

Molecular Structure, Symmetry, and Shape as Design Elements in the Fabrication of Molecular Crystals for Second Harmonic Generation and the Role of Molecules-in-Materials

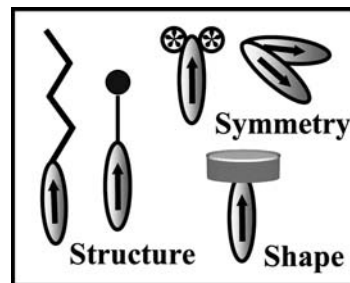
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CONSPECTUS

Molecular materials have emerged as a major theme in contemporary science and technology, thanks to the synergetic confluence of the power of synthetic chemistry, the predictive and analytical capability of condensed matter physics, and the versatility of materials science and engineering. The stringent demands in terms of molecular design and supramolecular assembly to be met in the fabrication of nonlinear optical (NLO) materials for applications such as optical second harmonic generation (SHG) make it a unique arena covering fascinating explorations in chemical synthesis, molecular and materials characterization, theoretical modeling, NLO studies, and photonics technology. Our search for conceptually novel and practically simple but effective approaches to the design of molecular building blocks for crystals exhibiting efficient SHG has led us to the avenues described in this Account. The focus has been on the incorporation of structural, symmetry, and shape features in dipolar NLO-phores to realize noncentrosymmetric or polar molecular assemblies suitable to elicit appreciable SHG responses. Attachment of *n*-alkyl chains of optimal length and remote functional groups were shown to be effective methods to steer the assembly of achiral NLO-phore units into SHG-active noncentrosymmetric lattices. Computational modeling of molecules, molecular clusters, and molecular assemblies in crystals provides valuable insight into the observed structure–function correlations. A systematic exploration of the impact of the placement of stereogenic centers in strongly zwitterionic NLO-phores on the molecular organization led us to the effective exploitation of C_2 -symmetric units to form helical superstructures capable of efficient SHG. New materials developed are based on organic and metal–organic molecules as well as coordination polymers. The potential utility of molecular shape could be demonstrated through the realization of perfectly polar organization in a family of screw-shaped dipolar molecules. Combination of optical transparency, thermal stability, and feasibility of fabricating thin films with orientationally ordered crystallites are important aspects of these materials. Several examples presented in this Account highlight the significance of molecules-in-materials by illustrating that not only the individual molecules and their organization in the crystal lattice but also the intermolecular interactions exert critical impact on the nonlinear optical response of the materials. The role of cooperative interactions in some of the cases is pointed out. This Account projects a range of design strategies for molecular SHG crystals and avenues for expanding further on the present observations; the need to address and exploit the contribution of intermolecular interactions is specially noted. The different examples presented illustrate not only the fabrication of new families of materials based on interesting models proposed earlier but also the emergence of new models from the novel materials developed.



Introduction

The latter half of the last century has witnessed the emergence of molecular materials as a thrust area of research at the interface of chemistry, physics, and materials science. Seminal discover-

ies that occurred periodically have brought to the limelight a wide range of novel materials and phenomena (Table 1). With the major efforts in this field directed at unraveling fundamental physical principles behind the attributes of novel chemical entities and their assemblies, and on developing

TABLE 1. Some Landmark Events in the Development of Molecular Materials over the Last Fifty Years^a

year	molecular materials discovered	ref
1954	perylene-Br: organic semiconductor	1
1960s	tetracyanoquinodimethane (TCNQ)-based semiconductors	2
1965	amino acid crystals: organic NLO materials	3
1969	poly(vinylidene fluoride): piezoelectric polymer	4
1973	tetrathiafulvalene (TTF)–TCNQ: organic metal	5
1977	polyacetylene: conducting polymer	6
1980	(TMTSF) ₂ (PF ₆): organic superconductor	7
1984	NPP: organic SHG crystal	8
1987	AlQ ₃ : molecular electroluminescent material	9
1990	poly(<i>p</i> -phenylenevinylene) (PPV): electroluminescent polymer	10
1991	γ -nitrophenyl nitronyl nitroxide (γ -NPNN): organic ferromagnet	11
2005	phenazine–chloranilic acid: ferroelectric cocrystal	12

^a The list is by no means exhaustive.

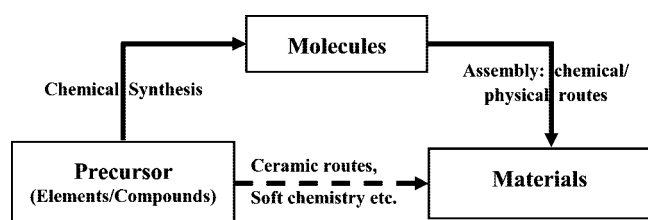


FIGURE 1. Two-level synthesis of molecular materials (full line arrows) contrasted with the direct route to traditional materials (broken line arrow).

their application potential, it is only natural that molecular materials are poised to play a vital role in the science and technology of the present century. The logical transition from molecules to supramolecular assemblies to bulk materials adds a new dimension to the current scenario wherein focus is shifting from macroscopic to nanolevel architectures.

