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Organic Nonlinear Optical Chromophores in an Inorganic Environment. Toward an Interplay between Magnetism, Conductivity, and Nonlinear Optics

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This review is devoted to hybrid materials made of organic quadratic nonlinear optical (NLO) chromophores embodied in various inorganic environments. In the first section are reported systems in which the inorganic moiety is a transparent mineral network (e.g., silica, zirconium phosphate, etc.) exhibiting good transparency, crystal stability, and mechanical hardness, but none of the electronic properties usually associated with material science. The second section focuses on NLO chromophores inserted into inorganic magnetic phases (more precisely, $Mn_2P_2S_6$ and $[Mn^{II}Cr^{III}(ox)_3]^-$ layered structures). The issue related to possible synergies between optical and magnetic behavior (Faraday effect) is adressed. The last section is devoted to organic/inorganic hybrid assemblies combining NLO and conducting behavior. Besides the obvious transparency/conductivity trade-off, the possibility for interplay occurring through intermolecular charge transfer is discussed.

I. Introduction

Molecular materials have emerged in many areas of material science for designing new magnets,[1] molecular assemblies for data storage,[2] conductors and superconductors,[3] or nonlinear optical (NLO) materials.[4−6] Traditional inorganic materials are usually submitted to very high temperatures during the synthetic process, which ensures thermodynamic stability, but leads to limited chemical flexibility. By contrast, molecular materials are obtained in two steps, the first step the design of a series of "building blocks", which can then be engineered in various solid-state environments, the second step. Indeed, there are hundreds of chemical modifications that can be envisioned for a molecular unit by means of organic synthesis. This allows modulation of the interactions between the blocks and, hence, the solid-state environment. Therefore, nearly identical molecular units can lead to different bulk properties, as illustrated here in a few examples.

$[MnCu(pba)(H_2O)_3]\cdot 2H_2O$ and $[MnCu(pbaOH)(H_2O)_3]$, with pba = 1,3-propylenebis(oxamato), are two almost identical compounds shown in Figure 1,[7] which reveal a ferrimagnetic interaction between the low spin ($S = {}^1/_2$) of the copper(II) centers and the high spin ($S = {}^5/_2$) of the manganese(II) centers. While the first compound orders antiferromagnetically below 2.2 K and, therefore, is not magnetic in the ground state, the introduction of a hydroxy substituent leads to slight modifications in the relative position of the chains, and consequently, $[MnCu(pbaOH)(H_2O)_3]$ becomes a magnet at 4.6 K. The second example is related to molecular conductors. Following the initial idea of Little,[8] organic structures with long-range π-overlap capabilities have been envisioned to design high-temperature superconductors. Indeed, stacks of tetrathiafulvalene (TTF, Figure 1) were the basis of the first organic conductor in 1973.[9] However, TTF usually gives one-dimensional stacks (β-phases) which undergo metal−insulator (Peierls) phase

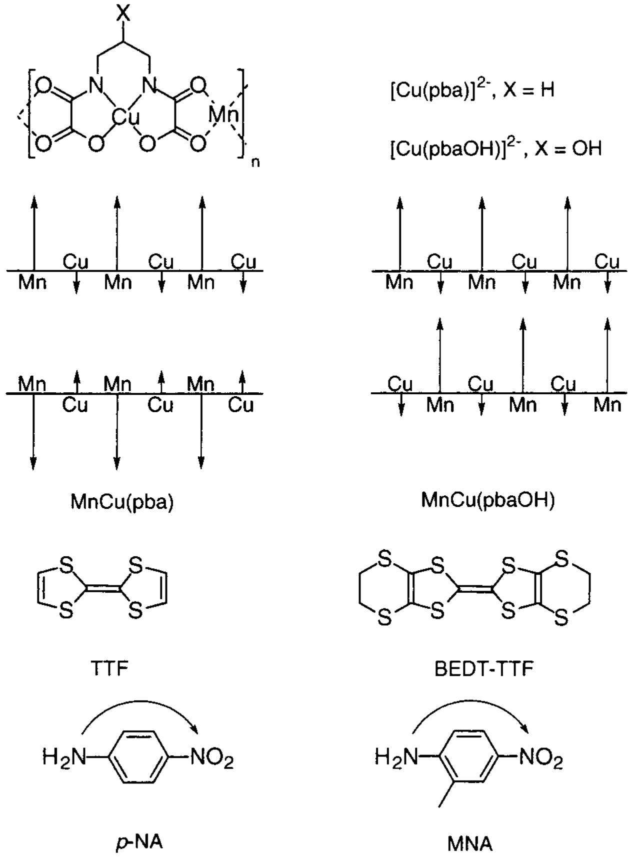

Figure 1. Buiding blocks leading to various macroscopic properties by virtue of different solid-state environments in molecular materials (see text). Examples are given for magnetic (top), conducting (middle), and NLO (bottom) materials.

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transitions,[10] and superconductivity has never been reported for any of these materials.[11] By contrast, the molecular structure of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, Figure 1) favors extended S···S contacts, which can increase the dimensionality (κ-phase), suppress the Peierls transition, and promote a superconducting state.[12] Quadratic NLO properties also strongly depend on the solid-state environment of the chromophores. *p*-Nitroaniline (*p*-NA, Figure 1) is a benchmark molecule which has been widely investigated since the mid 1970s.[13−15] Its NLO response is related to the "push−pull" character of the $\pi \rightarrow \pi^*$ charge transfer occurring between the amino and nitro substituent upon electron excitation. 2-Methyl 4-nitroaniline (MNA, Figure 1) is a related molecule, which exhibits the same π-electronic structure and therefore grossly the same NLO response. However, when *p*-NA crystallizes in a centrosymmetric environment, which leads to vanishing macroscopic quadratic effects, MNA crystallizes in the noncentrosymmetric *Cc* monoclinic space group and is a promising candidate for quadratic NLO applications.[16]

Besides this aforementioned capability for property modulation, the possibility of interplay between several properties at the molecular level is naturally adressed in molecular materials. Recent years have witnessed a growing interest for nanocomposite materials, which can be designed from suitable incorporations of ultrafine particles into polymeric matrixes.[17] Linking the properties in a "host−guest" structure at the molecular level would be an intriguing challenge, in relation to the concept of molecular switch, which is currently attracting great interest from a variety of perspectives.[18,19] "Hybrid materials" made of inorganic entities inserted into an organic host lead to an active research area.[20] However, the present review will be restricted to hybrid compounds made of organic entities bearing one property, inserted in an extended inorganic network.

We have found it to be of particular interest to focus on organic NLO chromophores. Organic magnets and conductors certainly offer theoretical and practical interest. Indeed, the first ferromagnetic transition in an organic material was reported in *p*-nitrophenyl nitronyl nitroxide radical by Kinoshita and co-workers[21] and the possibility to obtain ferromagnetic transitions in organic polymers was recognized many years ago.[22] Nevertheless, to the best of our knowledge, organic magnets obtained by insertion of organic radicals into inorganic structures have not appeared in the literature. Conducting properties have already been reported after intercalation of organic precursors into inorganic matrixes,[23] but the intrinsic properties of organic conductors and superconductors have been found to be invariably lower than those of inorganic candidates (e.g., gold metal and high T_c superconducting oxides). By contrast, organic molecules with quadratic NLO responses have long been recognized as exhibiting better capabilities than those of the inorganic materials currently available (e.g., KH_2PO_4 or $LiNbO_3$)[24] by virtue of their large hyperpolarizabilities (β), in addition to an ultrafast response time and large damage threshold.[4−6] Therefore, we have found it to be of particular interest to devote the present review to the incorporation of organic NLO chromophores in an inorganic environmement.

