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Reviews

Multilayer Deposition of Novel Organophosphonates with Zirconium(IV)

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This is a review covering transition-metal phosphonate surface multilayers investigated at AT&T. Dielectric, luminescent, photocharge generating, and nonlinear optical films have been designed and prepared. A wide range of data relating film structure and performance has been obtained. The future promise of these materials is in the construction of multilayers with more complex or multiple functions, taking advantage of the capability of arranging molecular subunits at specific spacings and relative orientations.

Thin films are the medium through which materials are generally utilized for integrated electronic and optical components.[1] They may serve passive functions such as corrosion protection, adhesion promotion, optical isolation, and pattern definition. More complex activity can include capacitance, rectification, transistor behavior, photoconduction, sensing, and electrooptical switching. To function properly, the films must be dense and often need to be thinner than typical spun polymer films. In addition, regardless of thickness, molecular-level organization is also desirable for certain purposes, and this may be difficult or impossible to obtain by spin-coating or vacuum deposition. Chemisorption of molecular film components onto densely functionalized substrates from solution ("multilayer deposition") provides an alternative method of film preparation where both thinness and organization are obtainable.

Much effort has been devoted to producing the appropriately functionalized, or "primed" surfaces ("monolayers") from which chemisorption-based film deposition may be initiated. Technologically important surfaces such as SiO_2, Au and GaAs, Al_2O_3, Pt, and most recently SiH have been matched with soluble and/or volatile reagents: silyl halides and alkoxides; organothiols; carboxylic acids; isonitriles; and terminal olefins, respectively.[2−6] The correct combination of surface and reagent often yields well-packed monolayers of 10–30 Å with complete masking of the surface. A high number density of the functional group located at the end of the reagent opposite to the surface-active end is projected from the surface and exposed for further interaction or reaction. Surface modification in this manner, by formation of monolayers, is sufficiently well-developed at this time to be considered routine.

On the other hand, *multilayer* deposition, where a sequence of chemisorption steps is repeated so that films 30–1000 Å thick can be prepared, is not nearly as advanced. Pioneering work at the Weizmann Institute[7] and Kodak[8] established silane condensation as a basis for multilayers. The propensity of halosilanes to react with hydroxy-rich surfaces, including silanol-terminated silicon oxides, enables layers to be deposited. Terminal functional groups on the adsorbed silanes that can be converted to hydroxyls through surface reactions allow the depositions to be repeated and layers to accumulate. Since then, this chemistry has been used to prepare films with high two-dimensional order[9] and optical nonlinearity.[10]

Other schemes for multilayer deposition are based on metal–ligand interactions, where distally difunctional ligands and multicoordinate metal ions are sequentially applied. Examples include pyrazines with Ru[11] and dithiols with Cu.[12] It is also possible to alternately deposit polymers with opposite charges;[13] for example, positively charged nitrogen-rich polymers and negatively charged polymeric sulfonates in turn. Very recently, it was shown that exfoliated sheets of the silicate mineral hectorite may play the role of the polyanion.[14]

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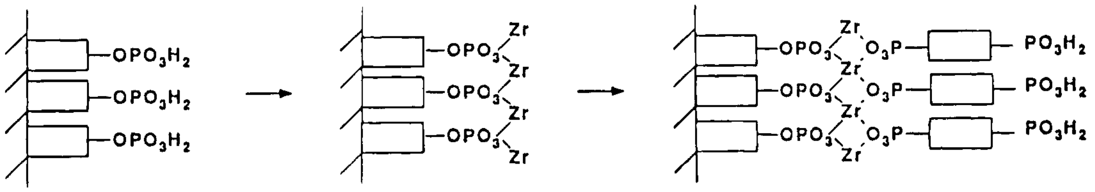
Scheme 1



One of the most versatile classes of multilayer materials is based on the high affinity of many transition metal ions for the phosphonate or phosphate ("P") group.[15] In solid-state chemistry, the metal–P interaction leads to a wide variety of layered and crystalline materials, including the prototypical α-zirconium phosphate, with high solvent resistance, intercalation ability, and the potential for catalytic activity.[16–17] Solvent-cast films of such compounds as microcrystallites on membranes were first prepared by Costantino and Alberti for ion-exchange applications.[18]

