CONCEPTS

Molecular Materials Possessing Switchable Quadratic Nonlinear Optical Properties

Benjamin J. Coe*[a]

Abstract: A diverse range of organic and metallo-organic molecular materials exhibit quadratic nonlinear optical (NLO) properties, for example, frequency doubling. The incorporation of switchability into the NLO behaviour of such materials will further increase their potential for novel applications in emerging optoelectronic and photonic technologies. Strategies for the molecular engineering of switchable NLO materials are outlined, and recent practical demonstrations of the switching of NLO responses, which utilize stimuli such as photoexcitation or redox reactions, are discussed.

Keywords: materials science · molecular switches · nonlinear optics · supramolecular chemistry

Introduction

General context: Recent years have witnessed a dramatic growth of multidisciplinary research activity involving materials that exhibit nonlinear optical (NLO) behaviour.[1–6] NLO effects are useful because they allow manipulation of the fundamental properties of laser light beams, for example in frequency doubling or tripling [*second* or *third harmonic generation* (SHG/THG), respectively]. Besides being already of widespread utility for SHG and THG in high-power laser systems, NLO materials are of great importance for emerging optoelectronic and photonic technologies relevant to applications such as optical computing. NLO activity can be found in semiconductors and inorganic crystals such as $LiNbO_3$,[1, 2] and also in various molecular organic materials.[3–6] The latter have attracted great interest owing to their potential advantages over the conventional inorganics for advanced applications. Furthermore, the inherent tailorability of molecular compounds renders them ideally suited for the creation of materials possessing switchable NLO properties.

[a] Dr. B. J. Coe
    Department of Chemistry, University of Manchester
    Oxford Road, Manchester M13 9PL (UK)
    Fax: (+44) 161-275-4598
    E-mail: b.coe@man.ac.uk

Origins of NLO behaviour in molecular materials: Although detailed mathematical explanations of the nature and origins of NLO effects are well beyond present scope, a brief discussion from a chemist's perspective is appropriate. At the molecular level, NLO phenomena arise from subtle interactions between polarizable electron density within a material and the very strong alternating electric field of a laser light beam. The resultant *induced polarization response* (P) of a molecule can be expressed as a power series in the applied field (E) according to the expression given in Equation (1).

$$P = \alpha E + \beta E^2 + \gamma E^3 + \dots \tag{1}$$

With normal values of E, the quadratic and cubic terms in Equation (1) can be neglected, and only linear optical behaviour is observed. The coefficient α is known as the *linear molecular polarizability* and is related to the refractive index of the material. However, under conditions where E approaches the magnitude of atomic field strengths, such as in a laser beam, the βE^2 and γE^3 terms in Equation (1) become important and it is these which give rise to quadratic (second-order) and cubic (third-order) NLO effects, respectively. The coefficients β and γ are termed *molecular hyperpolarizabilities*.

The equivalent form of Equation (1) at the macroscopic level is given in Equation (2), where the coefficients $\chi^{(2)}$ and

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \tag{2}$$

$\chi^{(3)}$ are the bulk hyperpolarizabilities of a molecular material. Because quadratic NLO effects arising from $\chi^{(2)}$ are considerably better understood and are also of greater immediate practical utility than their cubic counterparts, the latter are not considered further in this article.

Requirements for NLO activity: The vast majority of molecular compounds that possess large β values contain three basic components, namely, i) a powerful σ/π-electron donor group (D), ii) a powerful σ/π-electron acceptor group (A) and iii) a π-conjugated polarizable bridge connecting D to A. The linear optical properties of such dipolar, polarizable molecules are characterized by low-energy, intramolecular charge-transfer (ICT) transitions. Representative examples of

