Noncentrosymmetric monolayers from centrosymmetric molecules – A fresh approach to materials for frequency doubling

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The age we live in is often called the 'electronic age'. Some recent developments in physics, chemistry, materials science and engineering, however, indicate that a 'photonic era' is not too far in the future, when the role of electrons in information technology will be played much more efficiently by photons. Signs of the transition can already be seen, e.g. in fibre-optic communication systems utilizing electrooptic devices; many believe that all-photonic devices will soon appear. These devices for light transmission, processing and storage would be based on a variety of nonlinear optical (NLO) phenomena. The nonlinearity refers to the second- and higher-order terms in electric field (E) in the expres-

sion for the bulk electric polarization (P) of a medium $\chi^{(1)}$ refers to the linear electric susceptibility:

$$P = \chi^{(1)}E + \chi^{(2)}E \cdot E + \chi^{(3)}E \cdot E \cdot E \cdot + \ldots$$

and the other $\chi^{(n)}$ produce the different NLO effects; for example, $\chi^{(2)}$ leads to phenomena such as frequency doubling, also called second-harmonic generation (SHG). In a centrosymmertric medium, reversal of E should cause exact reversal of P, and, as seen from the above expression, this is possible only if all $\chi^{(n)}$ with even n are zero. In other words, nonzero even-order χ can be realized only in noncentrosymmetric systems. Frequency doublers in use today employ inorganic crystals like potassium dihydrogen phosphate, lithium niobate and β-barium borate which have noncentric arrangement of the atomic lattice. Recent efforts have been directed at exploiting the large hyperpolarizabilities of selected organic molecules (like donor–acceptor-substituted benzenes, quinones, stilbenes, etc.) gathered in a suitable noncentrosymmetric array in a crystal, polymer matrix or thin film. Large molecular hyperpolarizabilities which lead to high bulk $\chi^{(2)}$ values are usually associated with strong intramolecular charge transfer in the molecular dipoles.

Obtaining a noncentrosymmetric array of molecules is a challenging problem. A noncentrosymmetric molecule with a permanent ground state dipole moment does not guarantee a noncentrosymmetric crystal lattice. On the contrary, they often form centrosymmetric crystals. However, it is the common experience so far that if one is to fabricate noncentrosymmetric lattice, one should build it with a noncentrosymmetric molecule, not a centrosymmetric one, though there are rare exceptions where centrosymmetric molecules with octupolar moments have formed noncentric lattices which showed moderate SHG. Crystal engineering utilizing H-bond interactions, chirality, etc., to build noncentric lattices, growth of Langmuir–Blodgett (LB) films of the X or Z type, where molecules are deposited

in a head-to-tail fashion and electric field poling of molecular dipoles embedded in a matrix or attached to polymer chains are some of the common approaches to obtain noncentric arrangement necessary for SHG materials.

With this background the recent report by Ashwell and coworkers[1] on the detection of very strong SHG from centrosymmetric squarine dye molecules (Figure 1) deposited as LB films comes as an interesting surprise. Crystal structure of 1 is found to be centrosymmetric, belonging to the P2$_1$/c space group and the diphenyl-substituted squarine moiety is flat and centrosymmetric. As expected, the crystals showed no SHG but the LB films (though of poor quality) were found to be SHG-active. Ashwell and coworkers report that 2 and similar systems (with R = other alkyl groups) provide better films and reproducible SHG which is among the highest seen so far in LB films. Reflectivity studies indicated that the LB films consisted of monolayers with the chromophores lying nearly parallel to the substrate surface. Absorption spectra of the films showed characteristic bands due to intermolecular charge transfer in the 660–690 nm range depending on the film deposition pressure.