The Mallouk group first demonstrated that such materials could be grown on substrates by the deposition of individual layers of metal ions and P compounds.[19] Surfaces were primed with a high density of P groups and ion-exchanged with transition metal ions, particularly Zr^{+4} (Scheme 1). The bound ions are strongly coordinated to the surface P groups on one face but only weakly coordinated to chloride, carbonate, and/or hydroxide on the other. As such, application of a solution of a 1,ω-diP compound to the surface results in displacement of the weak ligands and formation of a monolayer of the diP molecule. Ideally, only one P from each molecule is attached to the surface, while the other is free. Repetition of the ion-exchange process on the free P's and reapplication of diP compound yields a multilayer. A wide range of data on this class of multilayers has been obtained and extensively reviewed.[19] The films are impenetrable to large electroactive ions but may be engineered with porosity that enables size- and shape-selective ion exchange and intercalation, useful for sensing, separation, and catalysis. Molecular recognition of amines and chiral discrimination of enentiomeric amino acid derivatives have been demonstrated.[19] In addition, the detailed structure of these multilayers has been investigated by various spectroscopies, especially FTIR[20,21] (vide infra).

We confirmed early on that the P groups are essential; neither the more weakly acidic biphenyldicarboxylic acid in DMSO nor the more strongly acidic (but more weakly ligating) biphenyldisulfonic acid in water form layers with Zr^{4+} under conditions where many other diphosphonic acids dissolved in aqueous ethanol or DMSO do form layers, with 1-h depositions at room temperature.[22] This is because only the P groups are dissociated and ligating at pH's where the metal ions are Lewis acidic. Many metal ions exist as electron-rich hydroxide or polyoxo complexes, often of low solubility, at pH >4, and are only Lewis acidic below this pH.[23] Since the P groups have first pK_a's of <2, they coordinate strongly to such metal ions in the pH range 1–4.

As we have aimed to incorporate rigid, electroactive subunits in multilayer films, a major synthetic effort has been necessary to prepare the desired subunits with suitably placed P functionality. The new synthetic methods we have uncovered are described in the individual references and will not be covered here. Instead, the structure and properties of various films that we have prepared will be summarized in light of their possible applications to electronics and optics and their potential to lead to interesting heterostructures not obtainable by other means.

Examples of organophosphonates that we have synthesized and deposited are pictured in Chart 1. Aliphatic compounds **1** and **2** were synthesized by standard Arbuzov reactions. Biphenyl compound **3** was prepared by a modified Arbuzov route using diiodobiphenyl and triethyl phosphite, with copper catalysis.[24] Compounds **4**,[25] **5**,[26] **6** and **10**,[27] **7** and **8**,[28] **9**,[29] **11**,[30] and **12–14**[31] were prepared as described in the corresponding original literature. As is obvious from the chart, all of our published work to date has employed relatively small molecules, and these are linked to surfaces and each other with Zr^{4+}. However, the deposition method is much more general than this. Many other transition metals are useful, including lanthanides[32] and first-row lowvalent metals including divalent Mn and Cu.[33] Each metal would have to be optimized for deposition conditions according to its solubility and pH-dependent coordination properties. In addition to monomeric ions,

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(15) In this paper, the symbol "P" will generally refer to phosphonic acid or phosphonate groups. However, in most cases, the chemistry would apply equally well to phosphate groups.