broadly dipolar molecules that exhibit pronounced quadratic NLO activities are shown in Figure 1. Of these species, **1**,[7] **3**[8] and **4**[9] all contain amino D groups, whilst **2** features an organometallic ferrocenyl D moiety.[10] The A units are an *N*-methylpyridinium group (in **1**), a coordinatively unsaturated molybdenum nitrosyl complex centre (in **2**), a nitro group (in **3**) and a 1,3-diethyl-2-thiobarbituric acid ring (in **4**).
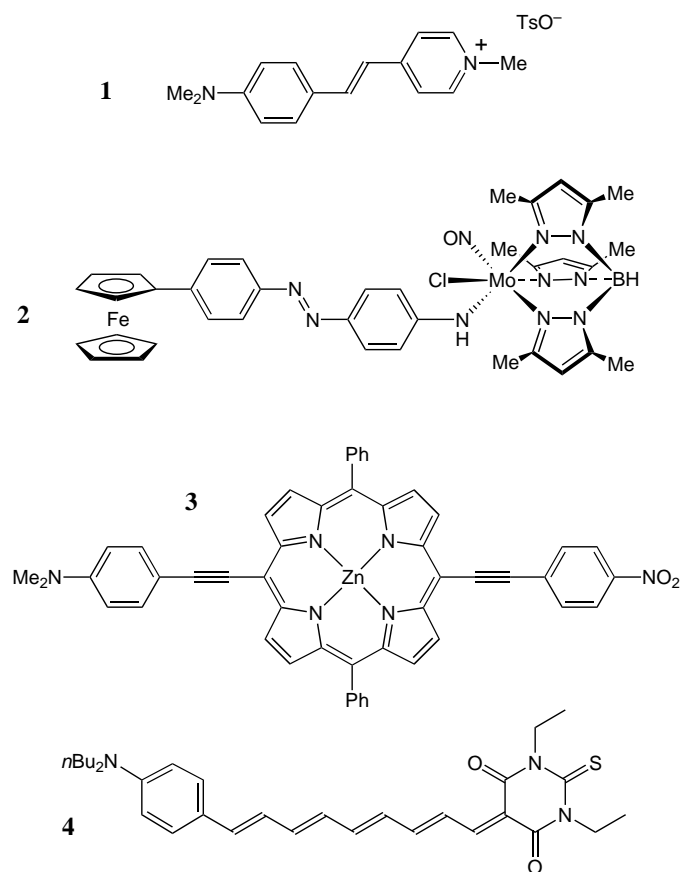

Figure 1. Representative examples of broadly dipolar molecules exhibiting large quadratic NLO responses (TsO⁻ = *p*-toluenesulfonate).

At the macroscopic level, the primary requirement for a nonzero $\chi^{(2)}$ value is a noncentrosymmetric material featuring some degree of alignment of the dipolar molecular constituents. The extent of potentially useful NLO activity hence depends not only on molecular structure, but also on crystal-packing arrangements (or the nature of the ordering within a thin-film or other material).

Measurement of NLO properties: Although numerous factors must be considered for device applications (e.g., thermal and photochemical stability, processability, etc.) the quadratic NLO properties of molecular materials are adequately discussed here by reference to β and $\chi^{(2)}$ coefficients. $\chi^{(2)}$ values are obtained from solid-state SHG experiments, whilst β coefficients are measured in solution, and until recently the only means for achieving this was the electric-field-induced SHG (EFISHG) technique.[11] Since SHG cannot be observed from an isotropic solution, poling with a strong external electric field is used to create a partially noncentrosymmetric macroscopic structure, and analysis of the second-harmonic light affords the component of β along the dipolar axis. Within the past few years the versatile hyper-Rayleigh scattering (HRS) technique has also become available.[12] This relies upon the fact that microscopic anisotropy within a solution can produce incoherent harmonic scattering; this allows the determination of different directional components of β. HRS has certain advantages over EFISHG, for example, it does not require knowledge of molecular dipole moments and is applicable to charged and octopolar compounds that are not ammenable to EFISHG study.

Measurements of β are typically made by the use of a 1064 nm NIR Nd³⁺:YAG laser fundamental (532 nm second harmonic), and the resultant β_{1064} values are increased by *resonance enhancement*. By using the two-level model,[13] which is valid for dipolar molecules in which β is primarily associated with a single ICT excitation, we can calculate β_0 values. β_0 is termed the *zero-frequency hyperpolarizability* and is an estimate of the intrinsic molecular hyperpolarizability in the absence of resonance effects. Applications of molecular NLO materials will generally involve NIR lasers operating in the region about 1000–1500 nm, and β_0 values represent molecular quadratic NLO responses at such off-resonance wavelengths.

Strategies for Switching of Quadratic NLO Responses in Molecular Materials

The intriguing concept of *molecular switches* has recently attracted great interest from a variety of perspectives.[14] A molecular-scale switch is a fundamental component of any true molecular electronic/photonic device, but the challenges inherent in the creation and operation of such an entity are formidable. An equally important, but more immediately realisable objective is the production of materials which exhibit useful bulk electronic/photonic properties that can be switched by stimulating changes at the molecular and/or macroscopic levels. As the molecular NLO field matures, it can be anticipated that materials which exhibit switchable NLO properties will find various novel applications.

