

A new form of analytical chemistry: distinguishing the molecular structure of photo-induced states from ground-states

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This paper introduces a new analytical technique from the field of crystallography, and the optoelectronics motivation that underpins this effort. The essence of the photocrystallography technique is explained in the context of a four-dimensional (space-time) structural probe, and the four technically distinct time-windows of enquiry are presented. This features the complementary needs of laboratory, synchrotron and Free-electron laser based X-ray diffraction experiments. The different scales of atomic resolution required for the technique to be able to probe various photochemical phenomena are described. Sample requirements for photocrystallography experiments are also considered. The paper concludes by forecasting the prospective fortune of this new analytical technique to respond to major current challenges in the photovoltaic, optical data storage, and non-linear optics industries.

Introduction

The optoelectronics industry is predicted to exceed \$1 trillion by 2015.¹ This is hardly surprising given that the world is becoming so dependent upon optical device technology. Such dependence ranges from digital light displays, to the telecommunication industry, to optical data storage media and to solar cell technology (photovoltaics). The world is experiencing a new form of light.

Optoelectronic materials provide the key sources of Red, Green and Blue light for RGB projection displays and laser applications, on account of their ability to act as wavelength converters. Fig. 1 shows one example of a non-linear optical material changing infra-red into blue light. Meanwhile, the wavelength modulation properties of electro-optical materials are fundamental to the telecommunications industry as they can turn binary code into light to effect its fastest possible long-distance transfer through optical fibres. Optoelectronic materials are also required to combat the world's data explosion.

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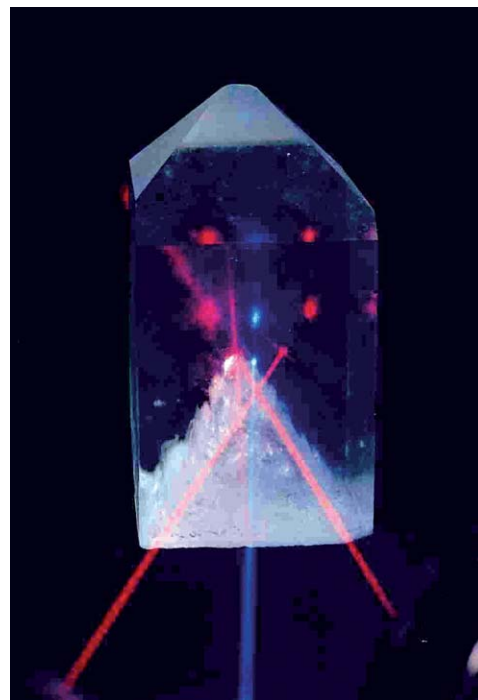


Fig. 1 An example of frequency doubling (infra-red to blue) effects in a crystal of ammonium dihydrogen phosphate, (NH₄)(H₂PO₄).

Holographic data storage, that relies on photorefraction, is one contender to supercede Blu-Ray. Hyped as being able to store a terabyte of data onto storage media the size of a sugar cube, this new technology stands to achieve the step-increase needed in optical data storage efficiency. And perhaps the most prominent of all optoelectronic properties is photovoltaics, since the associated solar-cell technology is predicted to source the world with 11% of its energy production by 2050.²

Despite these seminal roles of optoelectronics, there remains a serious bottleneck in the discovery of new optoelectronic materials that are suitable for industrial application. This is largely because optoelectronic properties are dictated by the electronic structure of a material, especially molecular charge-transfer effects that dominate the photo-excited-state; yet, the nature of this photo-excited state cannot be established in any direct or quantitative fashion. Until recently, only indirect and qualitative information could be revealed by well-established time-resolved UV/vis absorption or emission spectroscopy. Such methods necessitate pump-probe techniques where an optical source acts as the 'pump', while any electromagnetic source represents the 'probe'; the experiments proceed by alternating pump and probe in a stroboscopic fashion. More recently, time-resolved pump-probe IR spectroscopy has made an impact in solution-based photochemistry (*e.g.* ref. 3) and is being developed to study crystalline materials.⁴ However, this is not able to provide a three-dimensional impression of the electronic structural perturbations associated with optoelectronic properties.