The uniqueness of molecular materials stems from the fact that, upon disassembly via dissolution or perhaps melting/sublimation, they partition into the component molecules that in many of the cases preserve several of the characteristics they exhibited in the bulk state. This is indeed, a direct consequence of the assembly of molecular materials via the “two-level synthesis” (Figure 1) with the latter step involving relatively weak binding interactions. Even though the individuality of molecules is largely preserved in the bulk materials, in many instances they undergo significant structural changes, often conformational. At a more subtle level, the electronic structure and hence the properties of the molecules can manifest profound changes due to the interactions in the solid state. It is therefore meaningful to consider notions such as “molecules-in-materials”, highlighting the nontransferability of molecular features between the isolated and aggregated states and “molecular cooperatives”, where the interactions, even if weak, manifest signatures of cooperativity in the extended

assemblies. These considerations are fundamental, while addressing the electrical, optical, or magnetic attributes of molecular materials.

Fabrication of efficient second-order nonlinear optical (NLO) materials that exploit the fast and strong response of organic and metal–organic molecules is one of the fascinating problems in the field of molecular materials.¹³ Choice of the molecular building blocks, the intermediate stage in the two-level synthesis (Figure 1), is often dictated by the requirement of large hyperpolarizability (β) and for applications such as second harmonic generation (SHG) good transparency in the spectral region of interest.¹⁴ “Push–pull” systems with a dipolar π -conjugated structure, octupolar molecules, and nonconjugated structures with donor–acceptor groups have been investigated extensively. Realization of even-order NLO effects necessitates a noncentrosymmetric structure. Therefore the predilection of molecules to form centrosymmetric crystals¹⁵ has been one of the central problems addressed at the second level of materials synthesis. Beyond this essential condition, efficient SHG responses require an assembly of the NLO-phores with optimal orientations that effectively exploit their β tensor components; the well-known oriented gas model¹⁶ provides insight into this aspect. Several chemical and physical protocols have been explored for the assembly of molecular SHG materials. Incorporation of features like chirality,^{3,17} steric effects¹⁸ and H-bond functionalities^{19,20} in the molecule have led to crystals exhibiting strong SHG. Other approaches include salt formation,²¹ cocrystallization,²² and assembly of helical superstructures.²³ Techniques like electric field poling in polymers, intercalation in host lattices, physical vapor deposition, and ultrathin film assembly through layer-by-layer and Langmuir–Blodgett techniques have also been used to fabricate materials with strong SHG responses. Unlike conducting and magnetic materials where cooperativity of interactions is the essential basis for the materials attributes, in the case of molecular NLO materials, such effects have been less widely exploited.

Among the various forms of molecular materials, crystals afford the most direct access to the details of molecular organization and hence are best suited to derive correlations between the SHG response on the one hand and the molecular structure, intermolecular interactions, and assembly patterns on the other. The subtle interplay between the molecular structure, the assembly in crystals, and in turn, the impact of the assembly on the molecular and electronic structure determines the bulk SHG response. Since dipolar NLO-phores are the most extensively investigated in SHG applications, we have sought to explore novel approaches to their design

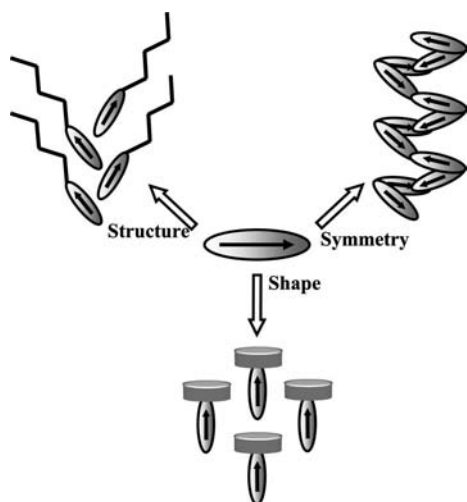


FIGURE 2. Schematic representation of design concepts exploiting the structure, symmetry, and shape of dipolar NLO-phore molecules for assembling SHG-active crystals.