The organization of the paper will be the following: in a first section will be reported hybrid solids made on organic NLO chromophores inserted in a "innocent" inorganic environment. This term will refer to inorganic structures exhibiting none of the electronic properties usually associated with materials science (e.g., conductivity, magnetism, or nonlinear optics). Therefore, the only property associated with the pure inorganic moieties will be related to the stability of the crystal packing or its mechanical hardness. In a second section, NLO organics will be associated with magnetic inorganic networks. Finally, the possibility of designing hybrid materials combining NLO and conducting properties will be envisioned. In the last two sections, the important issue related to interplay between the properties will be adressed.

II. Organic NLO Chromophores Embodied in "Innocent" Inorganic Environments

II.1. Engineering NLO Chromophores in Noncentrosymmetric Crystal Environments. Comprehensive introductions of the NLO properties of organic molecules have been reported in many reviews and textbooks[25,26] and, therefore, will not be presented here. Nevertheless, it might be helpful to remind the reader that the molecular NLO response is expressed from the polarization (μ) of the molecule subjected to a laser light:

$$\mu(E)= \mu_0 + \alpha E + \beta E^2 + ... \qquad (1)$$

In this expression, μ_0 is the permanent dipole moment, α the linear polarizability, and β the quadratic hyperpolarizability (origin of the NLO response), E being the electric field component of the laser. The largest β values are obtained when the molecules contain π-electronic systems with charge asymmetry arising from contributions of the substituents-induced asymmetry. This situation is optimized with "push−pull" molecules in which the magnitude of β can be correlated with the electron-donating and -accepting strength of the substituents. The archetypal model that fulfills these requirements is *p*-nitroaniline (*p*-NA, Figure 1).

The polarization of a macroscopic material is again given by an expression analogous to (1), where the macroscopic polarization (P) is expressed as follows:

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + ... \qquad (2)$$

$\chi^{(2)}$ is the quadratic susceptibility and is related to the underlying β. An important point to note is that, for $\chi^{(2)}$ to be nonzero, the material needs to be noncentrosymmetric. Consequently, the search for materials with efficient quadratic nonlinearities has to be conducted in two steps for (i) designing molecular structures with large β and (ii) engineering the chromophores into noncentrosymmetric environments. The oldest strategy in solid-state engineering for $\chi^{(2)}$ NLO materials is based on noncentrosymmetric crystal growth. The bulk NLO properties of crystals is frequently evaluated from the efficiency of a powdered sample in second-harmonic generation (SHG)[27] or as the d_{33} component of the $\chi^{(2)}$ tensor in thin films materials. We will now report on various engineering approaches that have been pro-

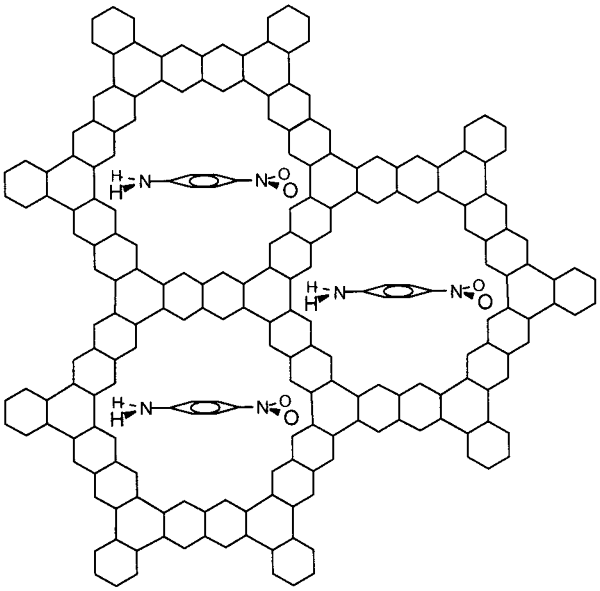

Figure 2. Cross-sectional view proposed for VPI-5 (*p*-NA) hybrid obtained by inclusion chemistry, according to ref 32a.

posed to obtain noncentrosymmetric organization of organic chromophores in inorganic host structures.

II.2. Inclusion Compounds. The first "host–guest" structures in which NLO chromophores were inserted to promote noncentrosymmetric solid-state environments were those of *p*-nitroaniline and derivatives in β-cyclodextrins.[28,29] Following the initial investigations, Eaton et al. have tested other host structures such as thiourea and tris(*o*-thymotide).[30] Although the resulting materials were purely organic, this general strategy for engineering NLO chromophores in various host structures pointed out that noncentrosymmetric crystals could be obtained even when neither the guest nor the host species alone crystallized in a noncentrosymmetric environment. Various dipolar molecules inserted into channel-type architectures of perydrotriphenylene were recently reported by Hulliger. Interestingly, the author uses Markov's theory to rationalize the polar self-assembly occurring during the synthetic process.[31]

The "host–guest" approach was extended to inorganic hosts (e.g., molecular sieves) by Stucky et al.[32] Various chromophores such as *p*-NA and MNA have been included in aluminophosphates molecular sieves such as ALPO-5,[33] ALPO-11,[34] and VPI-5,[35] which all offer one-dimensional channel structures, with diameters in the range 5–15 Å. These inorganic hosts have the advantages of rigidity as well as thermal and chemical stabilitiy over organic hosts. On the other hand, they are usually difficult to obtain as large single crystals, and limitations of this methodology come from the dilution of the chromophores, which occurs in the inclusion process, and from the diameter of the channels which prohibits the use of large guest species. Nevertheless, some SHG signals have been reported, which reach 10^3 times that of quartz in the best cases, a rather low value compared with that of pure MNA (10^6 times that of quartz).[36] Model structures have been proposed for these guest–host hybrids (Figure 2).

Porous zirconium phosphonate have also been reported to exhibit very high surface area with various potential applications.[37] In some cases, reactive hybrid materials have been obtained, in which photoreductions of the inserted organic species was observed.[38] A hybrid material made of (4′-(dimethylamino)-1-methylstilbazolium)$^+$ (DAMS$^+$, Figure 3) NLO cation intercalated in layered γ-ZrPO$_4$(H$_2$PO$_4$)$\cdot$2H$_2$O phases has been reported by Coradin et al. with a SHG efficiency equal to that of urea at 1.907 μm.[39] Compared with other host–guest systems built up from molecular sieves, layered materials can undergo large modulations of their basal spacing and therefore accommodate much larger chromophores.

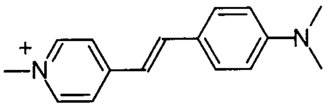

Figure 3. 4′-(Dimethylamino)-1-methylstilbazolium cationic dye (DAMS$^+$).

