Organic nonlinear optical materials: where we have been and where we are going

Seth R. Marder

Nonlinear optical (NLO) materials can be useful for a variety of applications varying from modulation of optical signals facilitated by the electro-optic effect—the effect whereby the refractive index of a material changes in response to an applied electric field—to microfabrication, sensing, imaging, and cancer therapy facilitated by multiphoton absorption, wherein molecules simultaneously absorb two or more photons of light. This short Focus article is a brief personal perspective of some of the key advances in second-order NLO materials and in multiphoton-absorbing materials, and of how and why these advances have led to renewed interest in organic NLO materials.

Electro-optic polymers

In the 1970s a concerted effort was made to investigate the second-order nonlinear optical effects in polarizable noncentrosymmetric molecules. One important class of molecules that has received significant attention is dipolar molecules in which the ease of polarization in one direction within the molecule is easier than that in the opposite direction. To rationalize the origin of the hyperpolarizability, β, in such systems and to guide the design of such molecules Oudar and Chemla

School of Chemistry and Biochemistry, and Center for Organic Photonics and Electronics, The Georgia Institute of Technology, Atlanta, GA, 30332, USA

suggested that in many systems β could be described well by a two-state model which could be used to guide the design of second-order NLO.[1] In this model,

$$\beta \propto \left(\frac{\mu_{ge}^2 \left(\mu_{ee} - \mu_{gg} \right)}{E_{ge}^2} \right) \qquad (1)$$

where μ and E are the dipole matrix element and transition energy, respectively, between the ground state (g) and the first strongly allowed charge-transfer excited state (e). Physically, the introduction of a ($\mu_{ee} - \mu_{gg}$) term meant that as the electrons interact with the oscillating electric field of light, they show a preference to shift from one direction relative to the other. Accordingly,

molecules for second-order NLO applications were based upon aromatic π-electron systems unsymmetrically endcapped with electron donating and accepting groups to impart the electronic bias. A prototypical NLO chromophore was 4-(N,N-dimethylamino)-4′-nitrostilbene (DANS) in which the two benzene rings and the double bond are the conjugated π-system and provide the polarizable electrons, and the dimethylamino group acts as the donor and the nitro group acts as the acceptor. This model guided the design of second-order NLO chromophores for quite some time and has been reviewed extensively.[2,3]

In the early 1990s I was fortunate to be part of the team that built on this model and helped to illustrate in a simple manner how the first hyperpolarizability, β, in organic molecules was related in a systematic manner to the degree of mesomeric charge transfer.

The degree of ground-state polarization, or in other words the degree of charge separation in the ground state, depends primarily on the chemical structure (for example, the structure of the π-conjugated system, or the strength of the donor and acceptor substituents), but also on its surroundings (for example, the polarity of the medium). In donor–acceptor polyenes, this variable is related to a geometrical parameter, the bond-length alternation (BLA) that is defined as the average of the difference in the length between adjacent carbon–carbon bonds in a polymethine (($CH)_n$) chain. Polyenes have alternating double and
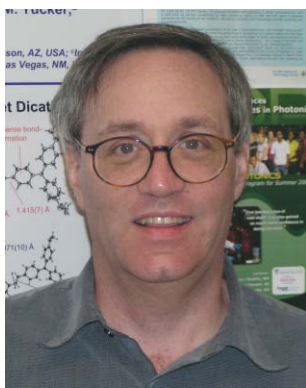
Seth Marder obtained his Bachelor of Arts in Chemistry from MIT in 1981 and his Doctorate, in Chemistry, from the University of Wisconsin-Madison in 1985. After postdoctoral studies at Oxford and at the California Institute of Technology and the Jet Propulsion Laboratory, he became a Member of the Technical Staff at the Jet Propulsion Laboratory and a Member of the Beckman Institute at the California Institute of Technology. In 1998 he moved to the University of Arizona where he was a professor of Chemistry and then also Optical Sciences. In 2003 he moved to The Georgia Institute of Technology where he is now a professor of Chemistry and Materials Science and Engineering as well as the director of Georgia Tech's Center for Organic Photonics and Electronics. He is a fellow of the American Association for the Advancement of Science and the Optical Society of America. His research interests include liquid crystals, transport phenomena, and nonlinear optical processes in organic and organometallic materials.