through incorporation of simple but effective molecular features. This Account provides an overview of the strategies we have developed for the fabrication of molecular crystals exhibiting efficient optical SHG. At the molecular level, introduction of features such as optimally long alkyl chains^{24–27} and remote functionalities^{28–31} facilitate new routes to the formation of noncentrosymmetric crystals. The former exploits the balance of different intermolecular interactions,²⁶ whereas the latter enables facile control on supramolecular organization and provides significant insight into structure–function correlations. Homochirality is a well-established tool to induce noncentrosymmetric lattice structure; new materials we have synthesized reveal the significance of the location of stereogenic centers in the molecule in driving optimal molecular orientations in the crystals.^{17,32} Extension of the approach led to the exploitation of C_2 -symmetric molecules for the fabrication of helical superstructures^{33–35} and coordination polymers^{36,37} exhibiting efficient SHG. Perfectly polar organization of dipolar molecules is relatively rare and of special interest in electro-optic materials. Simple screw-shaped metal–organic molecules were found to show a dominant tendency toward such organization in the solid state^{38–40} including vapor-deposited films.⁴¹ This Account outlines the conceptual basis for the design and development of the different classes of molecular crystals that exploit molecular structure, symmetry, and shape for the realization of efficient SHG responses (Figure 2). The critical role of intermolecular interactions including cooperative effects on the NLO responses of several of the materials is highlighted.

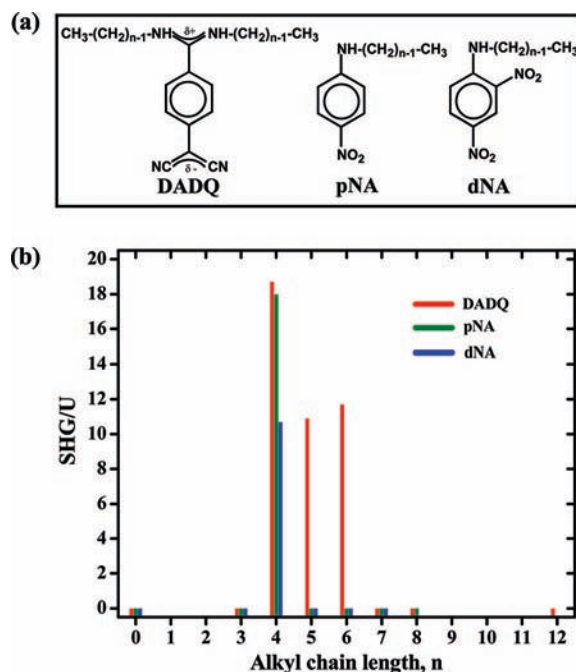


FIGURE 3. (a) Molecular structure of *N*-*n*-alkyl-substituted NLO-phores and (b) their SHG (1 U = SHG of urea); $n = 0$ indicates unsubstituted molecules (adapted from ref 27).

Structure as Design Element

Tuning the assembly by tinkering with the molecular structure has been one of the most popular approaches to the design of molecular SHG materials; several examples have been cited above. We have investigated extensively push–pull compounds having the diaminodicyanoquinodimethane (DADQ) framework. They possess large β values that are sensitive to environment effects,⁴² thus providing ideal test cases for the “molecule-in-a-crystal” concept⁴³ discussed later. The DADQ framework allows facile derivatization and hence varied molecular assemblies; their appreciable thermal stability is an additional asset. Among a series of achiral *n*-alkyl-substituted DADQs, we observed that only the butyl, pentyl, and hexyl derivatives showed SHG (Figure 3).^{24,27} The crystals of propyl, butyl, pentyl and octyl derivatives were amenable to structure elucidation; the butyl and pentyl ones are noncentrosymmetric, while the propyl and octyl ones are centrosymmetric. The intriguing effect of alkyl chain length on the structure and SHG of DADQs assumed more significance in view of the SHG reported for microcrystalline powders of *n*-alkyl derivatives of the prototypical NLO-phore, *p*-nitroaniline (pNA).⁴⁴ Our detailed investigations including crystallographic characterizations established that only the butyl derivative was noncentrosymmetric and SHG active (Figure 3).²⁵ When the same effects were noticed in 2,4-dinitroaniline (dNA) derivatives as well (Figure 3), we undertook a system-

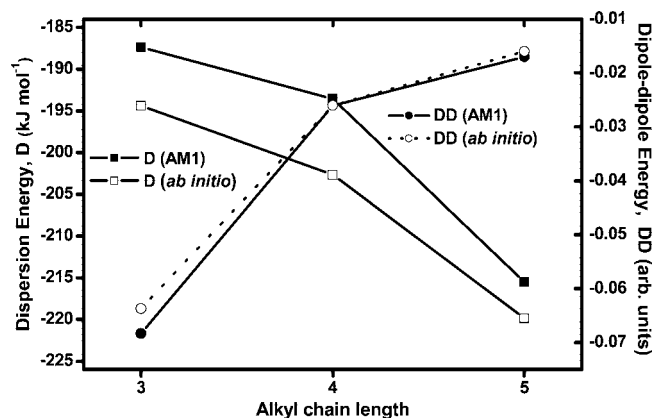


FIGURE 4. Computed dipole–dipole and dispersion energies for crystals of *N*-*n*-alkyl-substituted dNA, plotted against the alkyl chain length. Reproduced from ref 26. Copyright 2000 American Chemical Society.