For a classical D-π-A molecule, changes in the quadratic NLO response will occur upon alteration of the electronic properties of any, or all of, the individual functional units (Scheme 1). To achieve a pronounced switching effect, the molecule must be stable in two (or more) states that exhibit very different NLO properties. Complete reversibility and a high speed of switching are also highly desirable for practical applications. Whilst molecular-level changes can be readily effected by applying various stimuli (e.g., photoexcitation or redox reactions), the control of macroscopic structures is generally beyond the scope of current technology. Hence, almost all of the studies to date on the switching of NLO properties in molecular materials have involved the modulation of β responses.
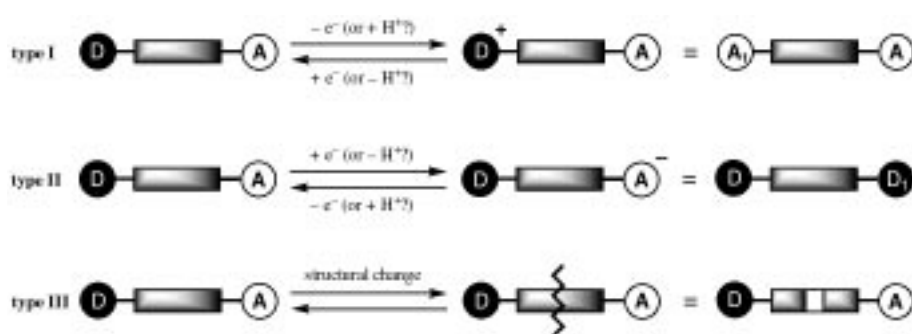
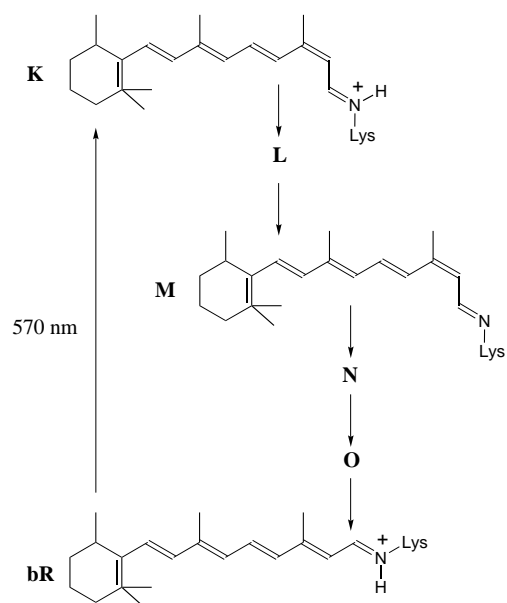Scheme 1. Schematic representations of strategies for switching of NLO responses in dipolar D-π-A molecules: type I = redox/proton transfer of D; type II = redox/proton transfer of A; type III = alteration of π-conjugation in bridge.
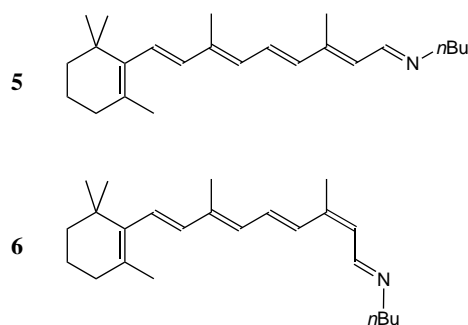
Compounds Possessing Switchable Quadratic NLO Properties

Bacteriorhodopsin chromophores: The protein *bacteriorhodopsin* (bR) is employed in nature as a photo-activated proton pump[15] and exhibits a diverse range of optical properties, which include pronounced NLO activity, that are suitable for various optoelectronic applications.[16] The bR photocycle features a series of ground-state intermediates that follow the simplified sequence bR(570) →K(620) →L(550) → M(410) →N(520) →(640) →bR(570) (the numbers in parentheses are the approximate absorption maxima in nm).[15] The chromophore in bR and related rhodopsins is a derivative of the polyene 6-s-*trans*-retinal, which is covalently attached through a protonated Schiff base linkage to a lysine residue of the protein backbone. The formation of the primary photoproduct (the K state) corresponds to a rotation around the C_{13}–C_{14} bond which occurs in <4 ps, forming the 13-*cis* isomer. Subsequent production of the M state coincides with the proton pumping and involves deprotonation by the $-CO_2^-$ group of an aspartate residue (Scheme 2).

Scheme 2. Selected forms of the chromophore in the photocycle of bacteriorhodopsin.

