Switching of molecular second-order polarisability in solution

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Second-order nonlinear optical (NLO) polarisabilities or first hyperpolarisabilities, β, of molecules may be manipulated by reversibly modifying the properties of specific parts of active molecules, usually by on/off switching. This may involve reducing the donor capacity of the electron-rich fragment of a typical donor–acceptor species, D–A, by oxidation or protonation. Conversely, the acceptor behaviour of A may be altered by reduction, or by deprotonation. Alteration of the first hyperpolarisability may also involve structural or chemical modification of the bridging group, thereby interfering with the communication between D and A. Much of the article focuses on redox behaviour of NLO-active metal-containing compounds, mainly describing dipolar species in which the donor fragment containing a metal is oxidised, but giving examples of switching behaviour in octopolar species and of protonation/deprotonation behaviour.

Introduction to nonlinear optics

Light, *i.e.*, a time-varying electromagnetic field, interacts with a material, inducing a polarisation in the molecules which constitute that material.[1] This results in an induced dipole moment μ_{ind} which, at low electric field strengths, is linearly proportional to the electric field E, the proportionality factor being the first-order polarisability α. However, at high electric field strengths, higher-order terms become relevant, and the induced dipole moment is then expressed as follows:

$$\mu_{ind} = \alpha E + \beta E^2 + \gamma E^3 + \dots,$$

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in which β represents the second-order polarisability or first hyperpolarisability and γ the third-order polarisability or second hyperpolarisability.

At the macroscopic level, the bulk polarisation is expressed as P_{ind} and equals:

$$P_{\text{ind}} = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots,$$

with $\chi^{(1)}$ the first-order susceptibility, $\chi^{(2)}$ and $\chi^{(3)}$ the second- and third-order nonlinear susceptibility, respectively.
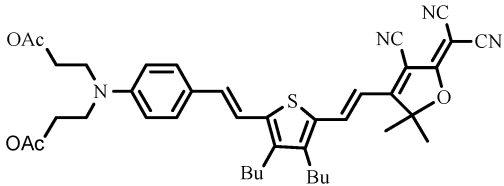
For molecular materials to exhibit second- or third-order nonlinear optical behaviour, the molecules which constitute them must have specific structural and/or electronic properties. For second-order processes, the manipulation of which is the main focus of this article, symmetry limitations are particularly important. The determination of NLO effects, as they are manipulated chemically or physically, also requires special facilities and these are also described in this article.

Molecular symmetry requirements

Compounds suitable for second-order nonlinear optics[3] fall into two categories, the larger of which contains molecules having C_{2v} or $C_{\infty v}$ symmetry. These molecules consist of an (strong) electron donor moiety attached to an (strong) electron acceptor moiety linked by a conjugated π-electron bridge, their linear optical properties being characterised by strong low-energy intramolecular charge transfer (ICT) transitions. A broad range of compounds[4] has been investigated and a specific example is shown in Table 1.

The second category of compounds, which is not so widely

Table 1 Absorption maxima (λ_{max}), hyperpolarisability (β_{333}) and static hyperpolarisability ($\beta_{333}[0]$) for a linear compound

λ_{max}/nm	$\beta_{333}/10^{-30}$ esu^a	$\beta_{333}[0]/10^{-30}$ esu
650	2058	635

^{a} Measured at 1064 nm by hyper-Rayleigh scattering, data taken from ref 2.

Table 2 Absorption maximum (λ_{max}), hyperpolarisability (β_{333}) and static hyperpolarisability ($\beta_{333}[0]$) for an octopolar compound

λ_{max}/nm	$\beta_{333}/10^{-30}$ esu^a	$\beta_{333}[0]/10^{-30}$ esu
650	2058	635

^{a} Measured at 800 nm by hyper-Rayleigh scattering, data taken from ref 6.

investigated, contains octopolar compounds, which have D_{3h}, D_2 or T_d symmetry.[5] The advantage of octopolar species is that they show the same optical transparency as their linear analogues but their second-order nonlinear response is much higher. However, these species do not possess a permanent dipole moment which makes them inaccessible for certain applications and is therefore a disadvantage. An example is shown in Table 2.

Measurement of second-order nonlinear effects

The second-order polarisability β or the second-order susceptibility $\chi^{(2)}$ are two parameters indicative of a second-order response. The first is a molecular parameter and is measured in solution, whereas the latter is measured by second-harmonic generation (SHG) in the solid state. Two major techniques are used for measurements in solution: electric-field induced second-harmonic generation (EFISHG) and hyper-Rayleigh scattering (HRS).

Second-harmonic effects require non-centrosymmetry at the molecular and macroscopic level. Since a solution containing nonlinear optical active molecules is isotropic, no SHG can occur on attempted polarisation. Therefore, in the EFISHG[7] experiment, a static electric field is applied to the solution, which induces alignment of dipolar molecules, thereby breaking the centrosymmetry. A probe beam is passed through the sample and the coherently frequency-doubled light may be

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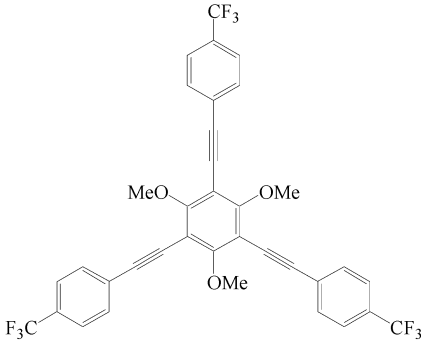
Jon McCleverty was Professor of Inorganic Chemistry first in Birmingham (1980–1990) and later in Bristol (1990–2003) where he is now Emeritus Professor. His interests are largely based in coordination chemistry, focusing on redox properties and the use of appropriate ligands for developing interesting and potentially applicable optical and magnetic behaviour.