Since X-ray crystallography is regarded as the 'gold-standard' for three-dimensional electronic structure determination, there has been much interest in studying photo-induced processes by pump-probe 'photocrystallography'. This paper introduces this developing crystallographic technique and describes how it represents a new analytical technique, distinguishing between the photo-excited state sought and the initial ground-state crystal structure. This new technique may be steady-state or time-resolved, and such space-time (*i.e.* four-dimensional) distillation of crystal structure will be illustrated here by studies across four discrete time-windows.

As a closing introductory statement, it should be noted that there are also complementary solid-state developments in pump-probe powder diffraction, EXAFS and electron microscopy currently underway in order to study photo-induced effects at the atomic level. The reader is referred to the respective articles and reviews on these techniques.⁵⁻⁷

Photocrystallography as a new analytical technique

When light is used to excite a crystal, complete photo conversion is very rare. Indeed, the light induced molecules tend to coexist with the original ground state molecules, as the minor component in the overall crystal lattice. 10 to 20% photo conversion is typical in photocrystallography experiments. Given that the refinable model for photocrystallographic data represents the crystal structure averaged over all unit cells, the co-existing light and ground state molecules will overlap within the space-averaged periodic boundaries of the unit cell. The photo-induced molecules do not generally appear to form in any periodic order. Therefore, the generation of a supercell would not help to distinguish between light-induced and ground-state

species. This contrasts with the concomitant modelling of minor and major molecular species in other contexts, *e.g.* molecular disorder. Instead, the distinction of light-induced and ground-state molecules is reliant upon data that is of high enough resolution to partition successfully electron density from partially overlapping atoms. Clearly, the greater the degree of atomic overlap, the higher the data quality and resolution needed.

In the extreme limit, where the atomic coordinates of a light-induced atom are coincident with a ground-state atom from a different part of molecule, the refinement of an atomic displacement parameter about that atomic site is the only way to distinguish between these two atomic species. The archetypal example of sodium nitroprusside is a case in point: here, the NO group rotates 180° from its ground-state position when photo-induced, and so N_{light} and O_{light} coincide with O_{ground} and N_{ground}, respectively. Thus, the photo-induced and ground-state spatial information obnubilate each other. This work has been the subject of both a neutron⁸ and X-ray⁹ diffraction study. In the neutron case, the NO photoisomerism is evidenced by changes in the anisotropic displacement parameters of the oxygen and nitrogen atoms: see Table 2b in ref. 8 although the authors do not interpret this change, in contrast to the X-ray case. The neutron study endeavours to convince the reader of photoisomerism *via* the small perturbations in Fe–N, Fe–C and N–O bond lengths along the *trans*-O–N–Fe–CN axis.

Indeed, bond-length perturbations are the most common means of demonstrating a light-induced structural change. Such bond-length changes are typically very small. This is especially true in cases where metal–ligand charge transfer (MLCT) is responsible for the light-induced structural changes. Here, the metal-to-ligand separation typically changes by 0.1–0.2 Å, but this could be much smaller. Light-induced charge-transfer effects in organic materials afford even smaller bond-length changes. This is because C–C bond lengths are inherently shorter than metal-to-ligand separations and so changes are correspondingly shorter for a given percentage change in length. Obtaining a sufficient level of atomic resolution to observe the structural perturbation sought thus presents a really major experimental challenge in this area.

Ultimately, one would in fact wish to be able to collect data with high enough resolution to perform three-dimensional electron density distribution mapping *via* a full multipole charge-density refinement, although such studies are likely to remain beyond our capabilities for some time yet.¹⁰ In the meantime, we are therefore reliant upon the use of bond-length analysis of data with the highest-possible space-resolution.

Fig. 2 summarises these bond-length resolution challenges facing the various aspects of photocrystallography, categorising the different types of photo-induced phenomena and materials that are currently being studied. The typical range of bond-length errors associated with a conventional chemical crystal structure determination is also provided as a helpful reference.