The NLO properties of bR and related compounds have been investigated by using the HRS technique. An extremely large β_{1064} value was determined for bR (2100×10^{-30} esu),[17] and studies with model compounds derived from 6-s-*cis*-retinal (**5** and **6**) show that both 13-*cis* isomerization and *N*-deprotonation cause large decreases in β (Table 1). Deprotonation reduces the acceptor strength and iso-

merization attenuates the D–A electronic coupling, the combined effect of these two changes being a reduction in β of about an order of magnitude.[18]

Table 1. Electronic absorption and HRS data for retinal derivatives in methanol.[18]

	λ_{max} [nm]	β_{1064}	β_0
		[$\times 10^{30}$ esu]	
5	365	470	220
5H+	445	3600	900
6	ca. 365	260	ca. 120
6H+	ca. 445	2440	ca. 600

Song et al. have observed 532 nm SHG from aqueous suspensions of the purple membrane of the bacterium *Halobacterium halobium*, which contains orientated bR chromophores.[19] Furthermore, they found that formation of the M state of bR upon 570 nm photoexcitation causes a decrease in the intensity of the SHG signal within 1 μs, which reaches a minimum in less than 1 ms and returns to its original value as the photocycle is completed. A reduction in the SHG intensity of 60% was typically observed, but this increased to as much as 90% in more dilute samples. Given the HRS results obtained with bR[17] and model compounds,[18] this efficient switching effect is clearly a result of the large decrease in β caused by photoexcitation of the bR chromophores. This corresponds to a hybrid of the type II and III approaches outlined earlier (Scheme 1).

Azobenzene-containing polymers: Polymeric materials are particularly attractive for NLO applications owing to their favourable processability and stability characteristics. Electric

poling can be used to induce chromophore alignment within a heated polymer that is then cooled to below its glass-transition temperature (T_g), while the electric field is maintained. Long-term stability of the ordering in the absence of an external field is required for applications. SHG switching has recently been demonstrated in two types of polymer that contain prototypical azobenzene-derived NLO chromophores.

Delaire et al. found that 488 nm irradiation of films cast from solutions of the dye disperse red 1 (DR1, **7**) in poly-(methyl methacrylate) (PMMA) causes an irreversible decrease (ca. 30 %), followed by a reversible decrease (ca. 30 %) in the intensity of 532 nm SHG.[20] These effects, which occur on a timescale of seconds, are ascribed to partial *trans →cis* photoisomerization (Scheme 3) of the DR1 molecules occupying two different types of site within the PMMA matrix.
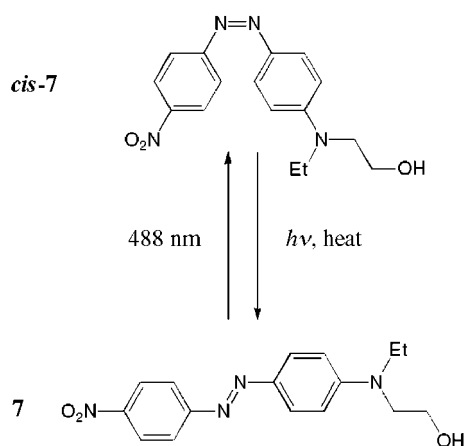
Scheme 3. Photoisomerization of the azo dye disperse red 1 (**7**).

The initial decline arises from irreversible disorientation of a portion of the molecules upon conversion back to their *trans* form (free molecules), whilst the reversible component is due to the fraction of molecules that can only recover their initial orientation (trapped molecules). By contrast, identical treatment of a DR1-functionalized PMMA copolymer (**8**) leads only to an irreversible loss of SHG. This indicates that all of the pendant DR1 units in films of **8** are free to undergo orientational changes upon isomerization. The suggestion that the reversible SHG switching arises from molecular-level changes is supported by MO calculations, which afford β_0 values for **7** and *cis*-**7** of 44.6×10^{-30} and 8.4×10^{-30} esu, respectively.[20] The smaller β_0 for *cis*-**7** is largely due to a departure from planarity of the azobenzene bridge.