NLO materials obtained by intercalation chemistry have been reviewed.[40] Besides zirconium phosphates, other layered inorganic hosts have been investigated such as bentonite, a cation-exchangeable clay in which DAMS$^+$ was successfully inserted at room temperature. The resulting hybrid exhibited a modest SHG efficiency (0.25 times that of urea at 1.34 μm).[41] Finally, the most efficient hybrid NLO material obtained from intercalation chemistry was DAMS$^+$ intercalated into Cd$_2$P$_2$S$_6$, a lamellar chalcogeno phosphate phase. The resulting compound of formula Cd$_{0.86}$PS$_3$\{DAMS\}$_{0.28}$ exhibits a SHG efficiency 750 times that of urea at 1.34 μm.[42] It may be interesting to emphasize that although the native Cd$_2$P$_2$S$_6$ crystallizes in a centrosymmetric space group, it can yield noncentrosymmetric intercalates. This surprising result was tentatively explained by the observation that the intercalated species undergo strong intermolecular interaction and form *J*-type aggregates along the inorganic galleries,[43] a situation previously reported to favor noncentrosymmetric packing of molecules and, hence, SHG properties.

II.3. Organomineral Hybrid Salts. To increase the intermolecular cohesion of organic crystals, several investigations have been aimed at combining organic NLO cations and inorganic anionic moieties. The resulting hybrid salts exhibit the SHG efficiency of the organic entity and the structural stability of the inorganic counterpart. The first materials have been based on the H$_2$PO$_4^-$ anion, an entity capable of long-range anion–anion interactions by means of hydrogen bonds, thus forming a mineral polyanionic structure.[44] A representative example that successfully applied this strategy is provided by the report of 2-amino-5-nitropyridinium-dihydrogenphosphate (ANPDP) by Kotler et al.[45] In this compound, the H$_2$PO$_4^-$ layers are strongly interacting with the pyridinium moieties, which leads to mineral networks with organic NLO chromophores tightly inserted between in a noncentrosymmetric solid-state environment. The d_{33} value is equal to 12 pm/V for ANPDP at 1.34 μm.

Various noncentrosymmetric structures built from 4-nitrophenol have also been obtained by the formation of metal phenolate. This route leads to the formation of a robust inorganic network with mechanical hardness and very stable crystal packing, while the hyperpolarizability of the phenolate is enhanced versus that of the phenol-based molecule.[46,47] In this series, a magnesium

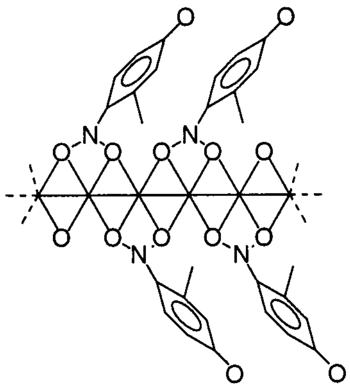

Figure 4. Herringbone motifs built through NaO_6 edge-shared octahedra in sodium 3-methyl-4-nitrophenolate dihydrate.

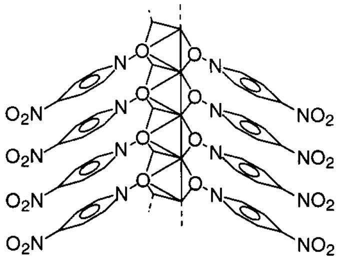

Figure 5. Schematic herringbone structure of bis-(4-nitropyridine-*N*-oxide) cadmium dichloride (*Fdd*2 space group).

derivative (magnesium bis-nitrophenolate dihydrate) of *C*2 symmetry has been reported.[48] However, most of these metal phenolates hybrid structures are based on sodium salts. Their common structural feature is the organization of the anions in herringbone motifs built through NaO_6 (usually edge-shared) octahedra. A representative example is the report by Nicoud and coworkers[46b] that 3-methyl-4-nitrophenolate sodium dihydrate (Figure 4), which crystallizes in the *Cc* space group, exhibits a SHG efficiency equal to that of the well-known 3-methy-4-nitropyridine-1-oxide (POM).[49]

Similarly, the anchorage of 4-nitropyridine-*N*-oxide onto $CdCl_2$ through metal−oxygen bonds has been achieved by Pécaut et al.[50] The structure of the resulting hybrid material is shown in Figure 5. 4-Nitropyridine-*N*-oxide is a neutral molecule, but the same herringbone pattern moieties makes this derivative very close to the NaO_6-based NLO materials previously reported. The SHG efficiency has been found to be equal to that of KH_2PO_4 at 1.064 μm.[24]

Among alternative anionic structures that have been under investigation, it may be interesting to mention that monohydrogentartrate lattices have received a lot of attention.[51−53] Although, L-tartaric acid is an organic acid, the resulting compounds may be considered as belonging to the same category of organomineral structures. Furthermore, L-tartaric acid is chiral, which guarantees that the crystallization of the hybrid material will occur in a noncentrosymmetric space group and therefore ensures a nonzero SHG efficiency.

II.4. Sol−Gel Inorganic Matrix Bearing NLO Chromophores. The sol−gel process, which is mainly based on inorganic polymerization, is a chemical synthesis method initially used for the preparation of glasses and ceramics. Because of unique low-temperature processing characteristics, the design of many organic/inorganic hybrid materials by the sol−gel approach has rapidly become an important field of research in materials science.[54] Because of the inherent properties of the silica matrix, the physical properties of these hybrid compounds address most of the issues related to practical device fabrication related to NLO materials: thermal stability, low optical loss, and high glass transition temperature (T_g). In this respect, hybrid materials obtain by sol−gel processes offer an alternative to the traditional poled polymers, which suffer from orientational relaxation problems, once the NLO chromophores have been poled above T_g under strong electric fields. Although several promising high T_g polymers (e.g., polyimides) have been recently reported,[55] relaxation problems remain an intrinsic weakness in the poled polymer approach.

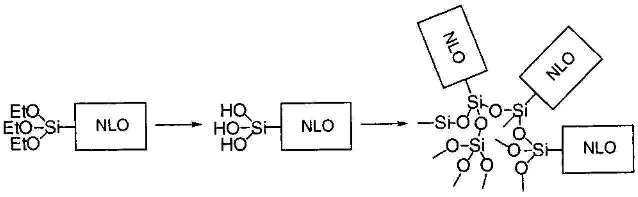

Figure 6. Chemical bonding of NLO chromophores into sol−gel matrixes.

Early NLO studies based on the sol−gel procedure have been reviewed by Dalton et al.[6b] Up to now, the most usual precursors that have been extensively used are based on organic NLO chromophores, which are chemically bound to tri(alkoxy)silanes before hydrolysis and polycondensation in the presence of an electric field.[56] This basic strategy is illustrated in Figure 6. The polycondensation reaction is extremely slow at room temperature for the sol−gel silica film system. This is why the chromophores are still able to align under the electric field. Owing to the high T_g of the silica matrix (>1000 °C), these hybrid systems prepared by sol−gel processes are the candidates which may retain the largest temporal stabilities.