The crystals of 1 consist of noncentric chromophore dimers which arrange themselves in a centrosymmetric lattice. The authors, therefore, suggest that in the LB films of 2 and similar molecules, noncentric dimers may be present which, however, form a noncentrosymmetric array, thus enabling $X^{(2)}$ to be nonzero. Since the chromophores themselves are centrosymmetric, intramolecular charge transfers do not contribute to SHG. Interfacial effects cannot give rise to such strong SHG as seen in these LB films. Therefore, the authors attribute the strong SHG to intermolecular charge transfer interactions in the dimer units. These charge transfers occur between the dialkylaminophenyl group of one molecule and the squarine moiety of the other in the dimer unit. It is also notable that a good correlation exists between the absorption wavelength variation from 656
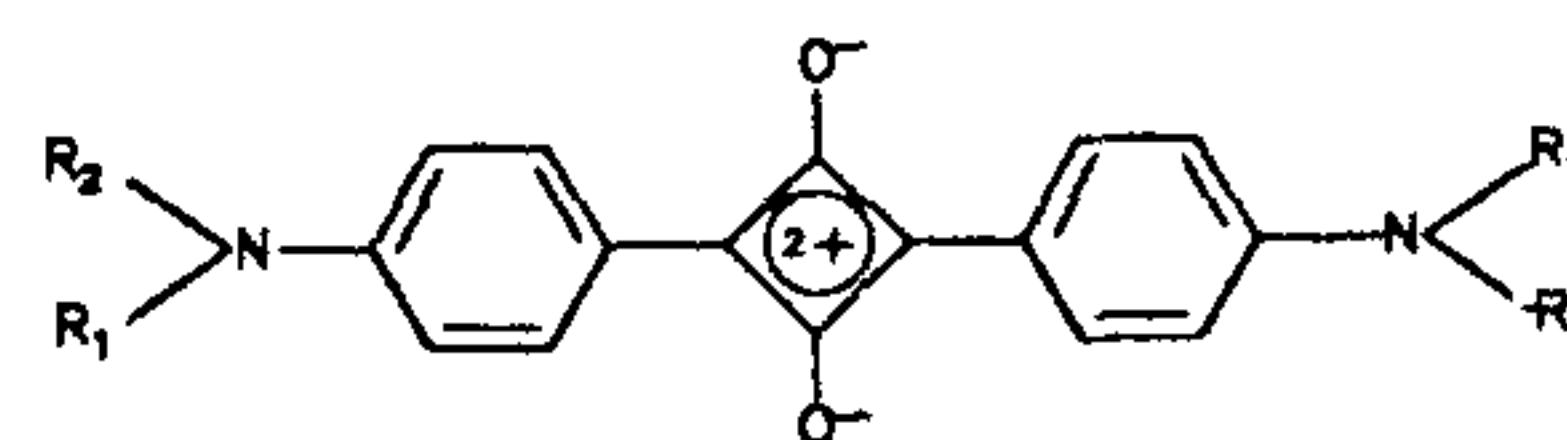
Figure 1. Squarine dye molecules deposited in LB films by Ashwell et al.[1].

to 694 nm and the increase of SHG efficiency as a function of film deposition pressure. The compression process appears to influence strongly the orientation of the chromophores (or chromophore dimers) in the noncentrosymmetric array.

The LB film structure is not fully understood and, therefore, the mechanism by which the strong SHG arises has to be treated as tentative. Film characterizations were carried out on samples deposited on silver-coated slides, but different film characteristics for samples deposited on plane glass slides used in the SHG studies cannot be ruled out. Though some of these questions remain, the discovery of Ashwell and coworkers is notable for the following important insights gained. There is no reason to believe any more that centrosymmetric molecules cannot be coaxed into noncentric arrays useful for SHG. Intermolecular charge transfers can be an efficient mechanism to obtain large bulk optical nonlinearities. This work is likely to initiate a fresh approach to the fabrication of quadratic nonlinear optical materials. The technological promise of these materials is enticing enough to justify detailed investigation and appraisal of such novel ideas.

1. Ashwell, G. J., Jefferies, G., Hamilton, D. G., Lynch, D. E., Roberts, M. P. S., Bahra, G. S and Brown, C. R., *Nature*, 1995, **375**, 385–387

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