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Jon McCleverty

detected. In contrast, in the HRS technique,[8] no static field is applied, and the incoherently frequency-doubled scattered light is detected. The inherent centrosymmetry in the solution is broken by the local (in time and space) microscopic anisotropy in the solution. The advantage of the HRS technique over EFISHG is that the second-order response of molecules without a permanent dipole, *e.g.*, octopoles, and ions can be measured. The EFISHG technique, however, is more "efficient", being a coherent technique.

For SHG in thin solid films,[9] the non-centrosymmetry rule remains. This requires the sample to be ordered in one way. Two major techniques are used for obtaining this ordering. One is either to dissolve the molecular chromophores in a polymer blend or to attach them to a polymer backbone, and then spin-coating to generate a thin film. These films are poled above the glass transition temperature T_g and then cooled while poling is maintained. Another method involves Langmuir–Blodgett (LB) techniques, which afford highly-ordered thin films derived from amphiphilic molecules. The second-order susceptibility $\chi^{(2)}$ is obtained by detecting the coherently generated frequency-doubled light from the sample in transmission or reflection.

Is it possible to switch the second-order nonlinear optical response?

To be effective as a switch several points need to be considered. It is important that the two forms ('on' and 'off') are stable, that they can preferably be switched from one to the other in an easily controlled way and that the response time is relatively fast. To alter the second-order nonlinear optical properties, modifications at the molecular level should be made. Since most of the second-order chromophores are of the donor–π–acceptor type all alterations can be categorised into three types, as proposed by Coe[10] and illustrated in Scheme 1.

All types of molecular switching can be reduced to these three forms. **Type I** includes all forms of switching in which the hyperpolarisability is altered by reducing the donor capacity of the donor moiety (D). This can be done by oxidation of, or proton transfer to, the donor. The donor can then be considered as a competing acceptor moiety A′. **Type II** is the reverse. The β value is changed upon reduction of, or proton removal from, the acceptor (A) moiety which becomes competitive with the donor [A changes into D′]. All switching mechanisms induced by alteration of the π-bridge, *e.g. cis–trans* isomerisation, are grouped in **type III**, where, for example, the loss or gain of conjugation changes the NLO response of the compound. Although theoretical calculations have shown that switching by proton transfer[11] or electron transfer[12] should indeed be feasible, we have chosen to focus our attention on the experimental aspects of molecular switching.
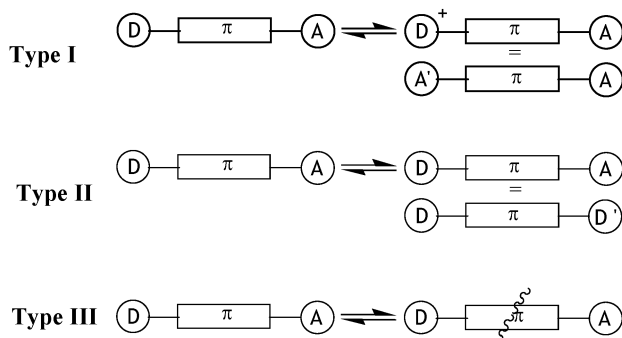
Switching by alteration of the π-bridge

Thiophene derivatives of perfluorocyclopentene are photochromic and possess high thermal and photochemical stabilities. Irie[13] has shown that this type of molecule can undergo photochromic reactions. Following irradiation at 313 nm, the electronic spectra of these compounds are changed, exhibiting a new absorption band at *ca.* 525 nm. This new band is due to the presence of a closed ring formed by the photochemical transformation.

Lehn *et al.*[14] have reported that the marked photochromism of compound **A** permits efficient switching of NLO responses. UV irradiation at 365 nm for 30 s causes a complete photocyclisation of yellow **A** to deep blue **A°**, and the process is reversed upon exposure to visible light of wavelength >600 nm for about 5 min (Scheme 2). The deep blue colour arises from intramolecular charge transfer from the 1,3-benzodithiole-2-ylidenyl donor to the dicyano-methylidenyl acceptor.