Organic/inorganic materials based on NLO species locked into a silica network are still attracting intense research activity. For instance, Jiang and Kakkar have recently reported on a compound based on the well-known Disperse Red One (DR1) dye, which exhibits a T_g equal to 297 °C and quadratic susceptibility ($\chi^{(2)}$) of 37×10^{-8} esu.[57] The hybrid structure is shown in Figure 7. No decay of the SHG signal was observed after 1 month at 80 °C.

Another promising idea is to introduce multialkoxysilane groups at both ends of a chromophore, which leads to a precursor used to prepare a viscous prepolymeric solution. The solution can be spin cast, and the resulting films are poled at high temperature to form heavily cross-linked three-dimensional silicate networks with both ends of the chromophore anchored. For instance, Dalton and co-workers[58] have reported on a 4-(2-hydroxyethylsulfonyl)-4′-[*N*,*N*-bis(2-hydroxyethyl)-amino] azobenzene dye (Figure 8), which, after incorporation into a silica matrix, exhibited a SHG response (d_{33}) of 27 pm/V at 1.064 μm and retained more than 80% of its initial value after 500 h at 100 °C. A related hybrid system was later optimized by Sung et al.[59] These authors obtained a thermally stable 4-[4″-aminophenyl)sulfonyl]-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]

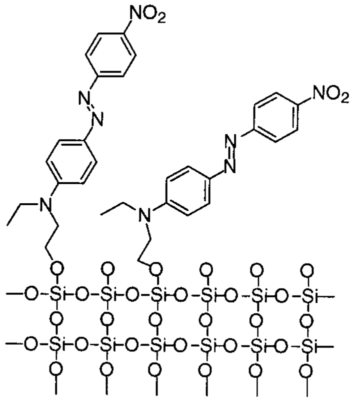

Figure 7. Disperse Red One (DR1) organic dye in a sol−gel silica matrix.

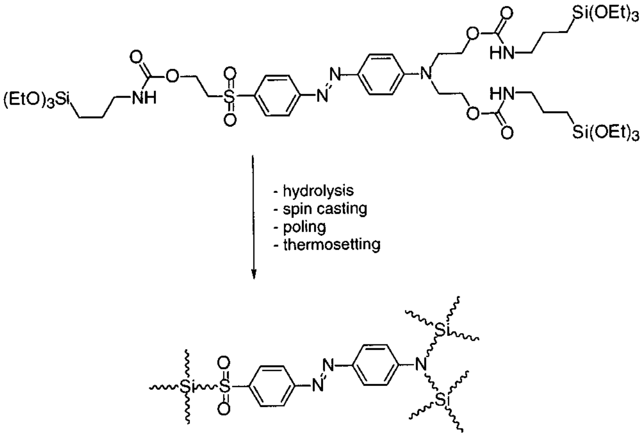

Figure 8. Example of NLO chromophore heavily cross-linked into a hardened sol−gel network.

azobenzene dye (decomposition temperature of 270 °C), which revealed a d_{33} value equal to 32 pm/V after incorporation into a silica matrix and no significant decay at temperatures up to 130 °C.

Various polymers containing NLO-active chromophores covalently bound to siloxane-linked backbones have also been prepared, with large NLO response and high glass transition temperature. However, they belong to the field of high T_g polymers rather than sol−gel materials.[60]

II.5. Self-assembled Hybrid Materials. By contrast to the previous inclusion (or intercalation) approaches, which are one-step strategies, self-assembly implies the repeated addition of monolayers onto a planar substrate. The bulk materials arise from multilayer interfacial organizations constructed at the solid/liquid interface. The resulting structures are close to those obtained by intercalation chemistry, but the alignement of the chromophores (and hence the non-zero SHG response of the materials) is guaranteed by the appropriate layer-by-layer synthetic procedure. Although the development of this technique seems to be hampered by the long time required by the sequential treatments, progress has been achieved, and film thickness around 1 μm may be obtained within a couple of weeks.[61]

The first substrate for such investigations is silica. In 1990, Marks and co-workers reported on an organosilicon-derived material composed of alternating inorganic and organic layers (Figure 9a).[62] In this material, the NLO chromophores are bifunctional stilbazole precursors locked in place by siloxane condensation reactions. The resulting hybrid material revealed a robust structure and a $\chi^{(2)}$ value in excess of 10^{-7} esu.

Another self-assembled hybrid system is based on zirconium phosphate. The capabilities of metal phosphate and phosphonate for the design of organic/inorganic molecular materials with various applications have been reviewed.[63] In particular, Katz et al. have reported that zirconium phosphonate-based self-assembled structures could lead to efficient NLO materials.[64] The resulting multilayer films are illustrated in Figure 9b. A NLO response of the same order of magnitude as $LiNbO_3$ was observed. Compared to Langmuir−Blodgett films, all these composite systems show better stability and very good transparencies.

III. Organic Chromophores in Magnetic Inorganic Structures

The following section will be divided into three parts to distinguish hybrid materials obtained by (i) intercalation or (ii) insertion chemistry. A last part (iii) will be devoted to a critical evaluation of the possibility to achieve an efficient interplay between magnetism and NLO properties.

III.1. Hybrid Materials Designed by Intercalation Chemistry. Intercalation (vs insertion) is used here to describe a process in which the host inorganic structure is present before the synthesis takes place. Therefore, intercalations imply heterogeneous reactions between solid phases and solutes containing the guest species. As a major consequence, it is usually not possible to obtain single crystals with this technique, and few structural data are available on these hybrid systems. Of course, this limitation will not be applied to insertion chemistry.

In section II.2., the intercalation of $DAMS^+$ (Figure 3) into $Cd_2P_2S_6$ has been mentioned, which leads to a highly SHG efficient hybrid material. $Cd_2P_2S_6$ belongs to a class of metal hexathiohypodiphosphates of general formula $(M^{II})_2[P_2S_6]^{4-}$ extensively studied by Hahn and Klingen.[65] These materials exhibit various types of intercalation chemistry.[66] In particular, Clément et al. have shown that $Mn_2P_2S_6$ reacts spontaneously with aqueous solution of various salts (C^+A^-) to give a compound of general formula $Mn_{1-x}PS_3\{C\}_{2x}$.[67] In these compounds, charge balance is maintained by loss of one Mn^{2+} ion from the intralayer region for every two C^+ intercalated in the interlayer region. Moreover, while the pristine host lattice $Mn_2P_2S_6$ is a two-dimensional Heisenberg antiferromagnet, with a Néel temperature of 78 K,[66] several of its intercalation compounds are found to exhibit spontaneous magnetization below 40 K.[67]

A compound of formula $Mn_{0.86}PS_3\{DAMS\}_{0.28}$ was obtained by intercalation of $DAMS^+$ into $Mn_2P_2S_6$.[42] The hybrid material exhibits a SHG efficiency 300 times that of urea, which reveals a spontaneous poling of the dyes between the slabs. Beside the large NLO response, the $Mn_{0.86}PS_3\{DAMS\}_{0.28}$ intercalate becomes a magnet at 40 K with a magnetization around 400 emu. This behavior has been related to the intercalation process, which destroys the spin balance by creating ordered vacancies in the Mn^{II} ion sublattice.[68] This material was the first one exhibiting both large NLO response and

