

New organic compounds for optoelectronics are being engineered with the aid of neutron studies



Materials with a bright future

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Lasers can be found everywhere from light-shows to supermarket check-outs and CD players. They are also a key part of an optoelectronic revolution which is transforming communications. An important effect called second harmonic generation (SHG) plays a major role in how lasers are used in these technologies. SHG doubles the frequency of light and is used to change the colour of a laser beam.

The SHG effect results from certain subtle electronic changes in a crystalline material when a laser beam shines through it. The compounds used to generate the SHG effect have traditionally been *inorganic* – typically, potassium dihydrogen phosphate and lithium niobate – and rely on small perturbations of key ions in the crystal array. We are interested in investigating novel *organic* compounds which generate the same effect by transferring electronic charge across the constituent molecules. They generally have a flat structure with an asymmetric distribution of charge resulting in an electric dipole moment. Their optical response is much faster than that of the inorganic materials so we are hoping to identify much more efficient SHG materials.

Although both neutron and X-ray diffraction are core techniques in exploring the charge transfer process, neutrons are particularly effective at pinpointing hydrogen atoms, which are mostly positioned at the extremities of the molecules and may play a key role in the charge transfer process.

Mapping electron density

At the ILL, we have used a combination of X-ray and neutron diffraction data to map the electron density in several well-known organic SHG-active compounds such as methylbenzylamino-(di)-nitropyridine (MBADNP), below, in order to identify the critical regions of charge-transfer across the molecule. Moreover, these studies have also enabled us to evaluate the dipole moment. Experimental determination of not only the magnitude but also the sense of the dipole moment in the solid state is very difficult by any other means.

For second harmonic generation to work, the charge transfer must be propagated right through the crystal. This is promoted by a type of intermolecular interaction called hydrogen bonding. However, the ILL work has shown that some types of hydrogen bonding appear to be more favourable than others in enhancing SHG properties. The most promising structures often show a delicate and complicated compromise between a number of factors.

Our increasing understanding of the charge-transfer processes in organic compounds has led us to try to engineer better SHG-active compounds, based upon known, favourable structural attributes in a series of compounds. The ultimate goal is to design a material for a given optical application from the huge variety of possible organic compounds that can be made by substituting one small part of the molecule for a

different one. The prospects for organic SHG materials are very good, although they are not as thermally stable as their inorganic counterparts. In recent years, however, there has been progress in overcoming this problem. In addition, organometallic materials show promise, since they possess the fast optical response of organic materials while having good thermal stability. Further structural studies on these and other materials will ensure that the future of opto-electronics continues to look bright. ■

Figure A

The molecular structure of MBADNP as determined by single-crystal neutron diffraction at the ILL

Figure B

A contour map of the bonding-electron density in the pyridine part of the optically active molecule, MBADNP. Each blue, red and black contour represents a positive, negative and zero electron density respectively at increasing levels of one-tenth electron density per cubic angstrom