Delaire *et al.*[15] have demonstrated SHG switching in poled films derived from two types of polymers that contain the typical azobenzene-derived NLO chromophore disperse red 1 (DR1; Scheme 3, **B**). Irradiation at 488 nm of a film made up of a solution of polymethylmethacrylate (PMMA) and the chromophore DR1 induces an irreversible decrease (*ca.* 30%), followed by a reversible decrease (*ca.* 30%) of the SHG intensity at 532 nm. These effects are attributed to partial *trans-to-cis* photoisomerisation of the DR1 molecules. The effect of isomerisation has been studied with all-*trans versus* 9- and 13-*cis* retinal and derivatives as model compounds. In the all-*trans* isomers, the better electronic coupling between donor and acceptor groups results in a hyperpolarisability value that is
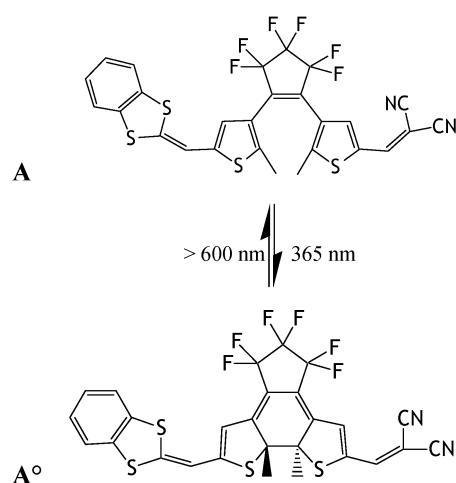
**Scheme 2** Photocyclisation of the bis(3-thienyl)ethene.
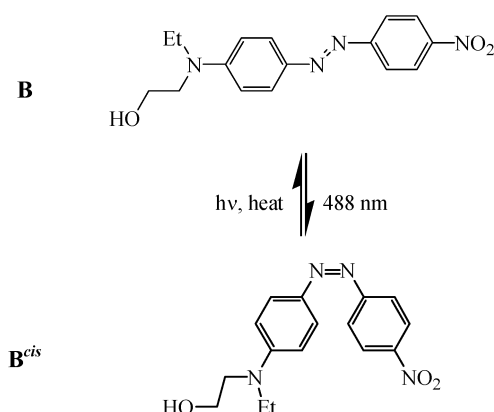
Scheme 3 Photoisomerisation of the azo dye disperse red 1 (**B**).

Scheme 1 Schematic representation of switching possibilities.

twice the value for the *cis* isomers.[16] Photoisomerisation has been shown to affect the frequency-doubling efficiency of the bacteriorhodopsin protein in a purple membrane suspension.[17] The initial decrease of SHG intensity arises from the irreversible disorientation of a portion of the molecules upon reconversion to their "*trans*" form (= free molecules). The reversible component is due to the fraction of molecules that can only recover their initial orientation (= trapped molecules).

Identical treatment of a DR1-functionalised PMMA copolymer leads only to an irreversible loss of the SHG, indicating that all the DR1 units are free to undergo irreversible orientational changes upon isomerisation. When considering a DR1 functionalised polysiloxane copolymer,[18] the polymer becomes uninteresting as a poled polymer NLO material due to its low T_g. This fact however has been exploited by Abe *et al.* who showed that the application of an electric field to a randomly oriented thin film causes a rapid (in seconds timescale) approximately five-fold increase in the SHG intensity at 532 nm. The effect reverses upon breaking the electric field. The switching can be repeated by applying the electric field again. This is an example of switching the NLO response by controlling the macroscopic ordering rather than by modulating the molecular properties.

Delaire *et al.*[19] have also probed the photochromic compound *N*-salicylidene-4-bromoaniline (Scheme 4, **C**) for SHG study at 532 nm. Upon irradiation at 365 nm the red colour of the tautomeric form of **C**^{pt} appears and reverts to **C** under visible radiation or on heating. This allows fully reversible SHG switching with an intensity decrease of approximately 60%. Given that the tautomerisation causes minimal structural change at the macroscopic level, the SHG switching is the result of β in **C** and **C**^{pt} being different.
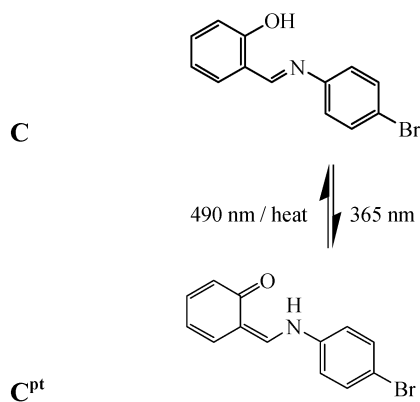
Scheme 4 Phototautomerisation of *N*-salicylidene-4-bromoaniline **C**.
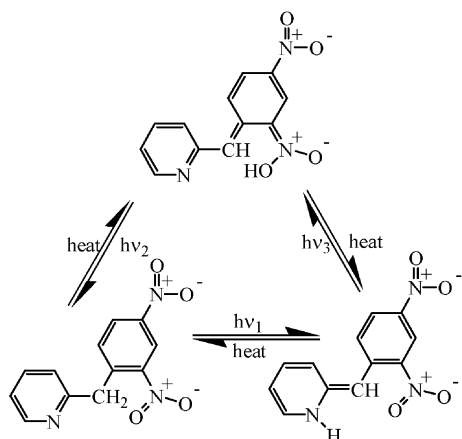
Scheme 5 Photochemical and thermal interconversion processes of 'CH', 'OH' and 'NH' tautomers of dinitrobenzyl pyridine.

The photochromic reaction of dinitrobenzyl pyridine[20] (DNBP), altering from a colourless to a deep blue form, involves a light-induced proton transfer. The mechanism of the process (Scheme 5) involves the transfer of a benzylic proton ('CH' form) to the *ortho*-nitro group forming the aci-nitro intermediate 'OH' ($\lambda_{max} = 380$ nm), and proton transfer to the pyridine nitrogen, resulting in the blue coloured tautomeric form 'NH' ($\lambda_{max} = 550$ nm). This process has the advantage that it does not require large structural changes and it can therefore also occur in the solid state or in a rigid matrix.

Since the lifetimes in solution of both photoproducts are rather short, the model compounds **D** and **E** (Scheme 6) have been used by Lehn *et al.* in hyper-Rayleigh measurements.[21] Large differences in hyperpolarisability were detected for **D** and **E** on excitation at 1064 nm in acetonitrile. β_0 has been determined as 1×10^{-30} esu for **D** and 62×10^{-30} esu for **E**. This study shows that the CH and OH or NH types of DNBP derivatives have strongly different molecular hyperpolarisabilities. As model compounds for photo-induced proton transfer, they demonstrate that DNBP derivatives have potential for optical modulation of the hyperpolarisability and thus for modulating the second-harmonic generation efficiency of NLO devices.