Polysiloxanes generally possess low T_g values, and are uninteresting as poled-polymer NLO materials as a result of ready relaxation of aligned chromophores. However, this fact has been exploited by Abe et al., who found that the application of an electric field to a once-annealed solid film of a side-chain liquid crystalline polysiloxane containing azobenzene chromophores (**9**) causes a rapid (timescale of seconds), approximate fivefold increase in the intensity of 532 nm SHG.[21] This effect reverses upon breaking the electric field, and the switching can be cycled repeatedly. The marked SHG enhancement was ascribed to field-induced
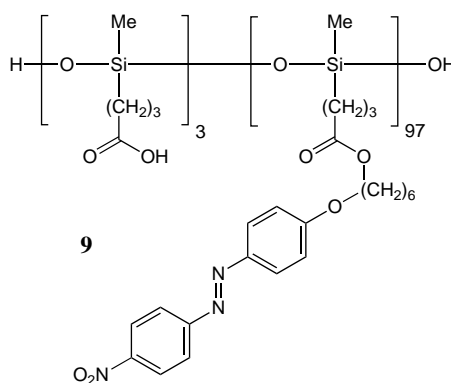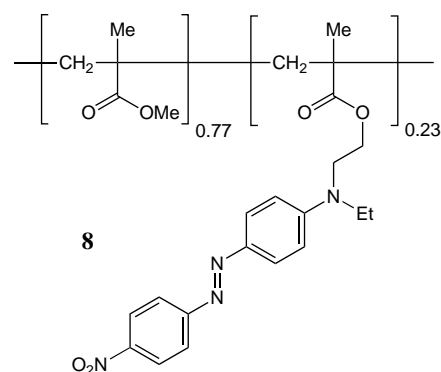
chromophore alignment (Scheme 4, p. 2468), made possible by the low T_g of the polymer, that is, even at room temperature, the siloxane backbones are sufficiently mobile to allow facile movement of the azobenzene units.[21] This report hence represents a rare example in which switching of NLO responses has been achieved by controlling macroscopic ordering rather than by modulating molecular hyperpolarizabilities.

A bis(3-thienyl)ethene derivative: Thiophene derivatives of perfluorocyclopentene are photochromic and possess high thermal and photochemical stabilities.[22] Lehn et al. have reported that the marked photochromism of compound **10** permits efficient switching of the NLO responses.[23] UV irradiation at 365 nm for about 30 s causes complete photocyclization of the yellow **10** to the deep blue **10ᶜ**, and this process is reversed upon exposure to visible light of wavelength > 600 nm for about 5 min (Scheme 5, p. 2468). Repeated cycling causes no significant decomposition. The colour of **10ᶜ** arises from a NIR absorption band due to ICT from the 1,3-benzodithiole-2-ylidenyl D group to the dicyanomethylidenyl A group.

Since the extent of D–A π-conjugation is clearly much greater in **10ᶜ** than in **10**, the former possesses the larger quadratic NLO response of the two molecules: 1064 nm EFISHG studies afford values for $\mu\beta(\mu\beta_0)$ of $260(127) \times 10^{-48}$ esu for **10** and $1100(620) \times 10^{-48}$ esu for **10ᶜ** (μ = dipole moment).[23] The β response is hence reversibly switched by a factor of approximately fourfold upon photoisomerization.
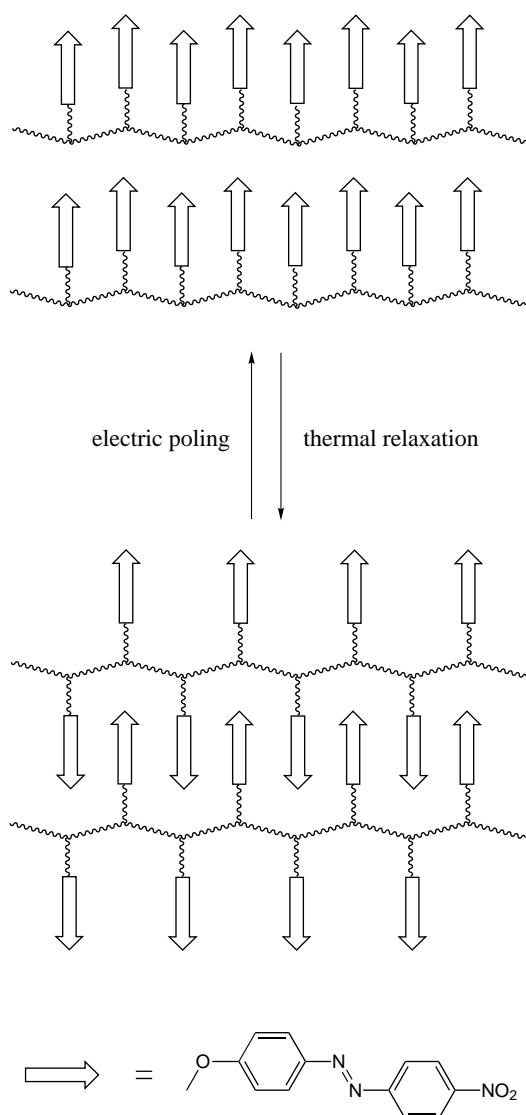
Scheme 4. Schematic representation of the (proposed) effect of electric poling on alignment of the dipolar chromophores in the functionalized polysiloxane **9**.