single bonds (bond lengths equal to 1.34 Å and 1.45 Å, respectively) and thus show a high degree of BLA (+0.11 Å). In a similar manner the bond-order alternation (BOA) can defined as the average of the difference in bond-order between adjacent carbon–carbon bonds in a polymethine chain. We found that hyperpolarizabilities in polymethine and polyene dyes were correlated with the BLA or BOA (Fig. 1, left).[4–7] Furthermore, it was shown that higher-order nonlinear polarizabilities could also be related in a systematic manner to this charge transfer; based largely on these principles, we and others synthesized molecules that exhibited molecular hyperpolarizabilities that were over an order-of-magnitude higher than that of DANS or the common work-horse azo-dye sold under the name Disperse Red 1 (a simple dialkylamino-nitro-substituted azobenzene).[6] In 1996 we reported on the development of a polymeric material incorporating a highly nonlinear chromophore (Fig. 1, center) and displaying an electro-optic coefficient, r_{33}, of 55 pm/V (which may be compared to a value of 30.8 pm/V for lithium niobate).[7] A poled polymer refers to one in which the noncentrosymmetry required for second-order NLO effects (such as the electro-optic effect) is induced by orienting dipolar NLO chromophores by application of an external electric field. While, at the time, the result was a nice demonstration, the facts that the materials were not chemically stable at temperatures in excess of 200 °C and that their orientational stability was pretty poor (i.e. they tended to lose noncentric alignment) above room

temperature were still significant limitations. At roughly this time, I was fortunate to begin collaborating with Larry Dalton (then at the University of Southern California, now at the University of Washington) and Alex Jen (then at Eni-Chem America, now also at the University of Washington). Both of their groups were working on developing more stable materials and more nonlinear materials using new types of poling schemes, post-poling cross-linking strategies, and π-conjugated bridges based on heterocyclic rings that had improved stability relative to polyenes. Larry often expressed concern that, using the molecules with the very strong acceptors that we had popularized, his group was never able to achieve electro-optic coefficients as high as those he predicted were potentially achievable based upon an oriented gas model. In this model, chromophore–chromophore electrostatic interactions were neglected; Larry and his collaborators reasoned that molecules with dipole moments on the order of 10 D simply cannot be treated as non-interacting at the high chromophore loadings (> 30 weight%) one would want to use in the poled polymer systems. Larry, along with Bruce Robinson at the University of Washington, made specific predictions about how far chromophores need to be kept apart and what shape they should have to help minimize dipole–dipole interactions, thereby enabling efficient electric-field poling.[8] Larry made some aggressive predictions about making polymers with r_{33} between 500 and 1000 pm/V, which I regarded as extremely optimistic. Over the past five years, extensive synthetic efforts in the

Jen and Dalton groups at UW,[9] as well as by groups at Lumera Corporation in Bothell, Washington, and at Lockheed Martin Corporation in Palo Alto, have led to the development of a new generation of acceptors, which are designed both to be very electron deficient and to minimize chromophore aggregation, as well as of π-bridges that provide a good compromise between facilitating charge transfer, preventing aggregation and enabling the molecules to maintain reasonable thermal and photochemical stability. These efforts have culminated in recent reports of very large r_{33} values for polymers containing chromophores that have less of a propensity to aggregate (Fig. 1, right), and very recently systems with r_{33} values of several hundred pm/V have been reported at meetings. Recently, Tobin Marks' group, in collaboration with Mark Ratner (both at Northwestern University), has also independently developed a molecular design for chromophores with very high β that is rather different and is based upon a twisted zwitterionic structure and could lead to polymers with very large r_{33}.[10] There are still issues that need to be addressed in these new NLO materials; however, the advent of organic materials with r_{33} much higher than that of lithium niobate is a major milestone and, interestingly, companies in the US and around the world are once again exploring the utility of electro-optic polymers for a variety of applications.