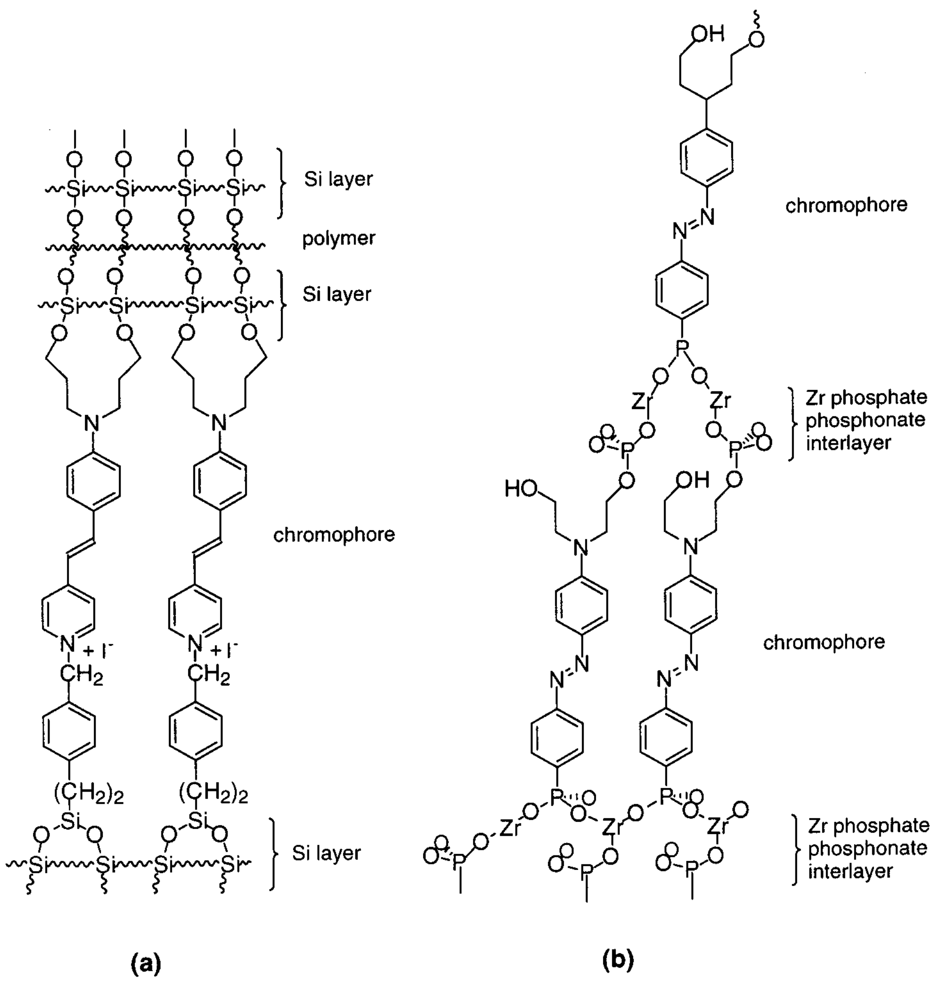

Figure 9. Schematic structure of self-assembled multilayer materials based on organosilicon (a) and zirconium phosphates (b).

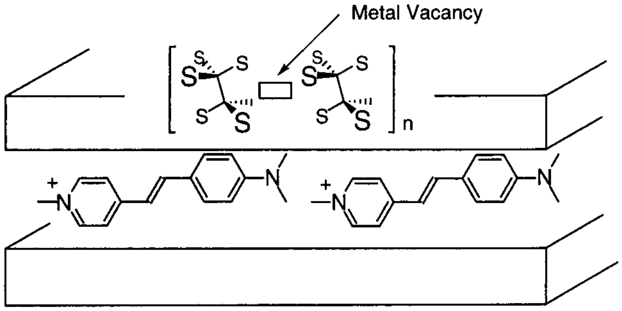

Figure 10. Model structure for the hybrid $Mn_2P_2S_6$ intercalated with $DAMS^+$.

permanent magnetization at rather high temperature.[69] Although some progress has been made by O'Hare et al. toward a comprehensive structural description of the intercalation compounds of $Mn_2P_2S_6$,[70] finding a rationale for a possible magnetic−NLO property relationship in these systems is hampered by the lack of a suitable single crystal. This remains a very challenging issue. Nevertheless, a schematic structure is presented in Figure 10. Owing to the 12.55-Å interlamellar spacing evidenced from the Seeman−Bohlin diffraction pattern, the $DAMS^+$ species undoubtly stand "edge on" or perpendicular with respect to the slabs.

Later on, this result was extended to few other organic dyes based on the same stilbazolium skeleton.[43] However, it is important to point out that this methodology must be restricted to a limited number of chemical modifications achieved on the $DAMS^+$ skeleton.

III.2. NLO Chromophores into Inorganic Ferromagnets. In the field of molecular magnetism, two-dimensional bimetallic oxalate-bridge networks have attracted increasing interest in recent years. This class of compounds shows a general stoichiometry of the type $(C)^+[M^{II}M'^{III}(ox)_3]^-$, where ox^{2-} is the oxalate $(C_2O_4)^{2-}$ and C^+ is an organic cation, most usually a bulky ammonium or phosphonium $[XR_4]^+$ species. Their interest arises from their ferro- or ferrimagnetic properties exhibited by the inorganic layers at low temperature.[71−74] The design of hybrid NLO−magnetic materials has recently been considered through a strategy aiming at replacing the "innocent" C^+ cation by a highly polarizable species. A first report by Gu et al. was based on $DAMS^+$, but no NLO properties were descibed.[75] Later on, Yu and co-workers observed that methoxyheptyl stilbazolium (MHS^+) cations embodied in $[Mn^{II}Cr^{III}(ox)_3]^-$ anionic layers lead to a derivative, which exhibits a SHG efficiency 100 times that of urea (at 1.907 μm) and a permanent magnetization, 5.7 K.[76] A schematic representation of both an organic cation and inorganic anionic layer is shown in Figure 11.

The only reported crystal structures in this series being those of $(NBu_4)[Mn^{II}Cr^{III}(ox)_3]$[77] and $(PPh_4)[Mn^{II}Cr^{III}(ox)_3]$,[78] the authors assumed that all these materials are lamellar and isostructural. The noncentrosymmetric *R*3*c* space group is consistent with the observation

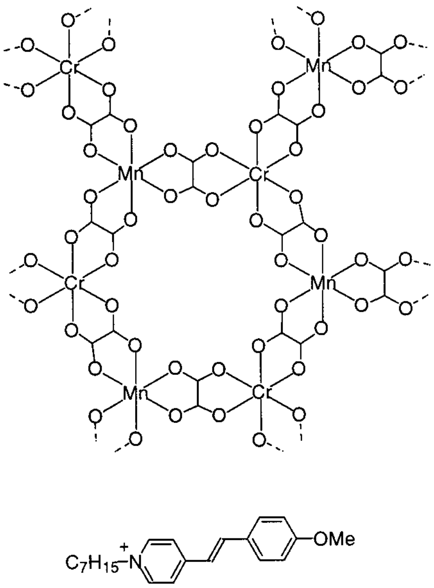

Figure 11. Schematic view of the anionic layer (top) and NLO cation (bottom) in $(MHS)^+[Mn^{II}Cr^{III}(ox)_3]^-$.