This is an excellent illustration of the modulation of molecular NLO properties by alteration of the π-bridge structure (type III, Scheme 1), and extended molecules such as **10** can be regarded as a basis for photoswitchable *molecular wires*.[23]

Nitrobenzylpyridines: The colourless compound 2-(2,4-dinitrobenzyl)pyridine (**11**) undergoes a two-step, photoinduced proton transfer reaction to form a deep blue tautomer **11^{pt}** (Scheme 6).[24] Since **11** features a methylene linkage, whilst **11^{pt}** contains a fully conjugated D-π-A system, Lehn et al. have suggested that **11** (or related compounds) may act as photoswitchable NLO materials.[25] HRS was hence used to determine the β values of a series of molecules designed to act as models for the two tautomers **11** and **11^{pt}**,[25] **14** and **15** clearly bearing the closest similarity to **11**. The UV-visible absorption maxima and HRS data for **12 – 15** are summarised in Table 2.
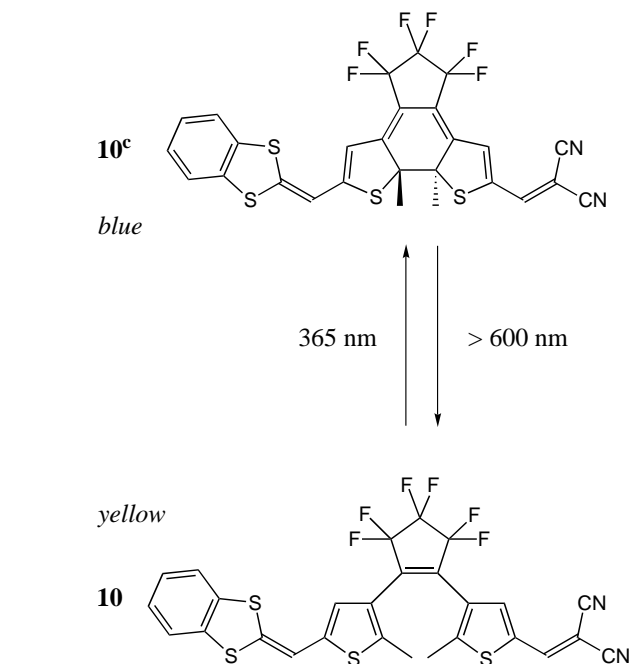

Scheme 5. Photocyclization of the bis(3-thienyl)ethene derivative **10**.

The very large β_{1064} differences between the pairs **12/13** and **14/15** are partly due to extensive resonance enhancements at 532 nm, which arise from the strong visible absorptions of **13** and **15**. However, **13** also shows a much larger β_0 value than its less conjugated counterpart **12**. Although the corresponding difference for **15** with respect to **14** is rather smaller, it is likely that β_0 for **15** is underestimated owing to limitations inherent in the two-level model. These data hence provide evidence that compounds such as **11** may indeed be amenable towards optical modulation of quadratic NLO responses.[25]
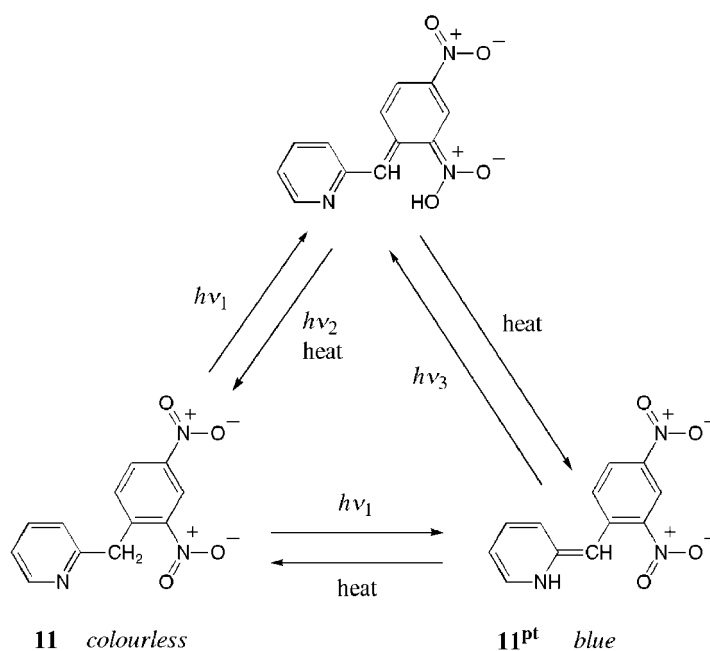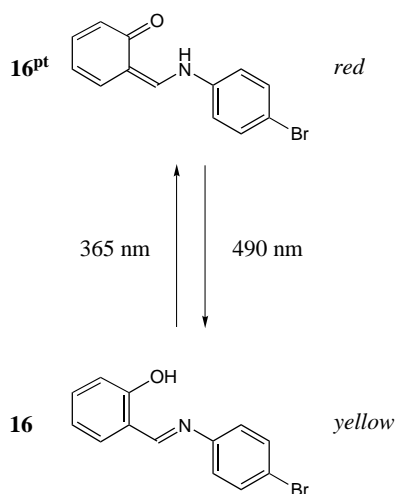