atic analysis of the role of the different intermolecular interactions in the crystal lattice.²⁶ In the dNA series, since intermolecular H-bonds were obviated due to strong intramolecular H-bonds, one has to contend primarily with only the dipolar and dispersion interactions. The essential lesson from this investigation was that as the alkyl chain length increases, the contribution of dispersion interactions increases, whereas that of the dipolar interactions decreases (Figure 4). Even though both dispersion and dipolar forces facilitate centrosymmetric packing,²⁴ different parts of the molecules promote these effects: the hydrocarbon tail promotes the former and the chromophore group the latter. Therefore it was surmised that a balance achieved with an optimal chain length leads to complex packing motifs including noncentrosymmetric structures. Preliminary observations suggest similar alkyl chain effect in *N*-*n*-alkyl-bis(4-nitrophenyl)amines as well.²⁷

We have explored a novel concept of molecular materials design based on what can be termed “remote functionalization”. In this approach, the NLO-phore is coupled with the so-called remote functional unit through saturated covalent bonds; the remote unit modulates the molecular organization without explicit interference in the NLO-phore response. Examples of systems that we have studied are shown in Figure 5. DMEDQ and AENA are achiral molecules forming centrosymmetric crystals. However the remote functionality facilitated the fabrication of their salts, leading to interesting noncentrosymmetric and SHG active materials. For example, DMEDQ/terephthalic acid showed a SHG of ~ 9 U²⁸ and AENA/*S*-camphorsulfonic acid showed appreciable SHG of ~ 18 U; in the latter case, the role of the chiral counterion is not critical as demonstrated by the contrasting case of the salt of pNA, which showed no detectable SHG.²⁹ Molecular pack-

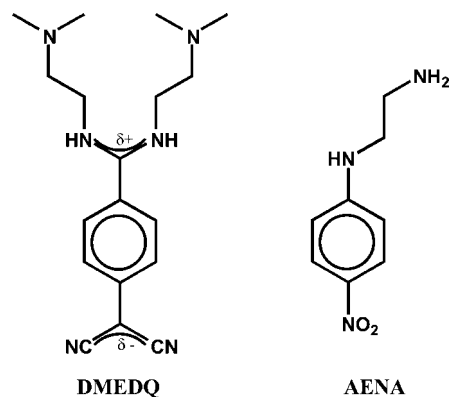


FIGURE 5. Molecular structure of “remote functionalized” NLO-phores, 7,7-bis(*N,N*-dimethylethylenediamino)-8,8-dicyanoquinodimethane (DMEDQ) and *N*-(2-aminoethyl)-4-nitroaniline (AENA).

TABLE 2. Effective NLO Susceptibility Coefficient for SHG (d_{12}) Estimated Using Crystal Structure and Oriented Gas Model, Experimental SHG and Static Hyperpolarizability (β_0) per Molecule from AM1/TDHF Calculation on Dimers Extracted from the Crystal Lattice of Salts of AENA with Acetate, Propionate and Butyrate Counterions (Figure 6)

	AENA acetate	AENA propionate	AENA butyrate
$b_{2yy}^{\text{eff}}(d_{12})$	0.149	0.268	0.360
SHG, U	25.5	22.0	4.1
β_0 per molecule (10^{-30} esu)	6.072	5.069	0.538

ing in the AENA salt induced by the interactions mediated by the remote functionality leads to strong SHG. Recently, we found that the homologous series of salts of AENA with the achiral acids, acetic, propionic, and butyric, form noncentrosymmetric crystals; the SHG activity decreases with increase in the size of the carboxylate ion, a trend opposite to that expected from an oriented gas model based analysis (Table 2).³⁰ Examination of intermolecular interactions reveals that the pNA moieties in AENA are linked into H-bonded chains in the acetate salt, whereas such interactions break down progressively in the propionate and butyrate salts (Figure 6) as a result of packing constraints. The impact of cooperative H-bonding on the molecular nonlinear responses provides a rationale for the observed SHG trends as discussed later. The “remote functionalization” concept was exploited in fabricating SHG-active metal complexes as well.³¹

Symmetry as Design Element

Among the strategies based on molecular modifications, the only one that absolutely ensures a noncentrosymmetric crystal lattice formation is the assembly of homochiral molecules. However, this does not guarantee optimal orientation of the molecules and hence strong SHG. We have probed the pos-