Potential-controlled electrolysis experiments were carried out by Ratera *et al.*[22] to confirm the possibility to reduce reversibly a polychlorotriphenylmethyl radical (**F**$^{•}$; Scheme 7). The reversible interconversion between radical **F**$^{•}$ and its corresponding anion **F**$^{-}$ is monitored by linear UV-Vis spectroscopy. This result indicates that there are no structural changes or decomposition in the time scale of the experiment. Unfortunately, in this case it did not result in an effective NLO switch since the anion (**F**$^{-}$) exhibits strong absorption at 532 nm ($\varepsilon \sim 25000$), which strongly interferes with the second-order nonlinear optical response, leading to an overestimated β-value for **F**$^{-}$. On the other hand, protonation and deprotonation of the anionic form **F**$^{-}$ is possible. The NLO response decreases as the pH of the solution increases. Acidic conditions generate the protonated species **F**^{H}. Experimental results show that its molecular hyperpolarisability was $\beta = 73 \times 10^{-30}$ esu, which is considerably lower than that obtained for its related octopolar open-shell radical **F**$^{•}$ ($\beta = 360 \times 10^{-30}$ esu).

Switching by alteration of the donor/acceptor unit

(a) Exploiting the basicity of donor fragments

The donating effect can be lowered upon protonation. We were able to demonstrate the reversible switching of the first hyperpolarisability of a substituted fullerene **G** (Scheme 8) upon protonation and deprotonation.[23] The electron donating ability of the dimethylamino unit is lowered upon addition of trifluoroacetic acid. The original HRS response is regenerated upon addition of Hünig's base (*N*-ethyldiisopropylamine).

Fig. 1 shows the reversibility of the switching of the hyper-Rayleigh response [$I_{2\omega}/I\omega^2$ with $I_{2\omega}$ the harmonic intensity and I_ω the fundamental intensity]. The left part of the *x*-axis

D   **E**
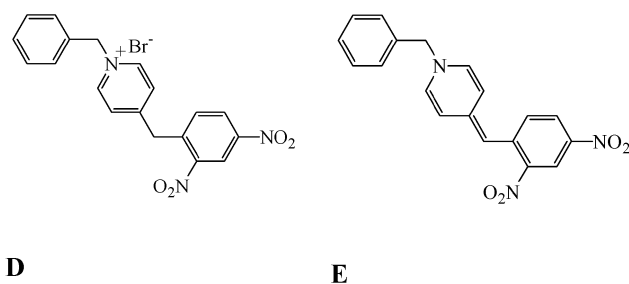
Scheme 6 Dinitrobenzyl pyridine derivatives **D** and **E** measured by hyper-Rayleigh scattering.

	F·	**F⁻**	**Fᴴ**
Open-Shell	ON	OFF	OFF
β (10^{-30} esu)	360	340	73
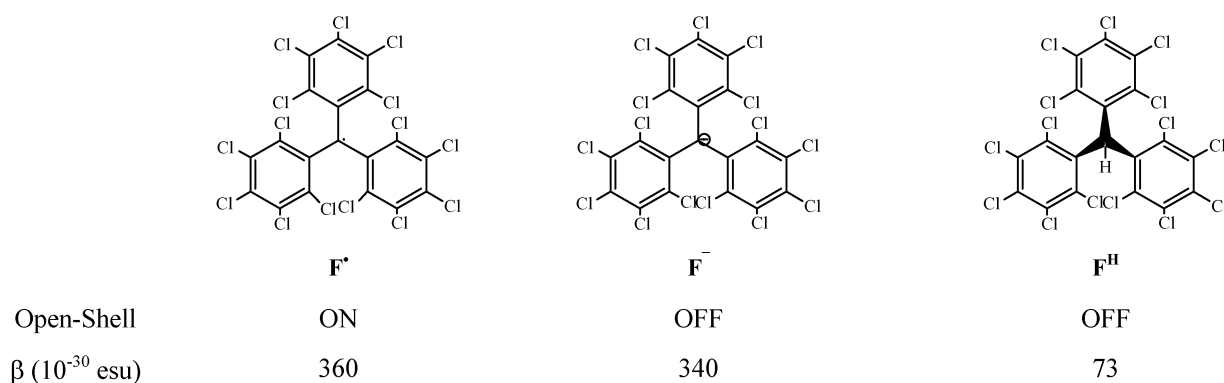
Scheme 7 Three step molecular switching array established for radical **F·** that is stimulated by two external pulses: a redox interconversion from the radical **F·** to the anion **F⁻** and an acid/base reaction that converts the anion to its protonated form **Fᴴ**.
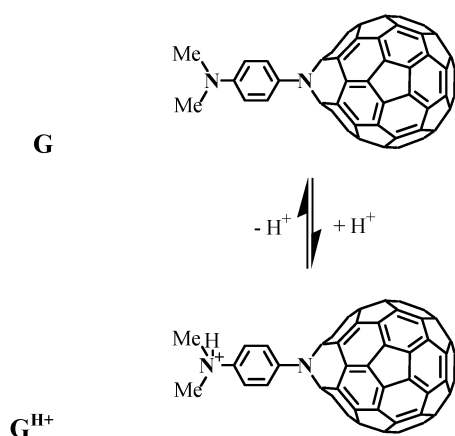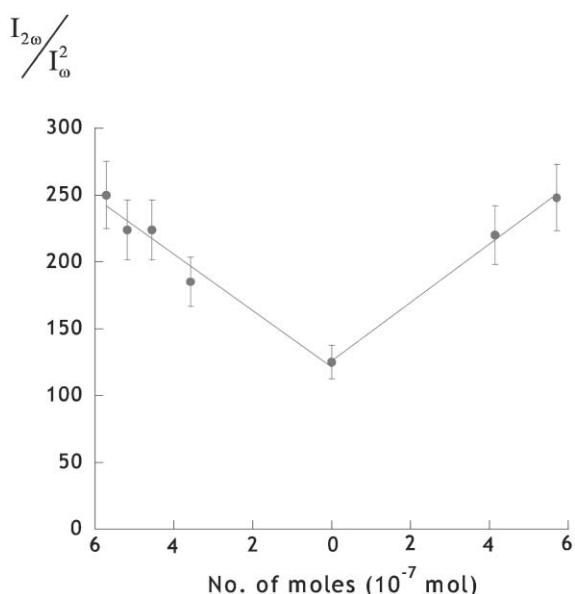