Scheme 6. Phototautomerization of 2-(2,4-dinitrobenzyl)pyridine (**11**).

12

13

14

15
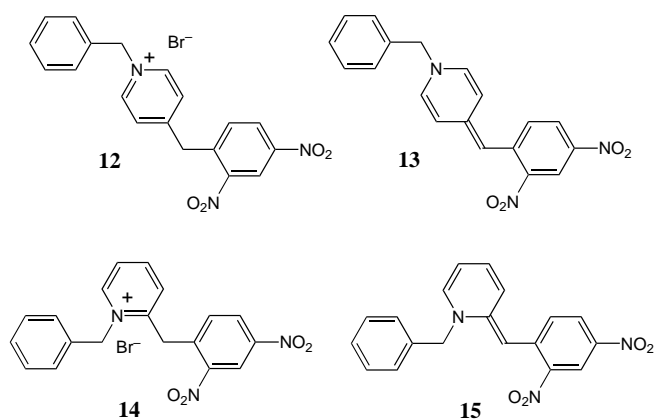
Table 2. Electronic absorption and HRS data for **12 – 15** in acetonitrile.[25]

	λ_{max} [nm]	β_{1064}	β_0
		[$\times 10^{30}$ esu]	
12	254	2	1
13	582	450	62
14	266	7	5
15	567	84	8

N-Salicylidene-4-bromoaniline: Delaire et al. chose the photochromic compound *N*-salicylidene-4-bromoaniline (**16**) for a SHG photoswitching study[26] because it adopts a favourable noncentrosymmetric crystal structure.[27] Upon 365 nm irradiation of **16**, the red colour of the tautomeric form **16^{pt}** appears; an equilibrium between the two forms is established after approximately 30 s.[26] Tautomer **16^{pt}** then reverts to **16** either thermally or under visible irradiation (Scheme 7), within about 30 s. This allows fully reversible SHG switching, with intensity decreases of approximately 60 % when a 1064 nm probe beam is used, and approximately 10 % with a 1907 nm fundamental. Given that the tautomerization causes minimal structural change at the macroscopic level, the SHG switching is likely to be a result of a difference in β between **16** and **16^{pt}**. The larger effect observed at 1064 nm may arise from strong absorption at 532 nm by **16^{pt}**; this more than offsets the increase in β due to resonance enhancement. In the absence of

experimental data, MO calculations provide β_0 values of 2.3×10^{-30} esu and 1.3×10^{-30} esu for **16** and **16^{pt}**, respectively; these values are in accord with the lower SHG intensity observed from **16^{pt}**.[26] The tautomerization converts an imino into an amino bridge, so the switching mechanism in this case is primarily of type III (Scheme 1).

Ruthenium(II) tris(2,2′-bipyridine) complexes: The presence of redox-active metal centres within a conjugated framework provides extensive opportunities for modulation of molecular NLO responses, and is hence a primary justification for the study of NLO-active metal complexes.[28] This was first addressed by Sakaguchi et al. in demonstrations of SHG photo switching from a derivative of [Ru^{II}(bpy)₃]²⁺ (bpy = 2,2′-bipyridine) (**17**) in Langmuir–Blodgett (LB) films (Figure 2).[29] Following 378 nm irradiation the SHG signal from a 590 nm dye laser decreased by 30 % in less than 2 ps and

