordinates, little by little, organic materials built from conjugated polar π-electron systems (the so-called "hyperpolarizable chromophores") were investigated, leading to the discovery of very efficient molecular materials in various condensed phases, such as single crystals, poled polymers, or Langmuir-Blodgett films (*4*).

The common requirement for all these materials is the lack of a center of symmetry in the bulk material, so that the control of noncentrosymmetric molecular arrangement is essential for obtaining effective macroscopic second-order nonlinearity. Several attempts have been made to that end, such as the use of chirality in crystals, high external electric field for poled polymers, and so on. But new methodologies for the induction of noncentrosymmetric structures in molecular materials are critical to the development of those having second-order NLO properties.

A new way to obtain such a control could come from the chemistry of layered materials and that of specific intercalated guest molecules, an approach that could lead to hybrid organic-inorganic composites spanning a broad range of fascinating properties.

The ease with which a thin sheet of mica can be peeled away and the lubricating qualities of graphite are related. Undergraduate students in chemistry or materials science learn that these properties merely reflect the strongly anisotropic structure of these substances, built up by the stacking of weakly interacting layers. For a long time, research chemists have been fascinated by the fact that such materials have an "internal" surface that is actually accessible to molecules, ions, and more recently, organic radicals and even polymers. Indeed, a wide variety of chemical species can penetrate the interlayer space under very mild conditions.



Contrary compound. The crystal structure of the organic-inorganic SnS_2-cobaltocene intercalation compound (*15*), an example that runs against the rule that crystal structures cannot be refined in intercalation chemistry. [Courtesy of D. O'Hare, University of Oxford]

Intercalation chemistry has been known for more than 150 years, but there was a resurgence of interest in the late 1960s, when Gamble *et al.* (*5*) found that the critical temperature (T_c) for the onset of superconductivity in $2H\text{-}TaS_2$ could be shifted from 0.8 to about 7 K upon amine intercalation. During the same period, improvements in x-ray methods of structure determination favored the discovery of numerous synthetic layered compounds (*6*).

For a long time, interest in these new materials was focused on the properties of the host lattice, the role of the guest species being merely to diffuse between the layers and cause charge transfer. It took quite a few years until chemists began to insert specifically functionalized molecules that would add some specific properties.

The work of Lacroix *et al.* illustrates this approach well (*1*); a specific cationic chromophore chosen for its large hyperpolarizability enters the interlayer space and triggers several consequences: metallic cations are expelled from their intralayer sites, leaving ordered vacancies, and the host-guest, and possibly guest-guest, interactions enforce spontaneous poling, leading to efficient second-harmonic generation.

This perspective also brings out the feature, common to nearly all studies of the intercalation of large species, that it is extremely difficult to achieve a complete structural characterization of the intercalated materials. Modern x-ray techniques can solve the structure of almost any perfectly crystallized material, even from polycrystalline powder samples. However, intercalation compounds constitute intermediate solids that are quite crystalline but contain many defects and retain some disorder that generally precludes full structural refinement, although a few exceptions exist (see figure).

Despite this difficulty, pioneering work was carried out in the early 80s by Pinnavaia *et al.* (*7*), who inserted a cationic organometallic rhodium complex in a layered silicate and showed that the guest species could still act as a catalyst for selective hydrogenation reactions. A key factor was that the interlayer spaces of silicates were able to swell because of the presence of a large amount of water. Such swelling would not occur in most other intercalation compounds, where the guest species are nearly close-packed so that external reagents cannot reach the catalyst.

In situ reactivity of inserted species is also exemplified by the photochemistry of inorganic complexes such as dimeric manganese-tricarbonyl–substituted cyclopentadienyl complex inserted into layered zirconium phosphate $\alpha\text{-}Zr(HPO_4)_2{\cdot}H_2O$, which is optically transparent for ultraviolet light. Irradiation leads to a steady decrease of the $\nu(CO)$ bands of the guest and to the increase of absorptions assigned to a phosphino-bound manganese dicarbonyl complex (*8*). Photosensitizers such as $Ru(bipy)_3^{2+}$ have also been inserted into layered MPS_3 and host to guest energy migration has been evidenced (*9*).