It is pertinent to add though that these atomic resolution requirements have been circumvented in a few cases where where high levels of photoconversion have been achieved.^{11,12} Here, the dominant species becomes the sought after photo-induced state rather than the original ground-state. This associated modelling of the photo-induced state is therefore significantly more facile, especially since a reference 'dark-state' is available to model the

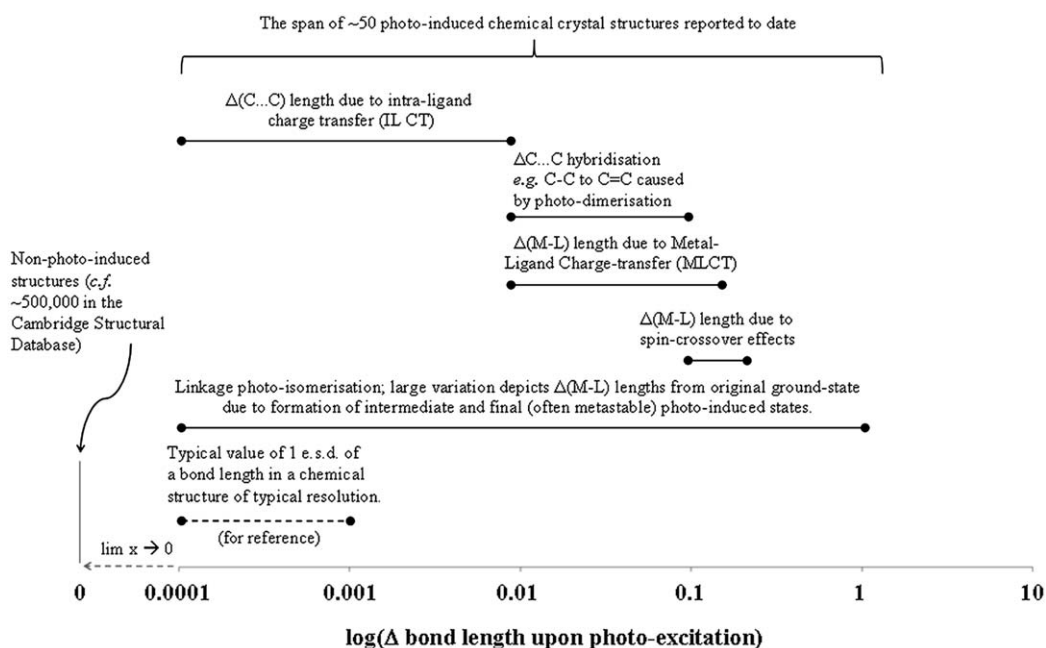


Fig. 2 Typical bond length changes associated with various types of photochemical phenomena.

structure of any minor residual component of the original ground-state.

Irrespective of these resolution challenges, one of the most exciting aspects of this work is that a new phase-space of crystallography is opening up. To date, there are ~50 photo-induced crystal structures reported; contrast this with ~620,000 conventional crystal structures present in the literature: ~500,000 (organic and organometallic) residing in the Cambridge Structural Database,¹³ and another ~120,000 in the Inorganic Crystal Structure Database.¹⁴ This almost entirely empty photo-induced phase space therefore provides a broad canvas of discovery opportunities and, in particular, it opens up an entire new area of solid-state photochemistry.

The four time-windows of separation

A comprehensive review of the experimental requirements for photocrystallography is given elsewhere.¹⁵ This paper aims to summarise the four discrete time-windows associated with the technique, the choice of which is dictated by the photo-active lifetime of a given compound.

Infinite to millisecond photo-active lifetimes

Light induced species with this range of lifetimes can be studied by lab-based single-crystal X-ray diffraction. If the photoactive state of a compound is metastable, *i.e.* has an infinite lifetime when maintained under certain experimental conditions, the experiment proceeds in a steady-state configuration, *i.e.* using the continuous X-ray source of a diffractometer. High-resolution ground-state data are first collected in much the same way as for a conventional structure determination. The crystal sample is then pumped with light of the appropriate wavelength and intensity while still mounted on the diffractometer (Fig. 3). Such optical-pumping is typically applied for a few hours. The *in situ*

nature of this light-activation allows a second data collection to be performed which is identical to the first with the important exception that the crystal now contains a percentage of a light-activated state. The difference between these two data collections, subject to unit cell normalisation, reveals the photo-active crystal structure sought.