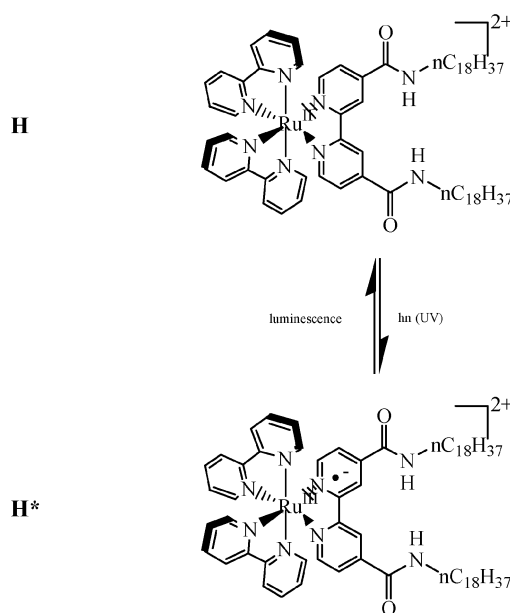**Scheme 8** (De)-Protonation reaction of compound **G**.

Fig. 1 Reversibility of the influence of protonation on the HRS response.

represents the decreasing number of moles of unprotonated azafulleroid upon protonation, starting from the initial number of moles in the cell, ending with zero upon complete protonation. The right part of the x-axis shows the increasing number of unprotonated molecules during the deprotonation with Hünig's base, starting from zero and ending with the original numbers of moles.
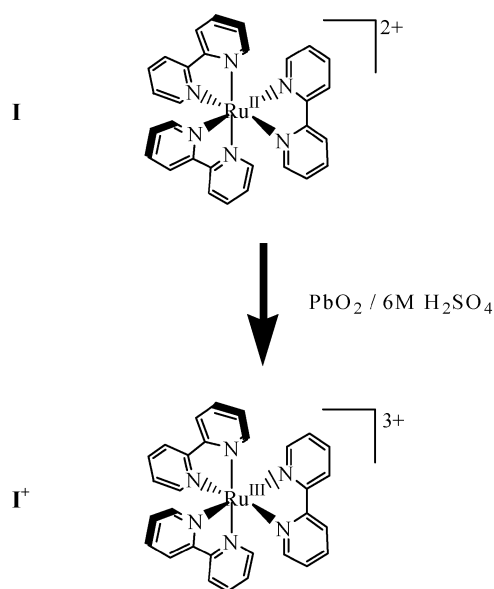
(b) Exploiting redox behaviour of donor and/or acceptor

The presence of a redox-active metal centre within a conjugated system provides excellent opportunities for modulation of the second-order nonlinear optical response. Sakaguchi et al.[24] first demonstrated the second-harmonic generation (SHG) photo-switching from appropriately modified tris(2,2′-dipyridyl) derivatives of Ru(II) tris(2,2′-bipyridine) complexes, **H** (Scheme 9), in Langmuir–Blodgett (LB) films.[25] The coherently generated second-harmonic signal from a 590 nm dye laser decreased by 30% in less than 2 ps upon irradiation at 378 nm. The initial value returned almost completely within several hundred ps. The same effect was observed for 355 nm radiation and a 1064 nm probe beam. The correlation between the SHG time profile and the luminescence decay of the metal-to-ligand charge transfer (MLCT) excited state indicates that the SHG switching is due to the change in β upon MLCT excitation. The β value at 1064 nm used in the photoswitching studies has been estimated to be 70×10^{-30} esu, but it is still unclear how the β response of **H** is affected by the MLCT excitations. The electron-withdrawing amide substituents will encourage MLCT into the π^* system of the substituted 2,2′-bipyridine ligand, leading to simultaneous oxidation of the Ru centre and reduction of a dipyridyl ligand, thereby giving a D^+–A^- structure: a combination of **type I** and **type II** strategies.