of a bulk NLO response in the hybrid material. Finally, a very recent paper by Clément et al. has provided a set of 35 layered compounds in the $[(C)^+[M^{II}Cr^{III}(ox)_3]^-$ series with five different metals (M = Mn, Fe, Co, Ni, Cu) and seven stilbazolium-shaped organic dyes.[79] All these hybrid structures order ferromagnetically at Curie temperature in the 6−13 K range, and two-thirds of them exhibits SHG efficiencies. Up to now, no crystal structure has been reported for the SHG active materials. Nevertheless, the structure−magnetic property relationships are well understood, and additionnal investigations conducted on this family of magnets have revealed that the magnetization is directed perpendicular to the anionic layer (easy axis of magnetization).[80,81]

III.3. An Interplay between Magnetism and Quadratic NLO Response? The issue of possible interplay between magnetism and NLO properties is naturally addressed in the aforementioned hybrid materials. The past few years have witnessed a growing interest in the incorporation of switchability into quadratic NLO materials.[82] Along this line, most investigations have been based on photoexcitation, and the NLO properties of photochromic materials have recently been reviewed by Delaire and Nakatani.[83] Up to now, very few reports have pointed out that NLO switches could be induced by a magnetic phenomenon. The possibility for a modulation of the cubic NLO response upon spin transition has been envisioned by Létard et al.[84] However, the effect has been suggested but not observed yet. A recent theoretical investigation has also revealed that the $S = 0 \rightarrow 2$ spin crossover in an iron(II) complex should result in an increase of the quadratic NLO response of about 25% of the initial value.[85] Nevertheless, to be fully convincing, a switch should be attached to “on and off” behavior, which has not been observed yet.

Hybrid materials in which the NLO species are located in close proximity to magnetized inorganic lattices might offer an alternative strategy toward a possible interplay. At this point, it has to be considered that the traditional NLO approach is based on the framework of a dielectric subjected to an electric field. In this approach, no magnetic effect will interfere with the NLO response. At a deeper theoretical level, the usual NLO framework could be enlarged to encompass both electric and magnetic dipole transitions, leading to generalized mixed electric−magnetic contributions to the NLO tensor.[86] However, in the present hybrid structures, the magnetic and NLO components are fairly well separated, and it can be assumed that the magnetization has no effect on β. By contrast, the propagation of the light is usually affected by magnetic properties, which should result in a modification of the NLO response.

Among various magneto-optical effects, the most familiar is the rotation of the axis of linearly polarized light which occurs upon passage through a magnetized material. This is commonly called the Faraday rotation.[87] For diamagnetic or paramagnetic materials, the magnetic rotation (θ) is expressed as

$$\theta = VBl \tag{3}$$

in which B is the applied magnetic field, l the thickness of the sample, and V the Verdet constant. Large V values are in the range 10−100 deg cm^{-1} T^{-1}, which corresponds to modest Faraday rotations. By contrast, θ no longer depends on the external magnetic field but on the internal magnetization in the case of propagation through a permanent magnet. The specific rotations (θ_F) of magnetic materials scale over many decades and can reach as high as 10^5−10^6 deg cm^{-1},[88,89] which leads to large rotations even upon transmission through thickness around 1 μm.

A quantification of the modifications occurring in the NLO response of a hybrid layered material such as $Mn_{0.86}PS_3\{DAMS\}_{0.28}$ or $(MHS)^+[Mn^{II}Cr^{III}(ox)_3]^-$, which undergoes a transition from a paramagnetic to a ferromagnetic state, has recently been proposed.[90] As previously mentioned, the magnetization is directed perpendicular to the anionic layer in these systems.[80,82] Owing to the elongated shape of the NLO chromophores in the stilbene series, it can be assumed that the hyperpolarizability tensor (β) will likely be parallel to the slabs and hence perpendicular to the magnetization in most of these hybrid materials. This situation is depicted in Figure 12, where a laser beam is polarized along OX ($E_0 = E_X$), and the magnetization directed along OZ. Within this model, the modulation of the light intensity (I) induced by Faraday effect has been calculated for $\theta_F = 10^4$ deg cm^{-1} in Figure 13. It appears that the effect is much larger on the SHG intensity than on the ω counterpart.[90] According to this analysis, the SHG signal is expected to be reduced upon passage through a magnetized material.

At this point, it is important to emphazise that such behavior has never been unambiguously observed. This would imply the design of a compound available as large and transparent single crystals, exhibiting large quadratic NLO response and high-temperature magnetic phase transition. To the best of our knowledge, materials fulfilling all the above requirements have never been reported. Nevertheless, a suggestive test has been performed on $Mn_{0.86}PS_3\{DAMS\}_{0.28}$.[90,91] Although the NLO properties had to be measured by reflection on a powdered sample, which prevents any quantitative estimation of the modulation, it was observed that a

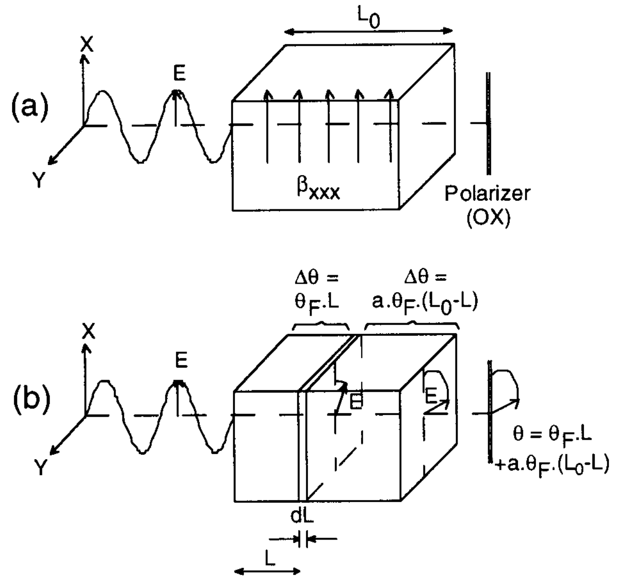

Figure 12. (a) Experimental setup assumed in the calculation of the effect of a magnetic transition on the NLO properties of an idealized one-dimensional material. The magnetization is along OZ. (b) Faraday rotation on *E* (redrawn from ref 90).

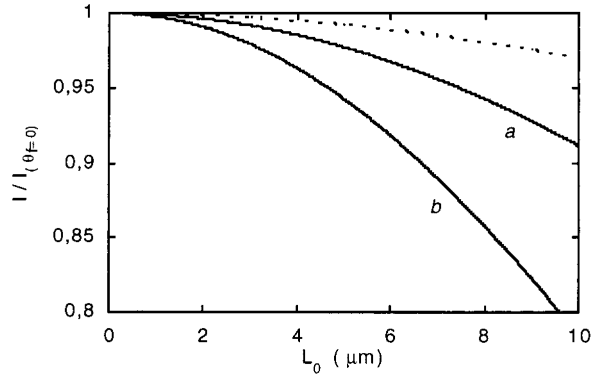

Figure 13. Modulation of the SHG light intensity induced by the Faraday effect ($I/I_{\theta_F=0}$) with $\theta_F = 10^{-4}$ deg cm^{-1}, for $\theta_{F(2\omega)} = 2\theta_{F(\omega)}$ (a) and $\theta_{F(2\omega)} = 4\theta_{F(\omega)}$ (b). The effect at ω frequency is given as a reference (dotted line). (Redrawn from ref 90.)

magnetic field causes a decrease of the SHG intensity of about 10%, as the temperature is lowered below T_c. Although not fully conclusive, this test suggests that the magnetic–NLO property relationship deserves more attention in the future.