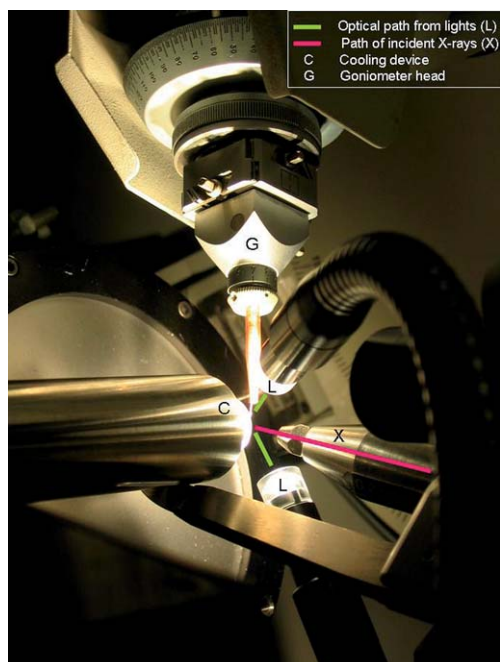


Fig. 3 A steady-state photo-crystallography experiment. The sample lies at the end of the fibre on the goniometer head (G), positioned in the centre of focus of the various incident auxiliary devices, comprising the collimated X-ray beam (X), two broad-band white light sources (L) and sample cooling apparatus (C).

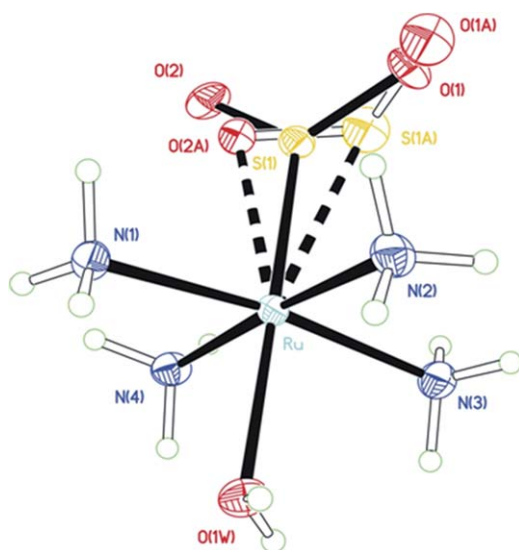


Fig. 4 η^1 to η^2 SO₂ photo-isomerism in [Ru(SO₂)(NH₃)₄(H₂O)](Tosylate)₂. η^1 -SO₂ (original ground-state) crystal structure: bold lines; η^2 SO₂ (photo-induced): hollow lines.

An example of such an experiment concerns the η^1 (end-bound) to η^2 (side-bound) SO₂ ligand photoisomerism of [Ru(SO₂)(NH₃)₄(H₂O)](Tosylate)₂ which is metastable pending the sample is maintained at $T = 100$ K. Monochromatic (532 or 488 nm) or broad-band (400–800 nm) white light can equally reveal the η^2 state as exemplified by Fig. 4.^{16–18} Curiously, photo-excitation at a much lower temperature, $T = 28$ K, affords further photoisomerism, that manifests a rare O-bound η^1 -SO₂ configuration.¹⁹ While the η^2 -state was first reported using a laboratory X-ray source, the O-bound η^1 -SO₂ state experiment was performed at a synchrotron X-ray source. The more complicated refinement of co-existing S-bound η^1 -SO₂ (ground-state), η^2 -SO₂ and O-bound η^1 -SO₂ photo-excited states necessitates high quality data that is promoted by the superior X-ray intensity of a synchrotron. This said, lab-based experiments are now sufficiently refined to produce such results, albeit with reduced quality compared with a synchrotron.

Where the photo-active lifetime is more ephemeral, down to millisecond lifetimes, the default continuous X-ray source of the diffractometer must be chopped at a frequency corresponding to the sample lifetime. This is achieved using a mechanical X-ray chopper. One such chopper has been designed specifically to access the millisecond range.²⁰ The data collection itself is a difference-experiment in the same (light + ground) – (ground state) fashion as described for the steady-state experiment.