In 1994 Bijnens et al.[26] studied the effect of the oxidation state on the value of the first hyperpolarisability. The Ru(II)
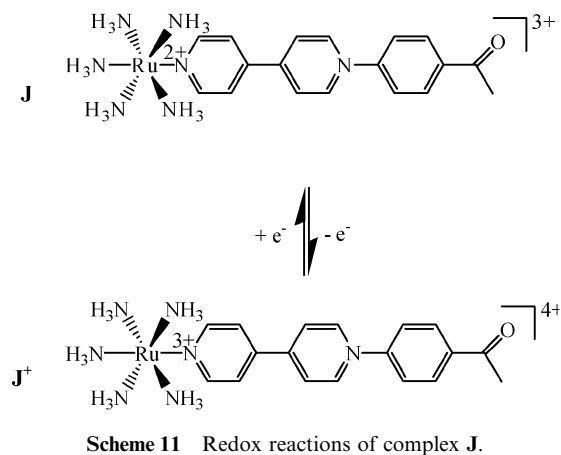

Scheme 9 MLCT excitation of complex **H**.

Scheme 10 Oxidation of complex **I**.
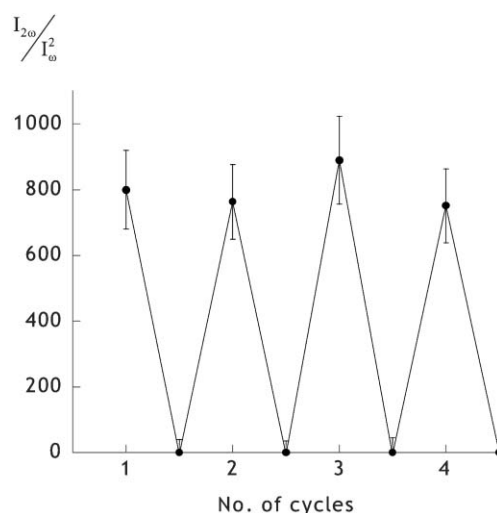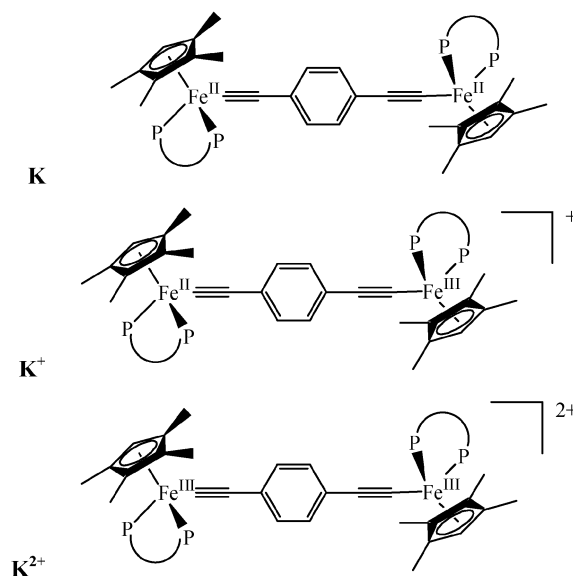

Scheme 11 Redox reactions of complex **J**.

Fig. 2 Redox switching of the second-order nonlinear optical response of complex **J** between its Ru^{II} and Ru^{III} (**J**$^+$) forms.

complex **I** could be oxidised by PbO_2 in concentrated sulfuric acid to **I**$^+$ (Scheme 10) and the position of the equilibrium is completely shifted to the oxidised form **I**$^+$ in 6 M H_2SO_4. This oxidation is accompanied by electronic spectral alterations, the strongest absorption in **I** shifting to the blue region with a drop in oscillator strength on conversion to **I**$^+$. Both **I** and **I**$^+$ have D_3 symmetry. Although these molecules are not dipolar, they are octopolar and therefore amenable to HRS investigations. Because of the D_3 symmetry, there is more than one major hyperpolarisability tensor component. However, based on the symmetry, the total number of 27 tensor components is reduced to ten non-zero components, with only two independent values. For this specific symmetry, the hyperpolarisability tensor cannot be further resolved and therefore the actual result is reported as $<\beta^2>^{1/2}$. The oxidation state also has its effect on the linear optical properties. The NLO properties of **I** and **I**$^+$ correlate well with their linear optical behaviour: the first hyperpolarisability of the oxidised form **I**$^+$ ($<\beta^2>^{1/2} = 21 \times 10^{-30}$ esu) being lower than for the reduced form **I** ($<\beta^2>^{1/2} = 40 \times 10^{-30}$ esu).

The effect of oxidation state on the first hyperpolarisability of ruthenium ammine complexes has been investigated by Coe *et al.*[27] using the HRS technique. The dipolar ruthenium(II) ammine complexes of 4,4′-bipyridinium ligands exhibit large tuneable β values associated with intense low-energy MLCT excitations, *e.g.* $\beta_{1064} = 1112 \times 10^{-30}$ esu and $\beta_0 = 354 \times 10^{-30}$ esu for compound **J**. The d^6 Ru(II) centre behaves as a powerful π-electron donor and is easily oxidised to its electron deficient d^5 Ru(III) analogue **J**$^+$. Oxidation of these Ru(II) complexes was achieved using 1 : 1 aqueous H_2O_2(30%)/2 M HCl and effectively quantitative re-reduction using 62% $N_2H_4\cdot2H_2O$ solution (Scheme 11). Oxidation was accompanied by loss of the low-energy MLCT band, which was fully reconstituted on re-reduction. The oxidised Ru(III) species produces very weak signals from which no meaningful hyperpolarisability value could be derived and consequently the loss of the low-energy MLCT (metal-to-ligand charge transfer) absorption on chemical oxidation of the Ru(II) complex results in a marked attenuation of the quadratic NLO response. This demonstrates effective switching of hyperpolarisability by chemical means. Fig. 2 shows the reversible switching of the NLO response. Since $I_{2\omega}/I^2_{\omega}$ is proportional to β^2, the reduction in hyperpolarisability on oxidation is estimated to be 10- to 20-fold, *i.e.*, at least an order of magnitude.