IV. Organic Chromophores in Conducting Inorganic Structures

IV.1. Combining Conductivity and Quadratic NLO Response. A review on organic/inorganic supramolecular assemblies exhibiting various conducting properties was reported in 1997 by Ouahab with a special focus on a possible synergy between conductivity and magnetism.[92] By contrast, the investigation of the interface between conducting and NLO properties is a rather new topic, which, however, might deserve some interest in the future for its potential applications in technologies aiming at combining both properties. For instance, the technology of optoelectronics, which needs to integrate photonic devices with standard semiconductor electronics to combine the information processing capabilities of electronics and the speed of the light, has made the need for photonic–electronic compatible materials pressing. The need for integrated optical interconnects in electronic systems is of prime importance, in relation to the fact that there is an exponential growth in cost per interconnect with the length of the interconnect.[93] Given this economical pressure, there is a driving force to condense more functions locally on the same system. NLO crystals such as $LiNbO_3$ are good candidates for photonics, but not easy to incorporate into electronic devices. On the other hand, silicon is the material of choice for semiconductor-based electronics, but it is not suitable for the implementation of optical functions such as light emission and modulation, although several strategies are being considered to realize Si-compatible optoelectronics.[94,95]

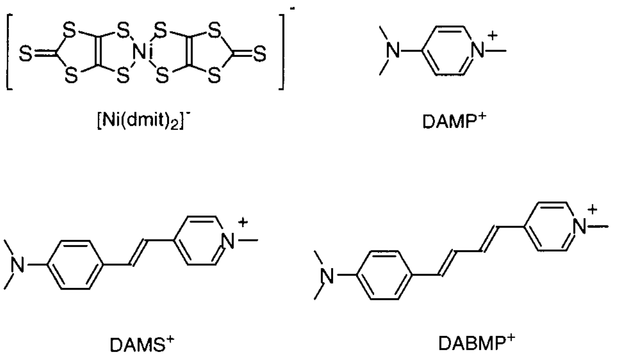

Figure 14. Building blocks used to design hybrid salts combining NLO chromophores and inorganic conducting network.

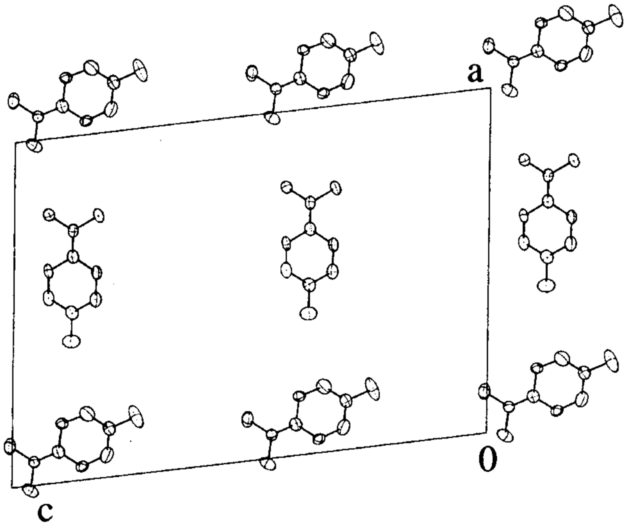

Figure 15. Projection of cationic layers onto the *ac* plane in $(DAMP)^+[Ni(dmit)_2]^-$ (redrawn from ref 107).

Linking conductivity and NLO properties at a molecular level is a challenging target, even if the possibility of using such materials in an operating electro-optical device may still remain somewhat speculative. First, the important issue of transparency/conductivity trade-off must be addressed for these hybrid systems. Electric conductivity usually requires the use of mixed valence compounds, in such a way that an electron can jump from one entity to the neighboring one. On the other hand, electron sharing is associated with broad electronic bands, which usually implies a modest transparency on a large frequency domain.[96] Although semiconductors may exhibit good transparency in the near-IR

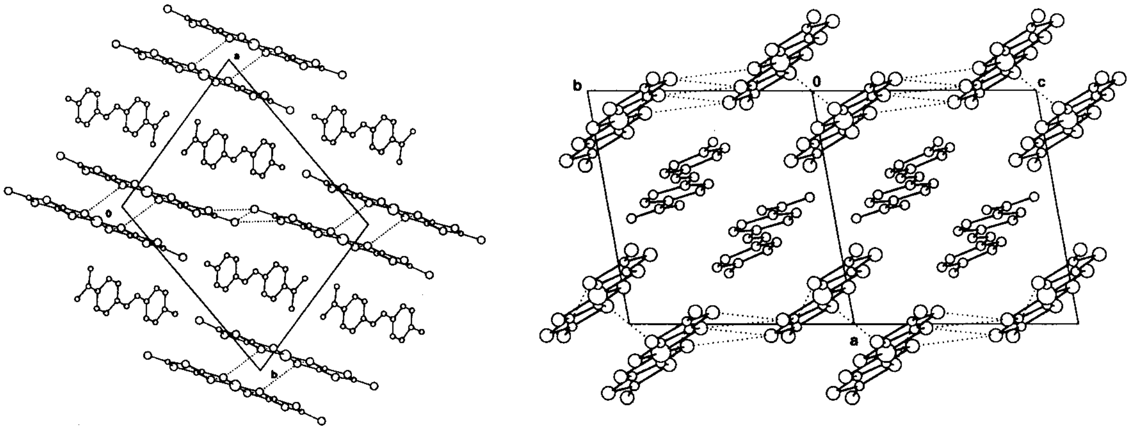

Figure 16. Projection of $(DAMS)^+[Ni(dmit)_2]^-$ onto the *ab* plane (left) and $(NOMS)^+[Ni(dmit)_2]^-$ onto the (011) plane (right), redrawn from ref 108. In the case of $NOMS^+$, the better adjustement between the redox potentials of cations and anions leads to strongly interacting species.

domain, where many optoelectronic devices are operative (1.3 and 1.5 μm),[95,97] molecular materials combining NLO and conductivity could either be poorly conducting or very absorbant. Nevertheless, future photonics, which requires ultra-short (sub-pico) pulses of light,[98] should benefit from the use of micrometer-thick materials to avoid velocity dispersion during the transversal of the devices. The absorbance of such devices could therefore be very limited.

At first, it seems possible to link NLO and conductivity in a salt, as both properties deal with the same general concept of charge transfer: an intermolecular charge transfer along stacks of ions in conducting systems and an intramolecular charge transfer between a donor (D) and an acceptor (A) counterpart in NLO systems. The possibility of π-overlaps between the ions could modulate the overall electronic structure, which would be desirable for linking the properties. In the next section, the very few examples in which NLO chromophores have been embodied in inorganic conducting structures by mean of this methodology will be summarized.