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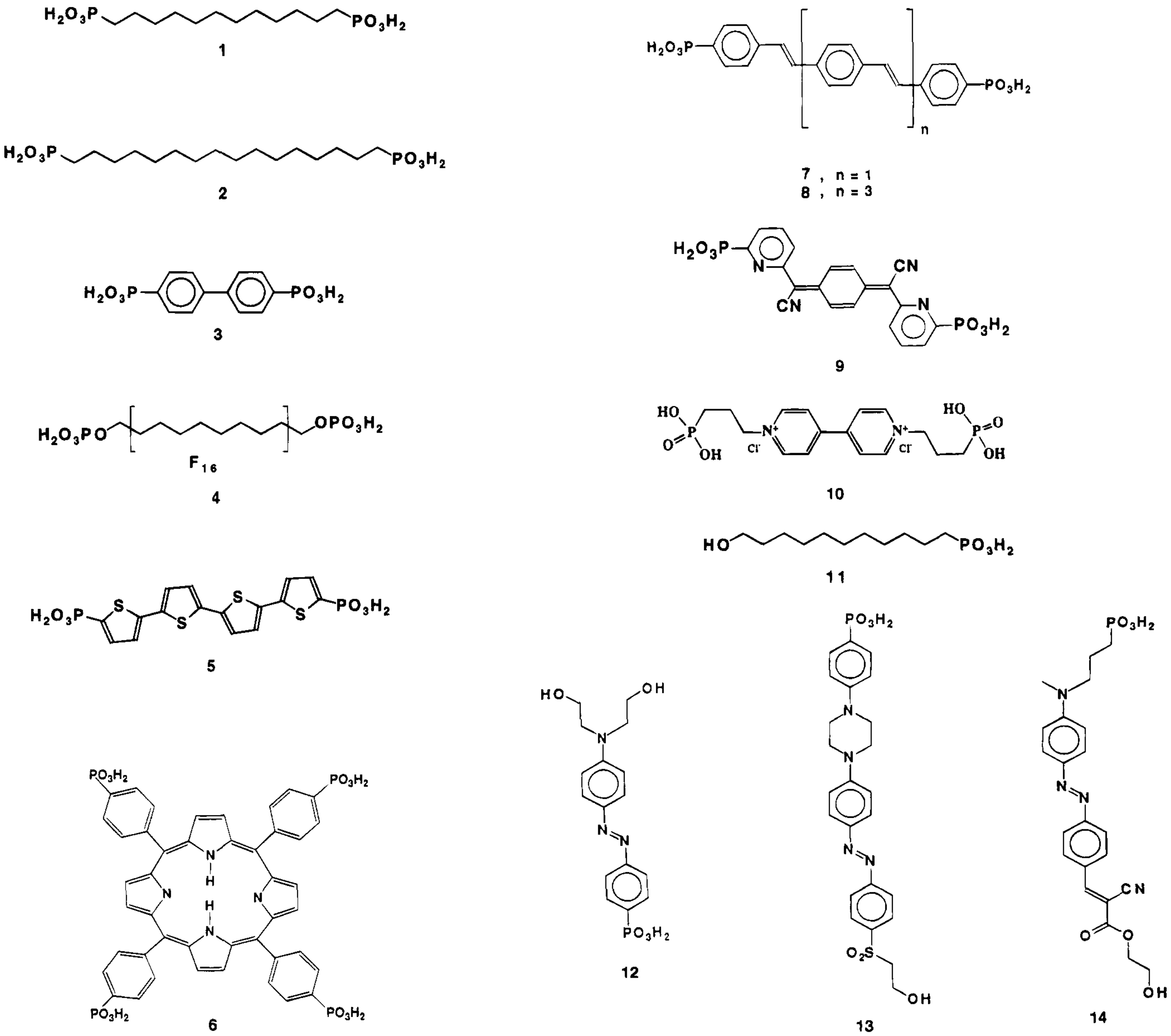
Chart 1



inorganic clusters could conceivably be pillared using this chemistry, as suggested by the recent surface-attachment studies of molecular sieve crystals,[34] semiconductor nanocrystals,[35] and an exfoliated layered silicate.[14] The organic components also need not be monomeric; by analogy to work by Ferguson[14] and also by Rubner,[13c,d] it is likely that P-functionalized polymers could be ion exchanged with excess Zr and then be layered onto the Zr-rich substrates. Furthermore, the P groups may be photodefined from acid-labile polymeric phosphonic ester precursors in thin films using photogenerated acid catalysts. Isopropyl and *tert*-butyl esters of styrylmethylphosphonic acids incorporated in polymers have been deprotected using photoacid generation followed by baking to define regions of the polymers on which dyes and catalysts for electroless metal deposition were selectively deposited.[36]

It is pertinent at this point to briefly compare metal−P multilayers to the much more widely studied Langmuir−Blodgett (LB) films. Both materials exist as very thin films on surfaces, with some degree of molecular organization. LB films are generally better ordered because the film is compressed to a two-dimensional crystal state at the air−water interface before it is applied to a substrate. However, the self-assembled films described here are more mechanically and solvolytically stable than LB films because they are held together by strong coordinative and ionic bonds, instead of weak van der Waals interactions that are the basis for LB film assembly. The self-assembled films can be prepared from molecules of a variety of shapes and functionalities and require no special deposition equipment, while LB films must be prepared in a trough using a film balance from molecules that are either amphiphilic or particularly suited to two-dimensional packing.