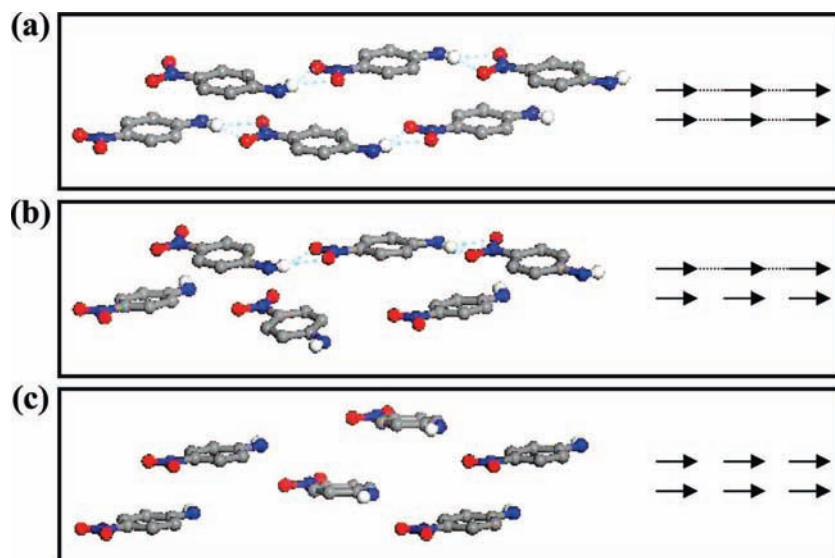


FIGURE 6. Organization of the pNA moieties in the crystals of (a) AENA acetate, (b) AENA propionate, and (c) AENA butyrate, and schematic drawing of the supramolecular structures showing the amino–nitro H-bonds where present: C (gray), H (white), N (blue), and O (red) atoms and H-bond (broken cyan/black line) are indicated (adapted from ref 30).

sible impact of the placement of stereogenic centers in the framework of dipolar molecules on the molecular orientations in the crystal lattice and hence on the SHG from the material. The limited but insightful exercise was focused on four DADQ molecules (Figure 7).^{20,32,45} They show a systematic variation in the position of the stereogenic site with respect to the molecular axis that is coincident with the strongest μ (dipole moment) and β components; the placement of the site could be quantified using a topological measure of chirality that we have defined.¹⁷ Most interestingly, we found that the effective nonlinear susceptibility estimated using an oriented gas model analysis of the molecular orientations in the crystals had a linear correlation with this chirality measure (Figure 7). In other words, the SHG response of this family of materials, controlled by the molecular orientations, could be related in a semiquantitative manner to the placement of the stereogenic center in the molecular structure. The factors promoting the deviation of molecules from a centrosymmetric assembly were found to be the number of stereogenic centers and their placement on rigid frameworks in close proximity to the dipole axis.

A logical extension of this exercise would be to have the element of chirality intimately associated with the largest β component. We envisaged that C_2 -symmetric push–pull molecules would be viable candidates. Since helical motifs often provide enhanced SHG responses,²³ formation of chiral supramolecular assemblies is desirable. *N,N'*-Bis(4-nitrophenyl)-1*R*,2*R*-cyclohexanediamine (BNDC) was found to satisfy these criteria. It forms helical superstructures in crystals, mediated by nitro group interactions (Figure 8), and exhibits strong

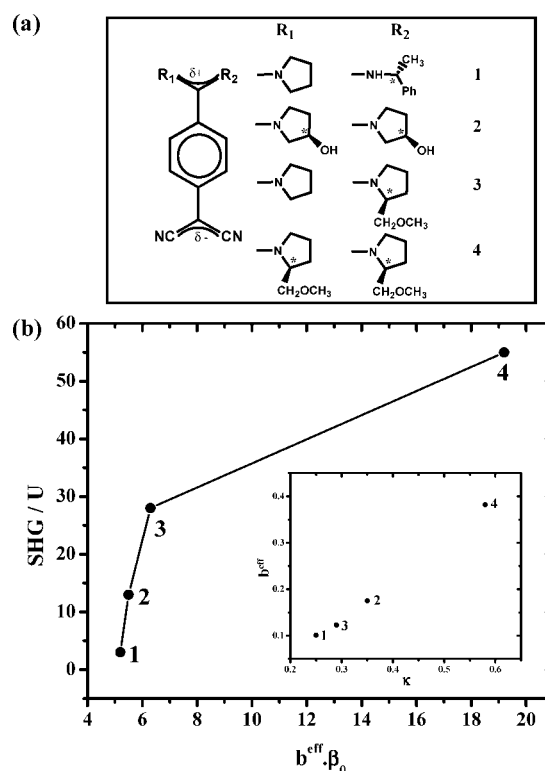


FIGURE 7. (a) Molecular structure of the chiral diaminodicyanoquinodimethanes and (b) variation of their solid-state SHG with $b^{\text{eff}}\beta_0$ (the line is only a guide to the eye); b^{eff} is estimated using the crystal structures and oriented gas model; β_0 is from AM1 computations; inset shows the correlation of b^{eff} with the chirality measure, κ , defined in ref 17 (adapted from ref 17).

solid-state SHG³³ comparable to the prototypical NPP.⁸ An oriented gas model analysis suggested that the response of BNDC crystals is dominated by cooperative interactions within the supramolecular assemblies; we return to this point later.