Multiphoton materials

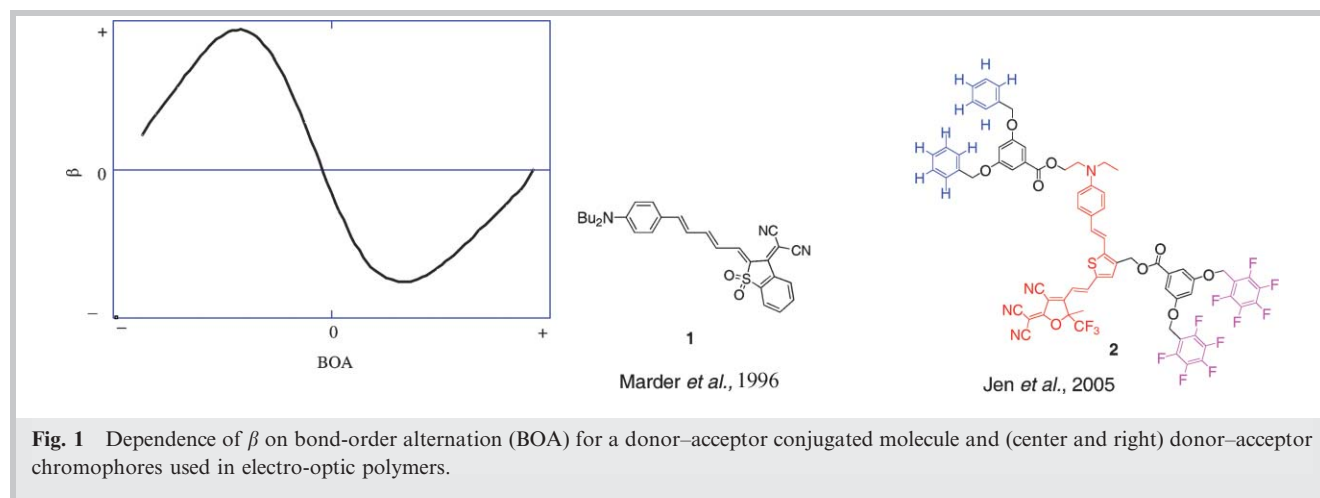Another research area that has grown rapidly over the past several years and

Fig. 1 Dependence of β on bond-order alternation (BOA) for a donor–acceptor conjugated molecule and (center and right) donor–acceptor chromophores used in electro-optic polymers.

which I believe will have broad technological impact is concerned with the applications of multiphoton-absorbing materials. Two-photon absorption (TPA) is a process whereby molecules *simultaneously* absorb two photons and is inherently weak at normal light intensities. TPA allows for the excitation of molecules with precise three-dimensional (3D) spatial confinement. This 3D control of excitation arises from the fact that the probability of TPA is proportional to the square of the intensity of the incident two-photon resonant light and that the intensity of a focused laser beam decreases quadratically with distance from the focal point; therefore, TPA falls off as the fourth power of distance from the focus. Consequently TPA above and below the focal plane is negligible. In addition, it is possible to excite molecules at some depth in a normally absorbing medium using TPA since the target molecules can be excited with photon energies well below that at which the medium exhibits single-photon absorption. Because of these two factors, various concepts to exploit TPA have been proposed; however, for many applications chromophores developed for one-photon excitation were being employed and had rather low efficiency for absorbing two photons, *i.e.* low TPA cross sections, δ. Accordingly, TPA really did not have a technological impact (except for its use in detailed spectroscopic studies) until the late 1980s and early 1990s. During this time period lasers delivering femtosecond pulses became more widely available and enabled advances; Peter Rentzepis *et al.* at UC-Irvine demonstrated high-density 3D optical memory[11] and Watt Webb *et al.* at Cornell University invented the two-photon scanning microscope[12] and demonstrated 3D microfabrication and terabit/cm^3 3D optical data storage. Prasad *et al.* at SUNY Buffalo demonstrated the utility of TPA for data storage and efficient optical pulse suppression in donor–acceptor π-conjugated molecules[13] in the mid 1990s, and, more recently, demonstrated two-photon-based photodynamic therapy.[14] Each of these applications could be greatly aided by the development of molecules with large δ, which would decrease the intensity required for an appreciable two-photon absorption rate, thus making
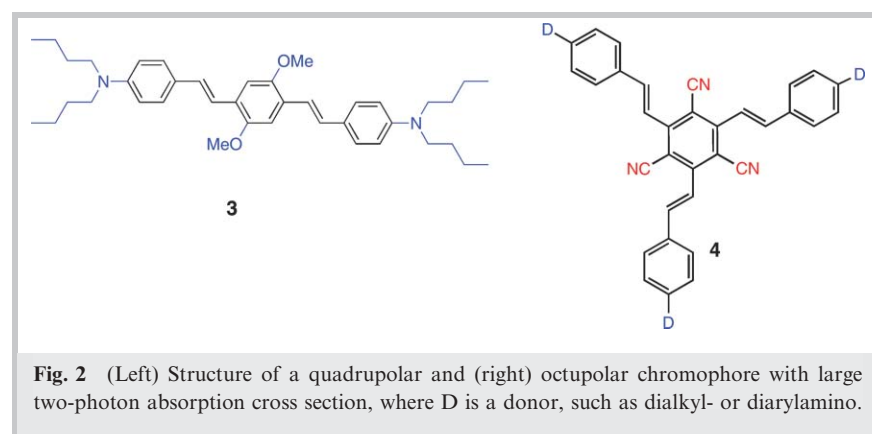
TPA applications more reliable and accessible since laser damage of molecules and surrounding materials could be diminished and lower power, less expensive lasers could be employed. In the mid 1990s, Joe Perry's group and my group, working in collaboration with Jean-Luc Brédas' group, discovered that π-conjugated molecules that undergo large changes of quadrupole moment (Fig. 2, left) upon excitation can show large two-photon absorption cross sections. In particular, we demonstrated that compounds with donor–π–donor, donor–acceptor–donor (D–A–D), and acceptor–donor–acceptor (A–D–A) structural motifs could exhibit exceptionally large values of δ.[15] Subsequently, numerous groups have successfully implemented this strategy and today a range of compounds with cross-sections hundreds to thousands of times that of a prototypical organic chromophore, *trans*-stilbene, is known. Other groups, in particular Cho *et al.*, have successfully extended this strategy to octupolar molecules (Fig. 2, right).[16]