Millisecond to microsecond photo-active lifetimes

To study photo-active species that live in this range of lifetimes, one needs to use a synchrotron X-ray source. This is because the X-ray duty cycle (photons per chopper repetition period) is simply too low at this chopping frequency for a laboratory X-ray source to produce sufficient incident X-ray intensity for a viable measurement. Various X-ray choppers have been designed for this task^{21–24} while the optical source is invariably a pulsed laser that specifies an intrinsic repetition rate. The experiment

proceeds *via* a stroboscopic (laser) pump and (X-ray) probe process where electronic time-gating is employed to synchronise the laser and X-ray pulses, incident to the crystal sample. The data collection itself is a difference experiment in the same way that was described in the previous section.

Microsecond to picosecond photo-active lifetimes

Photo-induced structures associated with this level of transiency need access to the temporal structure of the particle accelerator storage ring of a synchrotron. This provides the necessary time regime of X-ray pulses. The essence of this method was originally reported by Sandstrom and co-workers.²⁵ The X-ray pulses are sourced from synchrotron radiation that is generated from electron bunches in the synchrotron storage ring. Each electron bunch travels at a relativistic speed approaching that of light; consequently, it passes a fixed point within a picosecond or nanosecond time window, depending on the synchrotron being used. Corresponding ps-ns X-ray pulses can be harnessed by selecting spatially (and therefore temporally) separated electron bunch modes of a synchrotron. A synchrotron operates in one of various electron bunch modes (Fig. 5) at any given time of the year. The 16-bunch mode shown in Fig. 5 is particularly favourable since one can extract the ps-time-resolved synchrotron radiation from one of the 16 bunches using a chopper downstream,²⁶ where the X-rays travel off at a tangent from the storage ring, to the diffraction instrument. When the

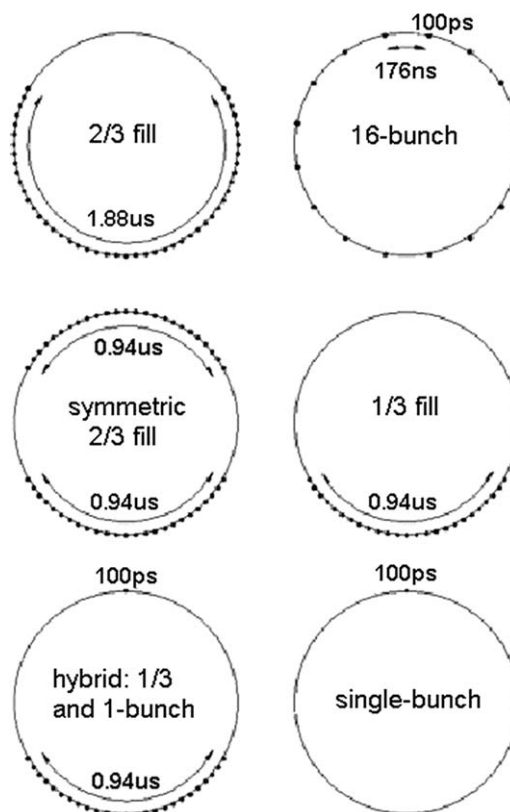


Fig. 5 The temporal structure of eight possible electron bunch modes in the particle accelerator storage ring at the European Synchrotron Radiation Facility.

resulting ps-time-resolved X-rays arrive at the instrument, stroboscopic (laser) pump and (X-ray) probe technology is employed, as per the description for the millisecond to microsecond photoactive lifetime regime. Electronic bunch clocks and associated equipment extend the time regime from picosecond up to microseconds.

Femtosecond photo-active lifetimes

This time-frame is too fast for a synchrotron to capture. Instead, the incipient X-ray Free Electron Laser (X-FEL) technology must be considered. This has been designed to create an X-ray pulse of ~ 100 fs generated from the linear acceleration of electrons over several kilometers. The sample lies at the end of this very extended linear accelerator where it receives a single, but extremely intense, X-ray pulse. This will likely destroy any sample, and so the diffraction data all emanate from the recording of this single-event. It is therefore known as a 'one-shot' experiment. The building and commissioning of three FELs, all with different design characteristics, is taking place in Japan (Spring-8), the USA (LCLS, Stanford) and Germany (X-FEL, Hamburg). Achieving the photo-active structure of such an ephemeral species is therefore at the current forefront of technical feasibility. Moreover, given that this time-frame is associated with that of bond-making and bond-breaking, it stands to also open-up new possibilities for the structural characterisation of photo-chemical reactions and mechanisms of their intermediates.