Deposition, Structure, and Dielectric Properties

Our films are deposited from concentrated solutions of the phosphonic acids at pH ~3. Heating the solutions above 70 °C greatly speeds the process relative to room-temperature deposition.[26] We have consistently em-

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ployed 5 mM aqueous $ZrOCl_2$ as the transition-metal ion source, as originally suggested,[19] although there is some latitude in the allowable concentration, pH, and counterions in the Zr solutions. The quality of the films is sensitive to substrate cleaning and the initial priming up to a point; use of long-chain thiols and silanes to prepare gold and silica surfaces, respectively, is more effective than shorter analogues. However, use of a poorly cleaned silicon substrate with a 19-carbon silane primer did not result in an inferior Zr–organophosphonate multilayer, even though the silane priming layer was in fact more disordered.[37]

Many analytical techniques have been used to ascertain the nature of the films, especially at early stages of growth.[38] Some of these techniques indicate that the deposition chemistry is very well controlled. Quantities of material chemisorbed in each step, as measured by ellipsometry, UV–vis spectroscopy, and X-ray photoelectron spectroscopy, are in agreement with the stoichiometry, density, and thickness of films predicted from molecular models and X-ray powder diffraction patterns of analogous solids. Atomic force microscopy shows that the films are conformal to the topography of the substrates, with no clumping of Zr salts except at concentrations and pH where cluster formation would be expected.[23a] Similar observations have been made on zinc-based multilayers deposited on gold.[33]

FTIR examination reveals that the quantity of organic material deposited is reproducible from layer to layer and that, in the case of long polymethylene chain compounds, some of it is well ordered.[37] However, there are also disordered and less dense domains, probably because of the poor two-dimensional lattice matching between the Zr–P and organic portions of the multilayers. Disorder in polymethylene multilayers is observed even when the films are grown on a close-packed LB film template[39] or alkanethiol monolayer on gold.[21] Besides the lattice mismatch, an additional cause of lower-than-desired order and density is the desorption of Zr from films during rinsing and P-deposition steps.[38]

This imperfection results in a variety of effects, some useful, but most deleterious. There is no UV–vis dichroism observed in films containing chromophores, even rigid, linear ones. X-ray diffraction peaks are not observed, except in the cases of films grown to extreme thickness,[40] on high surface area silica,[41] or over extremely well-ordered Langmuir–Blodgett film templates.[39] Second harmonic generation (SHG) is what would be expected for materials with fair, but not high, polar order (vide infra). Water and small electrolytes penetrate the films,[38,42] resulting in poor dielectric and electrochemical barriers and humidity-dependent electrical properties. The pores through which this penetration occurs may be desirable for sensors; indeed, porous materials have been synthesized intentionally by including P compounds of different[16a,43] sizes and by evaporating small molecules from the already-formed lattices.[19] However, the pores are a drawback to high electric field usage such as in capacitors and electrooptic devices.

Table 1. Electrical Properties of Zr Multilayers

compound	ϵ (1 MHz)	ρ_{DC} (Ω cm)
2	3.4	$>10^{11}$ [a]
3	5	10^{13}
4	2.5	$>10^{13}$
12	6	10^{12}
POP[b]	2.7	$>10^{10}$ [a]

[a] Lower limit based on 100 Hz data. [b] Pyrophosphoric acid.