Since TPA provides a means of exciting molecules with high spatial resolution in three dimensions, and since these excited molecules can potentially initiate a range of chemical or physical processes, it has facilitated the development of 3D optical imaging using fluorescent dyes, and 3D lithographic microfabrication (Fig. 3) using photochemically active chromophores in conjunction with either negative-tone[17,18] (where the materials become less soluble upon exposure) or positive-tone (where the materials become more soluble upon exposure) resists.[19] Joe Perry has shown that two-photon-excitable resins incorporating high-δ molecules as initiators can be used

to demonstrate two-photon-induced polymerization with an order-of-magnitude increase in photosensitivity relative to previous commercial resins incorporating dyes developed for one-photon excitation.[18] Features under 200 nm in diameter can be written using 700 nm excitation sources. There are currently efforts to commercialize the process and its application to the development of micro-electro-mechanical systems (MEMS) and to the patterning of surfaces; the latter area has potential applications in optics and, as templates, in tissue engineering. One particularly exciting optical application of 3D microfabrication that will likely receive more attention is the fabrication of photonic crystal templates.[18] In addition there has been an increased development of dyes that can be used for two-photon sensing and imaging applications. In particular, both Paras Prasad[20] and Mireille Blanchard-Desce[21] have shown that two-photon dyes can be designed for a variety of biological imaging applications. While the jury is still out on whether these approaches will be more advantageous relative to various luminescent semiconductor nanoparticle-based imaging approaches, it is clear that organic molecules can be designed to be target-specific and to respond to external stimuli. As I note below, I would not be surprised to see much research targeting hybrid nanoparticle/organic-dye systems for 3D imaging.

Perspectives for the future

A sustained level of fundamental research over the past ten years has left organic NLO well-positioned to make a technological impact in a variety of
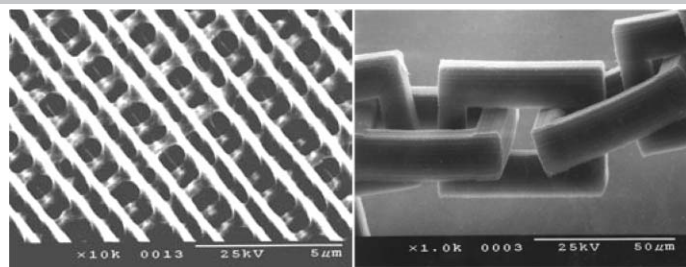

Fig. 2 (Left) Structure of a quadrupolar and (right) octupolar chromophore with large two-photon absorption cross section, where D is a donor, such as dialkyl- or diarylamino.