Some host lattices (V_2O_5, FeOCl) are oxidizing, and they can drive intercalation

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coupled with oxidative polymerization of specific monomers such as substituted pyrroles. These reactions yield a new type of layered nanocomposite in which sheets of polymers alternate with the host layers (*10*). Other host lattices (silicates, MPS_3) are also able to take up polyethyleneoxide, probably by a solvation mechanism (*11*, *12*). Tetrathiafulvalene, a fundamental molecule in the field of organic conductors, and some related species intercalate layered host lattices [FeOCl (*13*), $FePS_3$ (*14*)]; the guest species organize themselves as stacks that exhibit mixed valency and metallic conductivity. Other examples can be found in a recent review by O'Hare (*15*). Much remains to be discovered; in particular, the host lattice might prevent Peierls distortions from occurring and therefore favor superconductivity.

What is the future for layered nanocomposites? A number of exciting tracks are to be followed, which resemble what might be called two-dimensional supramolecular chemistry (*16*). One track is to combine on the molecular scale the mineral lattice and the organic species, with the hope that some synergies will occur. The possibility of such an effect is demonstrated by Lacroix *et al.* (*1*). The $Mn_{0.86}PS_3(DAMS)_{0.28}$ hybrid organic-inorganic composite actually becomes a magnet below about 40 K because of the spins of the Mn(II) cations of the host lattice (DAMS stands for the hyperpolarizable cationic chromophore 4'-dimethylamino-*N*-methylstilbazolium). This composite therefore associates both strong spontaneous second-order NLO properties and spontaneous magnetization up to quite high temperature by the standards of insulating transparent magnets (*17*). Therefore, the inorganic component provides the magnetic property, the organic chromophore provides the strong hyperpolarizability, and the synergy effect is represented by the orientational influence exerted by the host lattice on the guest organic species. This discovery opens a new avenue of research in the field of "multi-property" materials. Intercalation therefore provides an alternative to sol-gel methods for the synthesis of hybrid nanocomposites, at least in certain circumstances, bringing the advantage of a better crystallinity, a factor which can be of crucial importance when cooperative interactions are required.

One important condition for the future of intercalation is to carry out work at the frontier between organic and inorganic chemistry and to merge properties. If electronic devices operating at a molecular scale are to be developed in the future, it seems reasonable to think that the layered compounds will have a role to play as workbenches to tie down the molecular units. One can imagine x-rays or electron beams writing information by inducing some transformation on a molecule grafted on the surface of a layered material, which would be read by a scanning tunneling or atomic force microscope.

To be interesting, intercalation must not remain confined to laboratories specialized only in solid-state chemistry. It is by itself only a strategy to bring two or more components into intimate contact. It requires that several fields merge at many stages; this begins with, at the synthetic stage, organic and inorganic chemistry and materials science. Then, depending on what works, effort can turn to nonlinear optics, magnetism, energy migration, or photochemistry, and so on to other domains usually well separated. From this range of scientific endeavor, we see that intercalation chemistry is a multidisciplinary field, the development of which requires collaboration on a large scale.

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Remodeling Schemes of Intracellular Pathogens

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The successful microbial pathogen enters a specific host, finds a unique cellular niche, and multiplies even in the face of formidable host defenses (*1*). Many pathogenic bacteria are content to fight their way to the mucosal surface to multiply. Others, such as *Rickettsia* (causative agents of typhus and other arthropod-borne diseases) and *Chlamydia* (causative agents of trachoma and sexually transmitted disease), are obligate intracellular pathogens. To establish a successful infection, these organisms must invade (enter) a eukaryotic cell. The route of cell entry can have a profound influence on host-pathogen interactions hours and even days later in the infectious process. Although we know little about the process of entry, it is clear that microbes exploit normal internalization mechanisms of the host cell (*2*).

Most microbes that infect humans or that make up their normal flora are held at bay by innate physical and biochemical defense barriers. The microbe breaching these initial obstacles may meet strategically placed phagocytic cells whose major function is to destroy infectious agents. Almost perversely, some microorganisms take up residence in phagocytic macrophages. Among these are the bacteria that cause typhoid (*Salmonella typhi*), Legionnaire's disease (*Legionella pneumophila*), and tuberculosis (*Mycobacterium tuberculosis*), as well as several protozoan pathogens.

The macrophage presents unique advantages and disadvantages to the entering pathogen. It is a long-lived cell and thus provides a potential long-term habitat for the bacterial invader. In addition, because the macrophage serves as an antigen-presenting cell, it may offer the pathogen an opportunity to manipulate the immune system to its own advantage; indeed, survival and replication within the macrophage may even facilitate the journey of the pathogen to a preferred environmental niche. The route of entry into the macrophage is

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