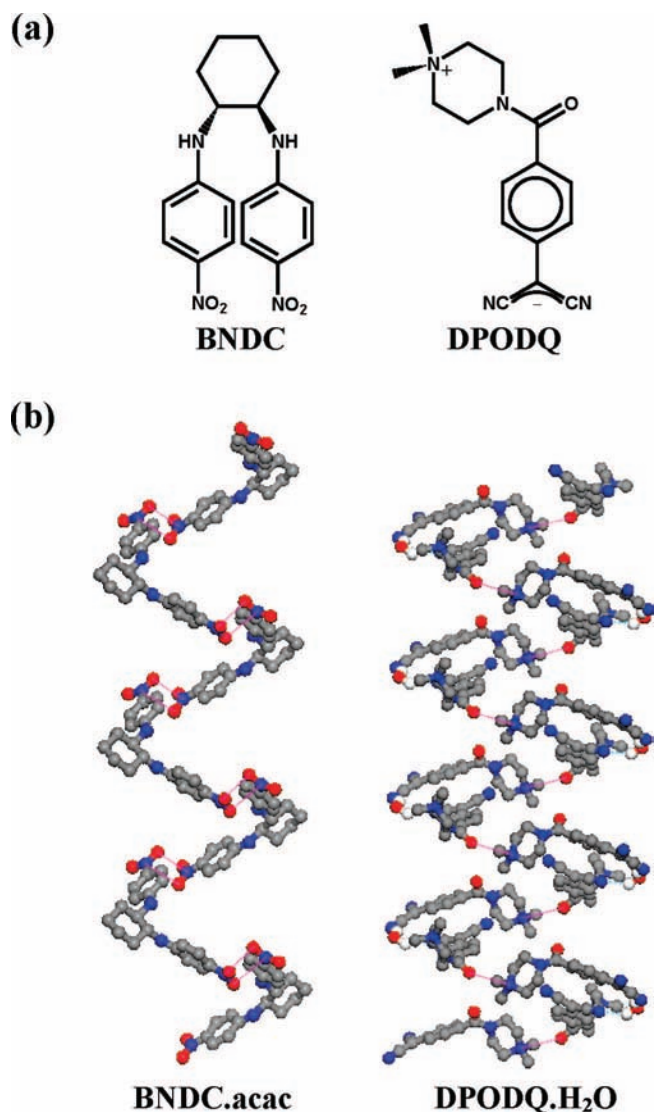


FIGURE 8. (a) Molecular structures of BNDC and DPODQ and (b) the helical superstructures in BNDC·acac (solvent molecules omitted for clarity) and DPODQ·H₂O crystals: C (gray), N (blue), and O (red) atoms, H-bonds (broken cyan line), and electrostatic interactions (magenta line) are indicated (adapted from refs 33 and 35).

Supramolecular helical structures were realized also with chiral C_2 -symmetric bis(amide) molecules; minor molecular structure variations alter the molecular organization from polar to helical and induce moderate SHG capability.³⁴ An interesting case of spontaneous resolution in the crystalline state was observed in a novel derivative of DADQ. 7-(*N,N*-Dimethylpiperazinium)-7-oxo-8,8-dicyanoquinodimethane (DPODQ) was synthesized in an unusual hydrolysis reaction, and this conformationally chiral molecule formed homochiral helices in crystals with concomitant SHG activity (Figure 8).³⁵ Another route to helical molecular organization and SHG materials is based on metal coordination polymers. We have exploited this route by designing the C_2 -symmetric ligand *N,N'*-bis(4-cyanophenyl)-(1*R*,2*R*)-diaminocyclohexane.^{36,37} Even though

the ligand does not form helical assemblies, the complex with Ag(I) formed a helical polymer with a nearly 10-fold increase in the SHG response.³⁶ Extension of the approach to other helical structures has been reported recently.⁴⁶ The examples discussed above, of helical superstructures built from organic molecules and metal complexes, indicate an elegant route to the construction of molecular SHG materials with potential to tap cooperative interactions and realize enhanced responses.