IV.2. Organic Chromophores between Nickel Bis(dithiolene) Slabs. Various materials combining conducting and quadratic NLO properties have appeared in the literature. Among them, photorefractive polymers have become a very active research area.[99−101] The photorefractive effect is based on a combination of photoconductivity and electro-optic response, a property related to the quadratic NLO behavior. In the field of molecular materials, few investigations have been reported in which NLO chromophores were combined with tetracyanoquinodimethane (TCNQ). The resulting materials were observed to exhibit conducting properties and quadratic optical nonlinerities in some cases.[102−104] A theoretical investigation by Di Bella et al. have also suggested that charge transfer between $TCNQ^-$ and appropriate counterions would lead to very large NLO responses.[105]

We have recently reported on a strategy aiming at combining conducting inorganic layers built up from nickel bis(dithiolene)metal complexes ($[Ni(dmit)_2]^-$)[106] and various highly polar cyanine dyes, 4-(dimethylamino)-1-methylpyridinium ($DAMP^+$), 4-(dimethylamino)-1-methylstilbazolium ($DAMS^+$), and 4-[4-(4-dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium ($DABMP^+$), shown in Figure 14.[107] The structures of these hybrid 1:1 salts are made of inorganic slabs of strongly interacting $[Ni(dmit)_2]^-$ units with organic cations inserted in between. Within each $[Ni(dmit)_2]^-$ layer, a two-dimensionnal S···S network ensures significant conductivity, which reaches $1.3 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ in the case of $(DAMP)^+[Ni(dmit)_2]^-$. This compounds reveals an additionnal interesting structural feature. Although the structure is monoclinic, with centrosymmetric space group ($P2_1/c$), the $DAMP^+$ cations are arranged in a noncentrosymmetric fashion within their own layer, as shown in Figure 15.

Later on, the possibility for π-overlaps between the inorganic moiety and the NLO cations has been discussed with the aim of finding a strategy toward a modulation of the overall electronic structure and hopefully a possible interplay. 4-Nitro-1-methylstilbazolium ($NOMS^+$), instead of $DAMS^+$, was combined with $[Ni(dmit)_2]^-$.[108] Interestingly, both cations have the same shapes and volumes, but different redox potentials ($NOMS^+$ being more reducible than $DAMS^+$). The differences between the crystal structures of $(NOMS)^+$-$[Ni(dmit)_2]^-$ and $(DAMS)^+[Ni(dmit)_2]^-$, which, to a large extent, accounts for the redox potential differences, reveal that $NOMS^+$ is more strongly interacting with the oxidable anionic layers than $DAMS^+$, with π-overlaps and short intermolecular distances between anions and cations (Figure 16). These structural features strongly suggest that the adjustment in the redox potentials of the cations (C^+/C^0) and the anions (A^-/A^0) is the key toward actual electron sharing.

Furthermore, the β dependence upon charge transfer has been theoretically investigated on $NOMS^+$ within the framework of the density functional theory (DFT). The data clearly show that a reduction process ($NOMS^+ + e^- \rightarrow NOMS^0$) can change the sign and magnitude of the hyperpolarizability (Figure 17), thus providing evidence for the possibility of tunable molecular NLO responses through intermolecular charge transfers in such systems.[108]

To conclude this section, it may be interesting to discuss several potential interactions, which could take place in these hybrid materials, to illustrate what properties could be combined and how. In the case of conducting layers with NLO species with redox properties inserted in between, it might be expected that a

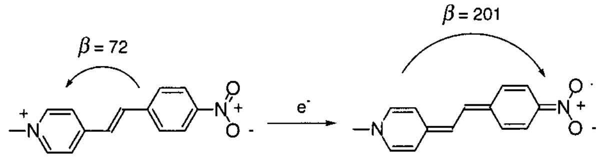

Figure 17. Tuning the hyperpolarizability upon the redox process in the NOMS$^+$/NOMS^0 system.

pulse of electric field would have the potential to stimulate charge transfers between the conducting and the NLO moieties. This behavior can affect the hyperpolarizability in the solid state, providing a route toward a modulation of the NLO response. In the case of chromophores with no expected redox process, the hyperpolarizability of the "insulating" chromophores is not affected by the electric field. However, this situation provides a hybrid device made of NLO materials, inserted between two electrodes at the nanoscale. Materials in which the optical properties can be changed by electric fields are of basic importance for optoelectronics. In particular, it is known that a quadratic NLO medium subjected to a static electric field undergoes a modulation of its refractive index (Pockels effect), which leads to the design of electro-optic modulators.[109] Along this line, the present structure would be the ultimate limit of nano-miniaturization for such an electro-optic device.

Concluding Remarks

Various strategies aiming at engineering organic chromophores into inorganic matrixes have been envisioned in the literature. In the first section we reported on sol−gel and self-assembled techniques which appear to be very general routes toward robust and stable structures. However, they lead to poorly crystallized materials, a weakness which might be of crucial importance when cooperative interactions (e.g., magnetism or conductivity) are to be considered.

Most magnets and conductors actually are centrosymmetric and consequently cannot exhibit any SHG activity. It is therefore not surprising that although the SHG behavior was detected in 1961 for the first time (in quartz),[110] the first observation of a SHG signal in a magnet was reported only recently by Nicoud et al.[111] Furthermore, the magnetization occurred at extremly low temperature in this compound (below 1 K). The report that $Mn_{0.86}PS_3\{DAMS\}_{0.28}$ exhibited a SHG efficiency 300 times that of urea with a spontaneous magnetization at 40 K was a breakthrough in this field.[42] There are now numerous noncentrosymmetric magnets in which various NLO chromophores have been inserted. The observation of an interplay between the properties remains a challenging issue in these hybrid systems, even if theoretical evidence suggests that it could be envisioned. One of the main bottlenecks to the comprehensive understanding of the capabilities of these systems is undoubtly related to the difficulties encountered in growing large crystals suitable for structure determination and single-crystal laser experiment. Although it has not been achieved yet, there is no reason to think that these problems should not be overpassed in the future.

As observed in the case of magnets, most molecular conductors crystallize in centrosymmetric space groups. A survey of the Cambridge Data Base reveals that only three structures based on $[Ni(dmit)_2]^-$ in more than 100 enties actually are noncentrosymmetric. The large size, centrosymmetric shape, and strong tendency for a two-dimensionnal S···S network observed in $[Ni(dmit)_2]^-$ can probably account for this structural feature, whatever the nature of the counterion. To overpass this difficulty, the design of hybrid materials made of chiral NLO chromophores embodied in $[Ni(dmit)_2]^-$ was recently explored.[112] However, the cations are packed in a pseudo-centrosymmetric environment, which leads to vanishing quadratic susceptibilities. Several strategies could be considered to favor more convincing NLO responses: for instance, by increasing the size of the substituents to enhance the "degree of chirality"[113] of these systems or by using hydrogen bonding to extend the range of intermolecular interactions, following an approach which has been fruitful in some cases.[114]

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