As we and others[44] have observed, the Zr–P films are inherently good insulators. Resistivities and dielectric constants of several of these materials (after moderate to vigorous drying using Hg top contacts and Au substrates) are listed in Table 1. The breakdown voltage is about 1 MV/cm, suitable for the observation of linear electrooptic and Stark effects. The resistivities are somewhat less than those of insulating polymers, while the dielectric constants and breakdown fields compare favorably with other ultrathin film materials except for silica and Teflon.[45] Conductivity and polarizability are much higher in freshly prepared, more hydrated films. A major problem has been the inability of most of these multilayers to hold up to evaporative metallization, which is the logical way to form electrical contacts such that electric fields drop across the multilayers. The only exception is **4**, where the organic core may be better lattice matched to the inorganic interlayers, providing denser films.[25] Metal–insulator–metal structures were indeed made from this compound. Deposition of buffer materials to protect the films against penetration by metals is an alternative to direct metallization but suffers from the possibility of the electric field dropping substantially across the buffer.

Luminescence and Electron Transfer

One of our main goals with multilayer materials has been to incorporate electron-donating and -accepting chromophores in order to observe designed optoelectronic effects and perhaps better understand luminescence processes in bulk materials. Three fluorescent photoelectron donors, **5**, **6**, and **8**, and two acceptors, **9** and **10**, have been synthesized for this purpose and characterized in multilayers.[46] Despite different geometries and degrees of flexibility, all form single organic-component multilayers with ellipsometric thicknesses well matched to the lengths of the organics. These compounds also form heterostructures in combination with inert spacer molecules and each other. Evidence of nearest neighbor interactions comes from UV–vis spectroscopy, where blue shifts in absorbance are noted in films of **5**[26] and **7**[28] compared to solutions of the same molecules. Multilayer deposition has proven to be a

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Table 2. Fluorescence Lifetimes and Viologen Quenching of Donors in Zr layers

	donor = **6**[36]	donor = **8**[39]
τ unquenched, ns	1.0, 3.5[a]	0.2[b]
τ quenched,[c] ns	0.3, 1.0[a]	0.1[b,d]
intensity quenched, rel to unquenched	0.6	0.02[d]

[a] Based on biexponential fit of decay curves. [b] Based on initial part of multiexponential decays. [c] With **10** in the adjacent layer. [d] To be submitted for publication; presented at the Fall 1993 and Spring 1994 MRS meetings.

convenient way to obtain transparent samples of those chromophores that are poorly soluble and hard to evaporate or disperse in polymers.

Extensive photoluminescence data have been obtained on **6**.[27] Distinct interlayer and intralayer energy-transfer processes, different from those in the bulk solid, were observed with this compound. Despite the nonlinear arrangement of the P ligands, a dense enough film was formed from **6** that a single layer of **1** was sufficient to isolate it from subsequently deposited chromophores.

The luminescence energies and dynamics of **7** and **8** as dilute solutions, sodium salts, monolayers, and multilayers were compared in order to better understand effects in samples of poly(phenylenevinylene) (PPV).[28] Shorter primary fluorescence lifetimes and tailing of residual emission to long times are both observed in all of the solid-phase samples, as well as in PPV. On the basis of our observations, the multilayers and PPV may be grouped as solidlike materials, very distinct from solutions of the oligomers in solvents or polymers. The dynamics and exciton migration effects in the oligomer multilayers and PPV are extremely close, suggesting that PPV is not photodynamically unique.

Donors **6** and **8** were prepared as layers with **10** as the acceptor in adjacent layers. In all cases, the acceptors caused the quenching of the donor fluorescence. Table 2 summarizes the results. While the **5**/**9** pair also showed quenching effects, this may have been due to energy transfer, and therefore the system was not extensively studied. The two cases with the viologen were almost certainly photoinduced electron-transfer phenomena, since the emission spectra of the donors do not overlap the absorbance spectra of the viologen, ruling out energy transfer as contributing to the fluorescence quenching in this case. The porphyrin donor–acceptor and donor–spacer–acceptor arrangements were repetitively stacked, creating heterostructures comprising a thicker film with the same fluorescence lifetimes as the single repeat units but with proportionately greater total fluorescence intensity, which would give greater sensitivity in measuring higher order optoelectronic effects such as photorefractivity.