Shape as Design Element

The critical role of molecular shape in the assembly of liquid-crystalline materials is well-known. Even though the relevance of molecular shape to crystal packing is implicit in classical approaches such as those due to Kitaigorodski,⁴⁷ it has not been used extensively for generating specific packing motifs, such as noncentrosymmetric structures of interest in quadratic NLO applications. A notable case in this connection is the design of polar assemblies proposed by Hulliger and co-workers for fabricating efficient electro-optic single-component molecular crystals.⁴⁸ The basic idea derives from models for the evolution of polar order in channel-type inclusion lattices and involves rod-shaped push-pull molecules with non-polarizable groups. A subtle balance of intermolecular acceptor-acceptor, donor-donor, and lateral interactions was proposed to lead to polar crystals. A potential design would involve a "screw-shaped" molecule having a dipolar backbone with large hyperpolarizability and a "head" that hinders lateral interactions but not the one-dimensional Coulombic interactions. Zn(II)(acac)₂L complexes with L = 4-(dimethylamino)pyridyl (ZNDA), 4-(pyrrolidino)pyridyl (ZNPPA), and 4-(morpholino)pyridyl (ZNMPA) possess such shape and, most interestingly, were found to crystallize in perfectly polar lattices (Figure 9).^{38,40,41} They show SHG responses comparable to that of urea and are of potential interest in electro-optic applications. Recently, Su and co-workers have shown that in addition to the "screw shape", appropriate ratio between the width of the head and length of the tail may be important for the assembly of these molecules, emphasizing again the role of molecular shape.⁴⁹

ZNPPA shows a special case of dimorphism with a centrosymmetric structure in addition to the perfectly polar one; an unusual cogrowth of the two forms was also observed in specific solvents.⁴⁰ The optical transparency and thermal stability of the Zn(II)(acac)₂L are important from the point of view of applications. They could also be fabricated as thin films by physical vapor deposition. X-ray diffraction and polarization-dependent SHG measurements demonstrated that the films

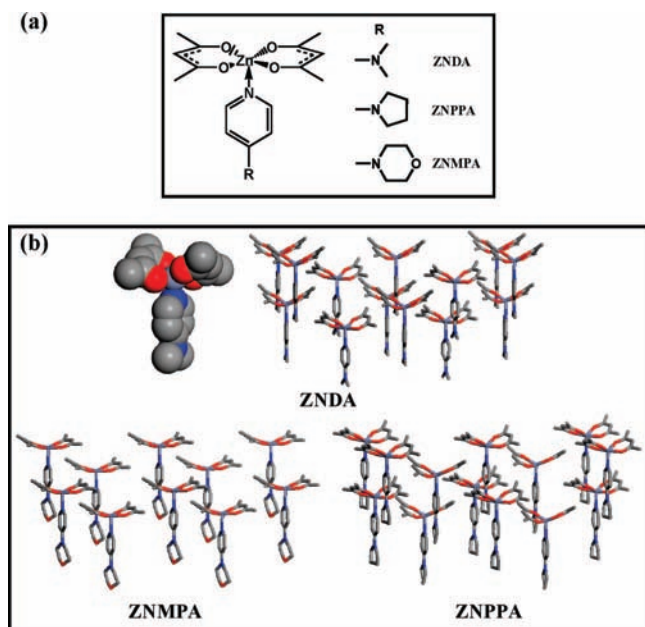


FIGURE 9. (a) Molecular structures of ZNDA, ZNPPA, and ZNMMPA and (b) the perfectly polar assembly in their crystals; the molecular shape is shown for ZNDA (adapted from refs 38, 40, and 41).

are constituted of polar crystallites with uniaxial orientational ordering.⁴¹ The rare phenomenon of perfectly polar assembly in these crystals, a signature of cooperative organization, is induced by the molecular shape and the balance of anisotropic intermolecular interactions. As noted earlier, polar assembly was realized also in a chiral vicinal bis(amide) molecule,³⁴ enabled by the unusual *syn* conformation of the amide groups.

Molecules-in-Materials and Molecular Cooperatives

Modeling the molecular structures existing in bulk materials, their electronic structure, and finally the molecular organization and materials properties is a challenging problem. It is possible to conceive an iterative process based on “embedding models”,⁵⁰ wherein knowledge of the crystal structure allows optimization of the molecular structure in presence of a framework of neighbors, followed by remodeling of the framework and repetition till self-consistency is achieved. A conceptually more simplistic, however practically more convenient, approach would involve mimicking the environment of a “molecule-in-a-crystal” using standard solvation models,⁵¹ with no crystal structure inputs. The effective dielectric medium that the model imposes on the molecule can significantly alter the molecular and electronic structures. Implicit in this idea is the assumption that the dominant effects are electrostatic in nature and that the anisotropic molecular environment that exists in the material may be simulated by an

appropriate cavity that assumes the shape of the molecular surface as defined by the solvation model employed. Successful implementation of such an approach includes modeling the structure of a boron–amine complex in the solid state by Schleyer⁵² and analysis of transition-state analogs by Sherer and co-workers.⁵³ We have shown that similar computations can effectively model the large dihedral twist exhibited by DADQ molecules in the solid state and that the dielectric constants imposed could be related meaningfully to the molecular features.⁴³ Since the hyperpolarizabilities of these molecules are sensitive to the molecular twist,⁵⁴ a correlation can be visualized between the molecular environment in the material and the molecular NLO response. We have extended such molecules-in-materials concepts to a variety of problems: charge redistribution and complexation in the solid state,^{35,55} electronic states that determine spectroscopic features of bulk materials,⁵⁶ and molecular assembly and polymorphism.^{40,57} Analysis of the molecular hyperpolarizability taking into account the environment effects is important for the effective design of molecular NLO materials; explorations in this direction using the “molecules-in-materials” concept would be interesting.