Sample considerations

The likelihood of a photocrystallography experiment revealing observable photo induced structural changes depends on a number of key factors. Three particularly important sample considerations are: crystal size, the level of photo-structural change expected, and optical absorption characteristics of the sample.

The ideal crystal size of the sample is in effect a best compromise between X-ray scattering intensity and optical penetration depth. On the one hand, a crystal must be large enough to exhibit sufficiently intense X-ray diffraction data for structural refinement to yield the desired results with adequate resolution. Due to the much greater X-ray intensity available at a synchrotron, compared with a laboratory X-ray source, there is much greater flexibility in crystal size optimisation at a synchrotron. On the other hand, the crystal must be small enough to allow light to penetrate through its entirety; otherwise, light energy will become trapped within the crystal and build up undesirable heat effects that can lead to part of the crystal being eaten away by the light (see Fig. 6) or, worse still, the crystal may explode. Optical bleaching effects may also need to be considered. This is where a progressive change in the optical absorption coefficient occurs as a function of light penetration depth through the crystal sample. As a result, the crystal exhibits non-Beer–Lambert law behaviour. Such effects are most commonly observed in time resolved (optical)pump-(X-ray)probe stroboscopic experiments since a short optical pulse can readily create optical shock-waves in the crystal. Molecular co-operativity effects may also influence the optical penetration depth in

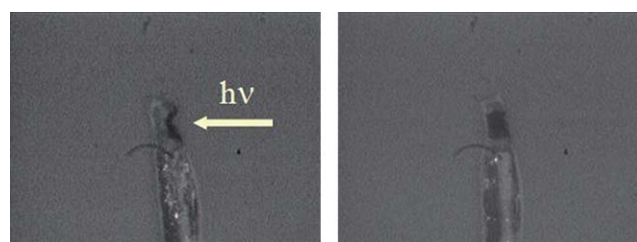


Fig. 6 Photographs of laser radiation damage to a crystal that has dimensions greater than the optical penetration depth at frequency, ν ; the result is an etched crystal. The etching is highlighted by the blackened area in each viewpoint perspective (the crystal is rotated through 90° between the two images); the affected crystal volume typically has a crystal thickness pertaining to this optical penetration depth. The crystal is mounted on a glass fibre.

a non-uniform fashion. This is where the photo-structural change of a molecule or a localised domain of molecules incites the same photo-structural changes in neighbouring molecules.

Concerning the level of photo structural change, this must of course be large enough to observe within the resolution limits of the photocrystallographic data. Furthermore, the light-induced structural change sought will preferentially lie in a spatially distinct crystallographic position from the pre-irradiated crystal structure. However, the photo structural change should not be so large that it imparts crystal lattice strain to the extent that the crystal fractures or explodes.

Optical absorption characteristics of the sample dictate the entire design of the photocrystallography experiment. In the first instance, the lifetime of the photo induced state chooses the basis of the experimental set-up according to one of the four time windows of opportunity described above. Meanwhile, the wavelength of photo excitation is selected from an assessment of the optical absorption profile of the sample. One usually excites in the tail of the optical absorption band rather than at the wavelength of maximum absorption, λ_{\max} , in order to observe the photo induced effect without excessive photo structural change that would damage the sample. For similar reasons, the energy of the incident optical source is limited; here, sample thermal stability considerations are also relevant. In addition, the quantum-yield associated with the photo-excitation is a useful spectroscopic parameter to know since this indicates the maximum achievable photo-excitation level in a photocrystallography experiment.

Prospective applications of photocrystallography

Distinguishing the photo-induced crystal structure from its conventional ground-state can be immensely useful in helping to solve a number of key research problems. A comprehensive review that describes the applications of photocrystallography is given by Cole.²⁷ Here, we summarise the salient aspects of four technologically important application areas: dye sensitised solar cells, optical data storage, light emitting diodes and nonlinear optics.

