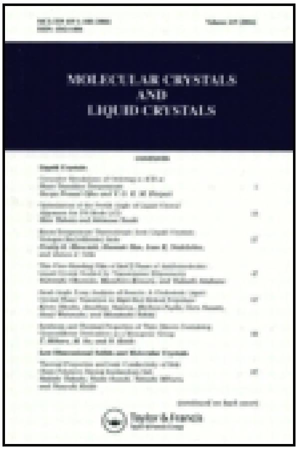

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Defeating Tradeoffs for Nonlinear Optical Materials

Christopher R. Moylan [a], I-Heng McComb [a], Robert D. Miller [a], Victor Y. Lee [a], Robert J. Twieg [a], Susan Ermer [b], Steven M. Lovejoy [b] & Doris S. Leung [b]

[a] IBM Almaden Research Center, San Jose, California, USA

[b] Lockheed-Martin Research Laboratories, Palo Alto, California, USA

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DEFEATING TRADEOFFS FOR NONLINEAR OPTICAL MATERIALS

CHRISTOPHER R. MOYLAN, I-HENG MCCOMB, ROBERT D. MILLER, VICTOR Y. LEE, and ROBERT J. TWIEG
IBM Almaden Research Center, San Jose, California, USA

SUSAN ERMER, STEVEN M. LOVEJOY, and DORIS S. LEUNG
Lockheed-Martin Research Laboratories, Palo Alto, California, USA

Abstract In order to be useful for electro-optic devices, nonlinear optical chromophores must be thermally stable, highly transparent, and have large hyperpolarizabilities. Although these qualities are to some extent mutually exclusive, a small group of chromophores has been prepared that meets the various criteria for applicability.

INTRODUCTION

Organic nonlinear optical materials generally consist of optically nonlinear chromophores oriented within polymer matrices. Such "poled polymers" show great promise for electro-optic, frequency doubling, and photorefractive applications. In order to be truly useful, nonlinear optical chromophores must have large molecular nonlinearities, high thermal decomposition temperatures, and low absorption coefficients at the application wavelengths. Yet it has been empirically observed that tradeoffs exist between nonlinearity and each of the other qualities (thermal stability and transparency). The ultimate success of organic nonlinear optical materials depends upon whether these tradeoffs can be defeated.

NONLINEARITY VS. THERMAL STABILITY

The origin of the tradeoff between nonlinearity and thermal stability is well understood. Thermal stability is typically enhanced by incorporating aromatic rings in the delocalized bridge moiety between a chromophore's electron donor and acceptor groups. But since the molecular hyperpolarizability β is a measure of the ease of coupling the ground state and a charge-transfer excited state with an electric field, any substitution that inhibits intramolecular charge transfer will cause β to decrease. If an aromatic ring lies along the electron transfer pathway, it must adopt a quinoidal bonding pattern for charge transfer to take place, which is heavily disfavored.

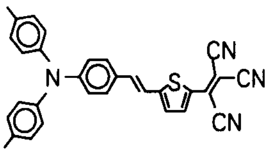
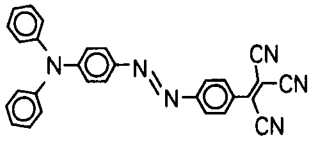
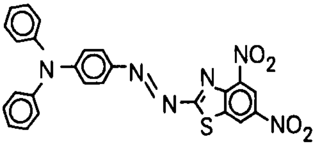
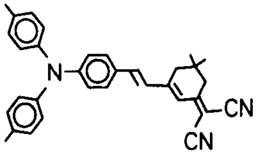
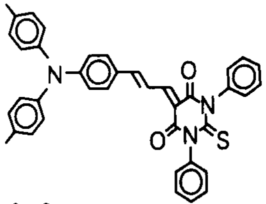
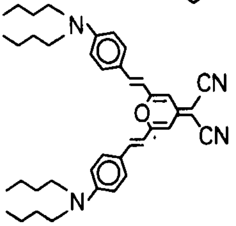
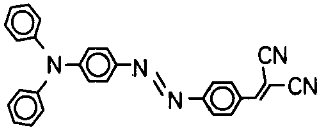
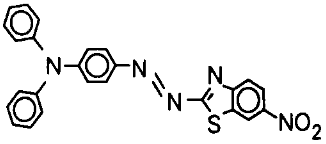
We have found that substitution of aryl groups "upstream" of the electron donor site rather than in the bridge,[1] combined with the use of cyanovinyl acceptor groups,[2] yields chromophores with high molecular nonlinearities as well as decomposition temperatures above 300 degrees C. For a limited number of compounds, the thermal stability tradeoff has therefore been defeated. Some of these are shown in Table I.

NONLINEARITY VS. TRANSPARENCY

The origin of the nonlinearity-transparency tradeoff is also well understood. The degree of coupling between the ground and excited states is inversely related to the energy difference between the two states. Thus, β is typically a strong function of λ_{max} for a given class of chromophores. It is customary to plot such data on a log-log scale and use the slope of the best fit straight line as a measure of the nonlinearity-transparency tradeoff. Such slopes are generally in the 6-7 range. If one has a very transparent chromophore with limited nonlinearity, this strong dependence is an advantage (small sacrifices in near-IR transparency yield large increases in nonlinearity). Unfortunately, though, it is becoming clear that transparency sacrifices previously viewed as small may in fact disqualify materials from potentially useful status.

Again, the way around the tradeoff is a new class of chromophores. If one can design compounds so that they have two low-lying excited states with similar energies and charge-transfer character, their molecular hyperpolarizabilities should be substantially higher with no change at all in transparency. One quality that often correlates with degenerate excited states is symmetry. Symmetric or quasi-symmetric chromophores have the potential to possess two ex-

TABLE I Chromophores with High Nonlinearities and Thermal Stabilities

Compound	λ_{max} (nm)	$\mu\beta/M$ (1.3 μm)	T_d (°C)
	680	14.2	331
	602	6.17	364
	594	5.28	324
	520	4.75	367
	594	3.66	320
	496	3.65	348
	526	3.20	383
	550	3.10	356

cited states that can each contribute substantially to β, rather than the single excited state that dominates the hyperpolarizability for most chromophores (those that are well-described by the two-level model).

The symmetric, "lambda-shaped" dicyano-4*H*-pyran compounds based on DCM laser dye and first synthesized by Ermer and coworkers[3] appear to be such a class. We have characterized DCM and several of its derivatives, and find all of the derivatives to be more nonlinear than their absorption maxima would imply. For example, the compound DADB appears in Table I as the only chromophore with a λ_{max} below 500 nm. All of the symmetric DCM derivatives exhibit apparent oscillator strengths greater than 1.0, and several of them clearly show multiple peaks in the lowest-energy absorption bands. We have therefore performed semiempirical calculations (DZDO) on a simple amino derivative. We find that there are indeed two charge-transfer excited states lying close together in energy. Interestingly, the pyran ring acts as the primary electron acceptor in these excited states, as opposed to the dicyanomethylene group.

As a result of the contributions of these two excited states, the log-log plot for the symmetric DCM derivative series has a slope of 10. Clearly, the nonlinearity-transparency tradeoff is much stronger for these compounds. For any given sacrifice in transparency (red-shifting of the absorption edge) a much greater increase in nonlinearity is obtained for the cyanopyrans than one gets from most other classes of chromophores. In this case, therefore, the best way to deal with the tradeoff is to enhance it rather than to eliminate it.

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