A further level of inquiry required to unravel the impact of assembly in molecular materials relates to cooperative effects of intermolecular interactions. Extended interactions leading to the formation of delocalized energy bands or internal magnetic fields are critical in conducting and magnetic materials. Cooperative interactions have been utilized less widely in the design of molecular NLO materials. The enhanced SHG from helical polymers has been attributed to coherent contributions from the supramolecular organization of the pendant NLO-phores.⁵⁸ Significant nonadditive effects have been invoked to explain hyperpolarizabilities of aggregates.⁵⁹ Computational studies have highlighted the impact of cooperative dipolar and H-bonding interactions on the quadratic NLO response of supramolecular structures.⁶⁰ Some of the materials that we have discussed above emphasize the significance of cooperative effects. The helical superstructures of BNDC formed through nitro–nitro interactions provides an illustrative case.³³ Since the BNDC molecule essentially consists of two *p*NA moieties, its β evaluated computationally could be meaningfully compared with that of NPP.⁸ Assuming further, noninteracting molecules within the framework of the oriented gas model, the relative SHG responses of the solids can be estimated using the information on molecular assemblies in the two crystals. It turns out that the experimentally determined SHG of BNDC is approximately ten times higher than such estimates. This is strongly suggestive of cooperative interactions

between the molecules in the helical superstructure. Another significant example is the case of the AENA carboxylic acid salts.³⁰ The trend in the experimental SHG is exactly the reverse of that predicted based on the β values of the individual pNA moieties and the molecular orientations in the crystals. Computations however revealed that the β value of the molecular clusters decreases from acetate to the butyrate salts (Table 2), a consequence of the decreasing number of chromophores involved in the "molecular cooperatives". This provides an unambiguous verification of the impact of supramolecular interactions on the SHG responses of the homologous series of crystals. Finally, we mention our recent study of a blue-luminescent molecular crystal⁶¹ showing a melting temperature of 348 °C (being centrosymmetric, it does not show SHG) that highlights the role of cooperative effects in the stability of molecular materials. The high thermal stability observed, even in the absence of large local dipoles or features conducive to strong, specific intermolecular interactions, could be explained using computations on oligomeric molecular assemblies that demonstrated cooperativity of interactions leading to sizable binding forces.

Conclusions

Following an overview of the emergence of molecular materials, the design and synthesis of quadratic NLO materials has been discussed in the general context of molecular assembly. Several examples of novel materials developed in our laboratory, exploiting molecular structure, symmetry, and shape were highlighted. Introduction of optimally long alkyl chains or remote functionalities on novel as well as known NLO-phores is extremely simple to implement from the standpoint of synthesis and opens up enormous possibilities for materials design. The remote functional group approach confers considerable flexibility on the control of molecular orientations in the crystal lattice through the generation of various intermolecular interactions. The selective incorporation of stereogenic elements in molecules that we have explored suggests a tailored approach to the use of homochiral building blocks for SHG active crystals. Exploitation of the shapes of molecules with large polarizability or hyperpolarizability in the design of specialized structures such as perfectly polar assemblies could have significant implications for the fabrication of electro-optic, ferroelectric, piezoelectric, and pyroelectric molecular materials.

The relevance of molecules-in-materials and the role of cooperative effects in realizing unusual molecular assemblies or achieving enhanced SHG responses are pointed out through examples presented in this Account. Cooperative intermolecular interactions can provide a powerful handle to

achieve enhanced nonlinear optical effects. The current illustrative cases provide impetus for developing new avenues to the fabrication of molecular NLO materials. It would be of interest to translate these concepts realized in molecular crystals into the realm of doped polymer films, host-guest systems, intercalation complexes, ultrathin films such as Langmuir-Blodgett films, and molecular nanostructures.

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Note Added after ASAP. This manuscript was published ASAP on February 9, 2008 with errors in Figures 8 and 9. The correct version was published on February 14, 2008.

BIOGRAPHICAL INFORMATION

T. P. Radhakrishnan was born in Kerala in 1960. After obtaining a masters degree from the Indian Institute of Technology, Chennai, in 1982, he worked with Prof. Zoltan Soos at Princeton University and received his Ph.D. degree in 1987. Following a postdoctoral stint with Prof. William Herndon at the University of Texas at El Paso, he joined the University of Hyderabad in 1989; he is currently a Professor in the School of Chemistry. His research interests span various domains and facets of molecular materials.

FOOTNOTES

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