Fig. 3 (Left) Photonic crystal lattice and (right) linked chains, fabricated by two-photon 3D microfabrication in a negative-tone material. (Images courtesy of J. W. Perry)[22].

disciplines. It would not be surprising if the initial applications that fueled the growth of the field around 20 years ago were to be eclipsed by a completely new set, enabled by our improved understanding of the detailed relationship between chemical structure and optical nonlinearity. In particular I expect to see:

that electro-optic coefficients of 500 pm/V will likely be achieved in poled polymers and may enable numerous applications beyond electro-optic modulation including efficient terahertz frequency generation, that can facilitate imaging for medical and security applications;

a resurgence of interest in the exploration of all-optical signal processing based upon third-order nonlinear optical materials;

rapid development and application of two-photon microfabrication, pushing the limits of achievable resolution below 100 nm and greatly expanding upon the range of materials that can be fabricated;

application of organic NLO materials for biomedical applications including imaging, sensing, treatment and tissue engineering;

the combination of efficient organic NLO materials with nanostructured metal clusters to provide dramatically enhanced NLO effects through surface-plasmon effects;

and the use of NLO materials in photonic crystals to provide tunability of their optical properties.

Many of these applications will benefit from new highly nonlinear molecules and materials. An increased level of control over, and understanding of, not only intramolecular effects, but also importantly intermolecular interactions will be essential in enabling these advances and, therefore, many challenges still face the chemical community in this field.

Acknowledgements

Notes and references

1 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664–2668.
2 D. S. Chemla, J. Zyss, Eds., *Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 1 and 2*, Academic Press, San Diego, 1987.
3 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, J. Wiley & Sons, Inc., New York, 1991.
4 S. R. Marder, D. N. Beratan and L. T. Cheng, *Science*, 1991, **252**, 103.
5 C. B. Gorman and S. R. Marder, *Proc. Natl. Acad. Sci. U. S. A.*, 1993, **90**, 11297.
6 F. Meyers, S. R. Marder, B. M. Pierce and J. L. Brédas, *J. Am. Chem. Soc.*, 1994, **116**, 10703.
7 M. Ahlheim, M. Barzoukas, P. V. Bedworth, M. Blanchard-Desce, A. Fort, Z.-Y. Hu, S. R. Marder, J. W. Perry, C. Runser, M. Staehelin and B. Zysset, *Science*, 1996, **271**, 335.
8 L. R. Dalton, A. W. Harper and B. H. Robinson, *Proc. Natl. Acad. Sci. U. S. A.*, 1997, **94**, 4842.
9 P. A. Sullivan, A. Akelaitis, J. Luo, M. Haller, Y. Liao, B. H. Robinson, A. K. Y. Jen and A. L. R. Dalton, *Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13–17, 2005*; American Chemical Society, Washington, DC (2005), ORGN-230.
10 I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 1998, **120**, 11174.
11 D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1999, **245**, 843.
12 W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73.
13 G. S. He, R. Gvishi, P. N. Prasad and B. Reinhardt, *Opt. Commun.*, 1995, **117**, 133.
14 J. D. Bhawalkar, N. D. Kumar, C.-F. Zhao and P. N. Prasad, *J. Clin. Laser Med. Surgery*, 1997, **15**, 201–204.
15 M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramanian, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653.
16 B. R. Cho, K. H. Son, S. H. Lee, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J. H. Choi, H. Lee and M. Cho, *J. Am. Chem. Soc.*, 2001, **123**, 10039.
17 S. Maruo, O. Nakamura and S. Katawa, *Opt. Lett.*, 1997, **22**, 132.
18 B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51.
19 W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry and S. R. Marder, *Science*, 2002, **296**, 1106.
20 X. L. Wang, J. Krebs, M. H. Al-Nuri, E. Pudavar, S. Ghosal, C. Liebow, A. A. Nagy, A. V. Schally and P. N. Prasad, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 11081.
21 L. Moreaux, O. Sandre, S. Charpak, M. Blanchard-Desce and J. Mertz, *Biophys. J.*, 2001, **80**, 1568.
22 S. M. Kuebler, M. Rumi, T. Watanabe, K. Braun, B. H. Cumpston, A. A. Heikal, L. L. Erskine, S. Thayumanavan, S. Barlow, S. R. Marder and J. W. Perry, *Photopolym. Sci. Technol.*, 2001, **14**, 657–668.