*Dye-sensitised solar cells (DSCs)*²⁸ are a strong contender for the dominant energy source in the next generation. The function of the dye in the DSC is a particular concern, given it has two key

operational roles: (a) providing the light-harvesting function of this solar cell and (b) initiating the electric current in the cell *via* a redox conversion process. There is currently a worldwide drive to generate better performing dyes since they impact heavily on the resultant DSC efficiencies which remain far from their intrinsic limit. By far the most successful, and therefore popular, dye is bis(tetrabutylammonium) *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II),²⁹ which is most commonly known as 'N719' (Fig. 7). Yet it is currently somewhat a mystery as to what makes this particular dye so special. Series upon series of similar Ru-complexes have been synthesised and tested in DSCs, with little comparable success. These findings make it abundantly clear that the quest for improved dye operational-efficiency is hostage to a more detailed and quantitative understanding of the precise electronic nature of the molecular charge-transfer and redox mechanisms with which the dye is involved in the DSC operation.

Photocrystallography is uniquely placed to respond to these challenges since it exposes the intimate secrets of dye functionality *via* the four-dimensional (space-time) characterisation of the electronic structure and dynamics of the photo-excited state, (dye)*. Comparing this with that of the ground-state (dye), one can discern the nature of the key electronic perturbations that pertain to molecular charge-transfer which controls the dye function.

Optical data storage technologies are currently hindered by a material supply bottleneck that plagues the commercialisation of new-generation data storage media. Holographic data storage, for example, would otherwise be seen as the next logical replacement for Blu-ray technology if suitable materials were available,³⁰ since it would enable a step-increase in data storage capacity; over 100 DVDs of data information could be stored onto a hologram the size of a sugar cube. And yet, the need for new optical data storage technologies is extremely urgent: with 1.5 billion people now connected to the Internet, with usage predicted to increase by over 10% each year,³¹ the demand for global data centres is escalating at a level that it will soon be beyond current optical data storage capacities.

Photocrystallography could help provide an elegant solution to this materials-centred problem *via* the quantitative molecular-level analysis of new photo-refractive materials, the properties of

which govern the operation of holograms. Suitable materials must have unique photo-refractive properties in three dimensions; they must be sufficiently light-sensitive to effect the holographic read-write process; photorefractive changes need to be readily distinguishable, and stable over time. Our aforementioned photocrystallography work on $[(\text{SO}_2)\text{Ru}(\text{NH}_3)_4\text{X}]\text{Y}$ complexes, for example, show these material-requirements can be met. In the first instance, these materials are exceptionally light-sensitive, responding to background lighting or ambient sunlight. Secondly, they exhibit photorefractive properties on account of the η^1 (end-bound) $\rightarrow \eta^2$ -(side-bound) SO_2 photo-structural change described earlier (Fig. 4); this manifests a marked change in ligand geometry and concomitant change in electric-dipole vector, thereby rendering an electro-optic modulation. This enables these materials to store data with 3-D sensitised characteristics when photo-excited in a suitable manner. Thirdly, these photo-isomers are metastable when suitably temperature-controlled. By judicious variation of ligand, X, and counterion, Y, ongoing research aims to be able to tune this metastable transition temperature, the desired level of electro-optical modulation and available wavelength-band to match the needs of device application.

Non-linear optics is fundamental to the telecommunications industry, given its key role in wavelength conversion, electro-optical modulation, and optical switching, during the course of optical transmission. Such features are behind many of the current innovations in the telecommunications industry which is currently having to develop rapidly to cope with the boom in the optoelectronics industry. High-bandwidth optical transmission, low-driving voltages, and all-optical switching are particularly attractive in new-generation technologies;³² for such properties, organic materials are far superior to the traditional inorganic non-linear optical materials.

Time-resolved photocrystallography could make a big impact here since the non-linear optical response in organic materials is governed by the nature of the molecular charge-transfer, enticed by light-activation. This causes the molecule to oscillate between a neutral and charge-separated canonical state over a very fast timescale, typically ns-fs. By employing photocrystallography to organic non-linear optical materials, one will be able to assess the level of photo-mixing of the charge-separated and neutral states of their electronic structure, compared with the ground-state electronic structure. This will provide a quantitative, and *in situ*, assessment of various structural characteristics of the photo-excited state, which are known to dictate the non-linear optical response:³³ in particular, the electron-donor, electron-acceptor and π -conjugation effectiveness, and bond-length alternation³⁴ parameter. Such information affords an unparalleled insight into the non-linear optical processes. Given the intrinsic link between structure and property, this information will be seminal in the future design of 'smart-materials' for enhanced non-linear optical performance.