Weyland *et al.*[28] have investigated the effect of oxidation state on the second-order nonlinear optical properties of a series of bimetallic organo-iron complexes which formally contain Fe^{II} and/or Fe^{III}. The mixed-valence complex (Scheme 12) **K**$^+$ [Fe^{II}/Fe^{III}; $\beta_{1046} = 400 \times 10^{-30}$ esu] exhibits a β value twice as big as that of its neutral precursor **K** [Fe^{II}/Fe^{II}; $\beta_{1046} = 180 \times 10^{-30}$ esu) and the fully oxidised derivative
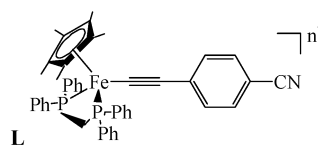

Scheme 12 Redox reactions of complex **K**.

K^{2+} (Fe^{III}/Fe^{III}; $\beta_{1046} = 200 \times 10^{-30}$ esu). Complex K^+ is a class II mixed-valence complex, retaining charge localisation but with enough electronic coupling between the redox centres to permit intense intervalence charge-transfer transitions. As the redox systems K/K^+ and K^+/K^{2+} are fully reversible, this system constitutes a reversible electronic switch of the molecular NLO response. In the case of the system K^{n+} there are three stable and defined forms for which the intermediate redox form gives a larger HRS response. An electro-switch can be activated in either oxidation or reduction modes. This type of molecule has clear potential for extension to switching of bulk NLO effects in electro-deposited films.

Paul et al.[29] have demonstrated the redox-switchable second-order molecular polarisabilities with electron-rich iron σ-aryl acetylides. A series of Fe(II) and their Fe(iii) analogues (L^{n+}) have been prepared and measured by the EFISH technique. For the cationic Fe(III) derivatives, $\mu\beta$ products are found to be smaller and overall negative values were found as compared to their Fe(II) parent compounds. An example is presented in Table 3.
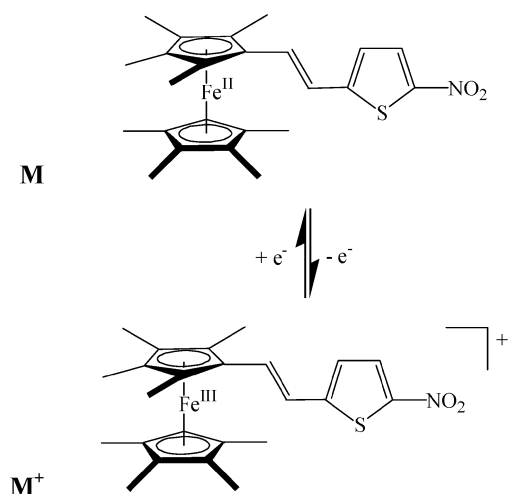
Ferrocenyl derivatives are ideal in the context of redox-active molecules with NLO potential since they are easy to prepare and contain the energetically convenient Fe^{II}/Fe^{III} couple. This has been demonstrated by Malaun et al.[30] using a combination of octamethylferrocenyl (D) and nitro-thiophenyl (A) chromophores (Scheme 13). Both M and its oxidised counterpart M^+ were shown crystallographically to be essentially identical. Oxidation of M to M^+ caused collapse of the two characteristic $D \rightarrow A$ charge transfer transitions in the former (644 nm and 477 nm in dichloromethane) and generation in the latter of the characteristic weak ligand-to-metal charge transfer (LMCT)

Table 3 Absorption maxima (λ_{max}), hyperpolarisability (β) and static hyperpolarisability ($\beta[0]$) for an iron σ-aryl acetylide

n	λ_{max}/nm	$\mu\beta/10^{-30}$ esu[a]	$\mu\beta[0]/10^{-30}$ esu
0	445	789	583
1	652	−56	−26

[a] Measured at 1.9 μm by electric field induced second harmonic generation (EFISHG), data taken from ref. 29.

transition of the ferrocenium unit (851 nm). M has a hyperpolarisability of 316×10^{-30} esu, which is lowered to 25×10^{-30} esu upon oxidation of the octamethylferrocene unit in M^+.

The redox interconversion of M and M^+ provides a basis for an effective switch for second-order NLO properties of the complex (Fig. 3). This was achieved chemically by oxidation using Bu_4NBr_3 and by reduction using $N_2H_4 \cdot 2H_2O$. Virtually identical results were obtained starting with M following an oxidation/reduction procedure, or using M^+ following a reduction/oxidation procedure.