Photoinduced electron transfer in viologen-containing multilayers has also been observed in bulk samples and multilayers lacking obvious photodonors; counterions and P functional groups have been implicated as partially sacrificial donors.[17b] The photoreduced viologen formed in these systems is envisioned as a reductant in photoactivated catalytic cycles.[43]

Polar Order and SHG

Polar thin films are necessary for certain physical phenomena, including piezo- and pyroelectricity, and especially second-order nonlinear optical effects including SHG for the generation of short-wavelength light for optical recording, and the linear electrooptic effect for electrooptic switching.[47] We have developed a modification of the standard metal–P deposition procedure that results in films with polar order (Scheme 2). One of the linkages between the organic residue and "P" is a phosphate ester bond that is formed by the reaction between a phosphorylating agent and a surface OH. This three-step process represents a simple, functional-group-tolerant alternative to the silane chemistry that has also been used to make polar multilayers.[10] The results are films that retain their polarity at significantly elevated temperatures.

After the techniques were worked out on aliphatic compound **11**,[30] three polar azo dye phosphonates were examined as multilayers by SHG.[48] Results are highlighted in Table 3. Quantities and polarities of material deposited were reproducible from sample to sample and among individual layers of single multilayer specimens. The nonpolar chromophore **7** was inserted between layers two and three of tetralayers of polar chromophores **12** and **13** with no effect on the observed SHG. This result implies that photomodulation of the SHG[49] via the incorporated photodonor might be possible in this system.

Because the sulfone and cyanovinyl compounds had well-defined chromophores with analogies in the poled polymer literature, it was possible to estimate order parameters $\langle \cos^3 \theta \rangle$ for films of those compounds, ~0.16 for the cyanovinyl compound and 0.2–0.3 for the sulfone. These are as good as those in well-poled polymers,[50] achieved in thermally stable systems without electric fields. However, the time and care it would take to prepare samples thick and dense enough for waveguiding and electrooptic switching are a drawback, and the apparent inability to exceed poled polymer order parameters is disappointing. The SHG might have been limited by local field effects ("H-aggregation")[51] that could have negated the signal from the best-oriented domains and given a falsely low estimation of the order parameter. Lowering of second-order NLO coefficients because of the close proximity of parallel, polar chromophores has recently been reported where the chromophores were rigidly held on anthracene-based frameworks.[52]

Of special importance is the potential for association of the nonlinear optical moieties with photodonors and acceptors with precise spacial and orientational control,[53] particularly for photorefractivity. This is a unique capability of the multilayer system, and the one that should be stressed in future work. An alternative

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Scheme 2

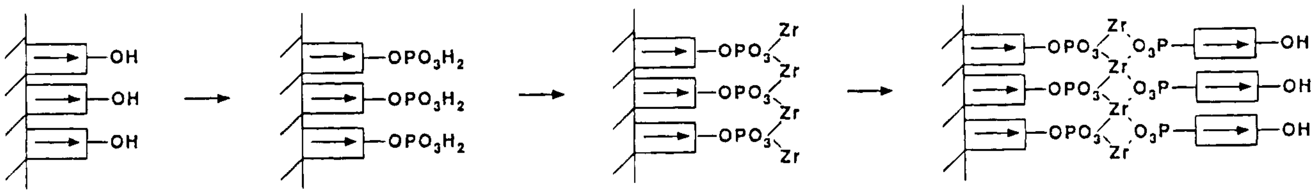

Table 3. SHG of Azo Dye Multilayer Films

compound	λ_{max} (EtOH, nm)	β, 10^{30} esu[a]	d_{zzz} 10^{-9} esu[b]
12	426		<96[c]
13	426	150	48
14	495	1060	280

[a] Estimated for 1.06 μm. [b] Measured at 1.06 μm. [c] d_{zzz} is not the sole contributor to the SHG.

approach to polar multilayers using monoprotected bis(phosphonates) and Hf has just been described.[54]

Conclusion

Many primary effects have been rigorously demonstrated in Zr–P multilayers. Materials that were designed to possess good dielectric properties, display photoinduced electron transfer, and generate second harmonic light have in fact done so. The challenge, and the opportunity, posed by this material class is to take advantage of the degree to which varied molecular species can be arranged at specific concentrations, orientations, and distances to produce heterostructures with interesting higher order effects, such as photorefractivity, sensory ability, and feedback-based logic. The realization of some of these effects would then justify the process research necessary for the optimization of film quality. Considering the vast number of metal ions, polymers, clusters, and newly synthesized organics that could be incorporated into these films, the chances for success in these endeavors are many.

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