Light-emitting diodes are becoming increasingly attractive as red, green and blue (RGB) sources in display technologies. Organometallic compounds that bear *trans*-ligands with suitable π -conjugation to form oligomers or polymers are particularly attractive materials. This is because they present metal-ligand, light-metal or intra-ligand charge transfer (MLCT, LMCT or IL) characteristics with energies that are well-placed to emit in the

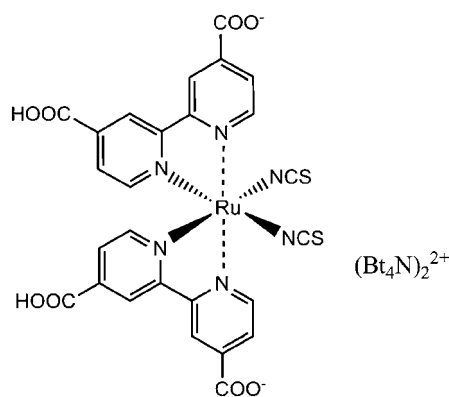


Fig. 7 A schematic illustration of the 'N719' dye, di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); ($\text{C}_{58}\text{H}_{86}\text{N}_8\text{O}_8\text{RuS}_2$).

visible region of the electromagnetic spectrum. Meanwhile, their propensity to form long chains *via* oligomerisation or polymerisation renders ease of manufacture with low-cost; this contrasts starkly with the situation for traditional inorganic LED sources.

In order to effect the best materials design for new LEDs, it is important to identify the nature of the charge transfer process associated with the dominant emissive character of a material. UV/vis spectroscopy is primarily used for this task and a wealth of qualitative information may be inferred from the associated spectra. However, a quantitative and direct assessment of the nature of charge transfer processes pertaining to the emissive state is not possible *via* this technique. Once again, photocrystallography comes to the rescue since it can fill this gap exactly. Four-dimensional (space-time) stroboscopic pump-probe photocrystallography experiments can reveal the crystal structure of the dominant emissive state. The nature and extent of the bond geometry changes, compared with that of its ground state, allow one to identify and quantify the nature and extent of charge-transfer processes taking place that are responsible for the light emission in these materials.

An addendum on practicalities There is clearly some way to go before materials design strategies, that employ photocrystallography, have a direct impact on the optoelectronics market. However, reports of photo-sensitive materials exhibiting high levels of photoconversion already herald the prospect of a single-crystal binary optical device with sub-nano pixellation. This said, not all photo-sensitive solid-state devices will exploit photo-induction in the single-crystal form. Based on current trends in the optoelectronic industry, thin-film technology will more likely house the photo-active materials. In that event, nano-sized single-crystals of photo-active species may be embedded into a polymer matrix to yield the desired optoelectronic properties.³⁵ Nonetheless, the photo-induced effect in question may propagate in several forms, *e.g.* polycrystalline or amorphous; although it would be unwise to speculate generally since each material will differ according to its individual photo-sensitive properties. Irrespective of the nature of the phase of material used ultimately in an application, photocrystallography offers the richest structural information when conducted in the single-crystalline state. As such, photocrystallography represents a key analytical tool in the future of solid-state optoelectronic design.

Concluding remarks

This paper has portfolioed photocrystallography as a new photochemical analytical technique with wide applicability to the field of optoelectronics. It still has some way to go before it can be fully established and mature as a standard analytical tool. Yet, its ability to provide a unique insight into the molecular control of optoelectronic properties, coupled with the very rapid growth in the optoelectronics industry, is a strong motivator for further development. Photocrystallography is already affording a growing database of excited-state structures. In due course, this will permit the realisation of excited-state structure-property relationships. This leads to the ultimate goal of 'structurally engineering' designer optoelectronic functionalities into new materials to suit a given device application.

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