The 'wet' chemical procedures effectively demonstrated the feasibility of hyperpolarisability switching but suffered from obvious disadvantages, including gradual degradation of the active species and difficulties in control of their concentration. However, electrochemical procedures potentially offer more attractive techniques for redox interconversion under controlled conditions. In situ electrochemical switching has the advantage that the redox-active portion of a molecule, even down to a single atom, can be addressed by applying a specific potential. Electrochemical switching of the third-order non-linear optical properties of the organometallic species N, which involves the Ru^{II}/Ru^{III} couple (Scheme 14), had previously been demonstrated by Cifuentes et al.[31] However, in order to
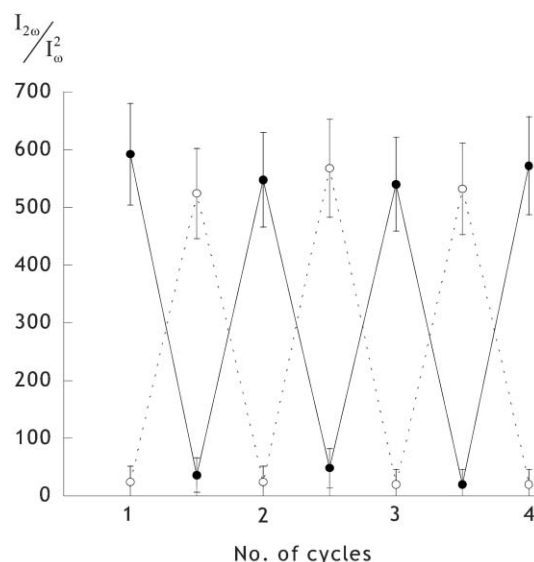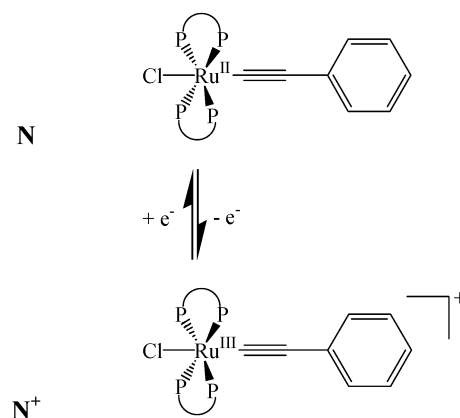

Fig. 3 Redox switching of the second-order nonlinear optical response of complex M between its Fe(II) and Fe(III) (M^+) forms starting from M and then alternately oxidising and re-reducing it (full line) or starting from M^+ and then alternately reducing and re-oxidising (dotted line).

Scheme 13 Redox reactions for complex M.

Scheme 14 Redox reaction for complex N.

utilise HRS techniques, a complete new cell design was necessary since the thin-layer electrochemical optical cell system adopted by Cifuentes *et al.* was not suitable.

For *in-situ* hyper-Rayleigh second-order scattering of electrochemically switched molecules, we developed a special cell (Fig. 4) to combine the optical constraints of second-order scattering with the physical limitations of electrochemistry.[32] The conventional cylindrical HRS cell has two reservoirs added to accommodate the electrodes. In one compartment the rotating Pt-gauze working electrode is housed together with the Ag/AgCl reference electrode. The other compartment hosts the Pt-counter electrode separated from the bulk solution by a porous glass frit. This cell has a capacity of 15 cm^3 and electrolysis takes 20–30 min.

Oxidation of **M** at an applied potential of 0.8 V occurred over a period of 20 min, and reduction of the oxidised species took 25 min at –0.7 V. The substantial decrease of the HRS response observed in the chemical procedure was duplicated in the electrochemical experiments (Fig. 5).

All examples given so far exploit the redox behaviour of the donor fragment (Fe$^{II/III}$ or Ru$^{II/III}$) and are based on type I switching (lowering the donor capacity). Type II switching (lowering the acceptor capacity of the acceptor fragment) has also been shown by reducing a molybdenum nitrosyl acceptor fragment.[33]

Conclusion

This article has shown several ways in which the first hyperpolarisability may be switched by exploiting the properties of various types of active molecules. Perhaps the most attractive procedures involve redox manipulation, particularly
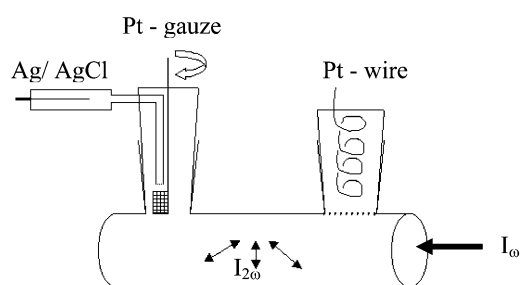
since this may be achieved, in principle at least, in solid state devices. Perhaps the next steps will involve the development of procedures which exploit reversible redox behaviour stimulated by laser irradiation at a different wavelength to that of normal NLO procedures. This could adopt NLO on/laser switch/NLO off protocols.

Fig. 4 Schematic view of the electrochemical/HRS cell.
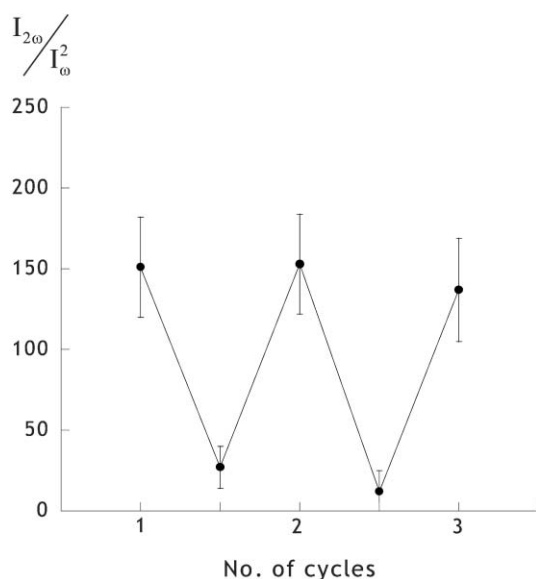
Fig. 5 Electrochemical switching of the HRS response between **M** and **M**$^+$.

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