glass slide

Scheme 7. Phototautomerization of *N*-salicylidene-4-bromoaniline (**16**).
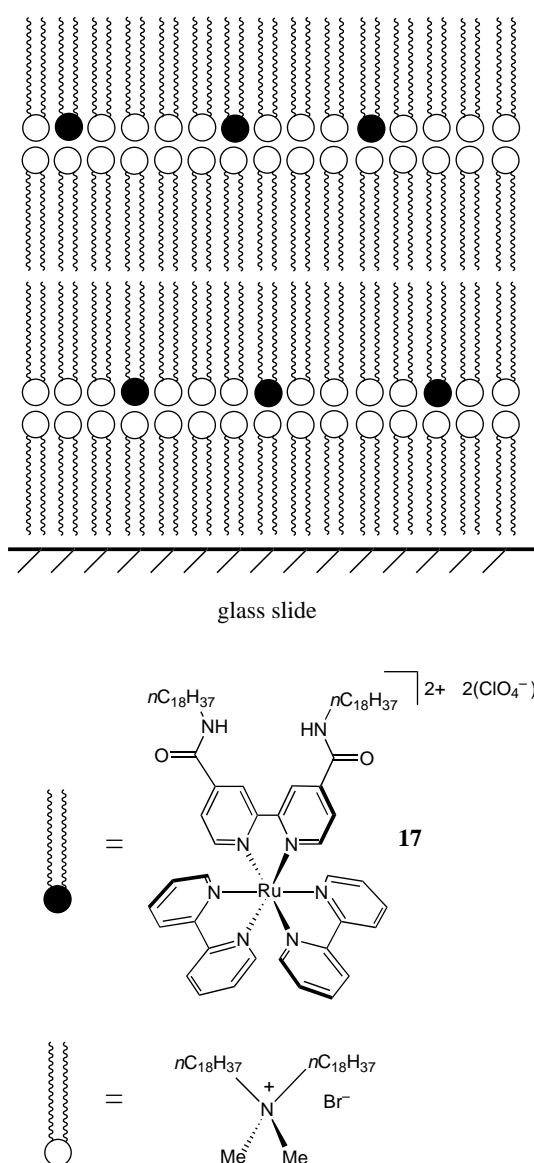
Figure 2. Schematic representation of alternating LB films containing the complex **17**. The actual samples featured 30 bilayers on each side of the support.

returned to almost its intial value within several hundred ps;[29b] a similar effect was observed with 355 nm excitation and a 1064 nm probe beam.[29c] A quantitative 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.[29]

Although $[\text{Ru}^{II}(\text{bpy})_3]^{2+}$ itself is an octopolar system, the symmetry is reduced by asymmetric ring substitutions such as those in **17**. β_{1064} of the LB films used in the photoswitching studies has been estimated at 70×10^{-30} esu,[30] but it is currently unclear how the β response of **17** will be affected by MLCT excitation.[29] The electron-withdrawing amide substituents will encourage MLCT into the π^* system of the substituted bpy ligand (Scheme 8), corresponding to simultaneous Ru oxidation and bpy reduction to give a $D^+ - A^-$ structure, that is, a combination of the type I and II strategies (Scheme 1).
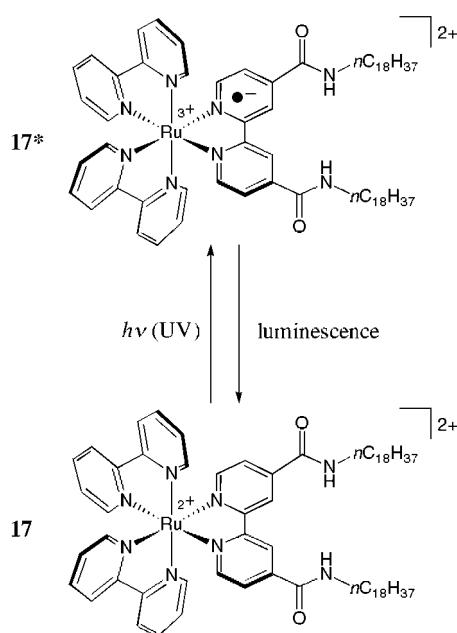

Scheme 8. MLCT excitation of complex **17**.

Ruthenium(II) ammine complexes: By using HRS measurements, Coe et al. have shown that dipolar ruthenium(II) ammine complexes of 4,4'-bipyridinium ligands exhibit very large, tunable β values, which are associated with intense, low-energy MLCT excitations.[31] For example, the $\beta_{1064}(\beta_0)$ values for **18** and **19** are $794(260) \times 10^{-30}$ esu and $1112(354) \times 10^{-30}$ esu, respectively.[31c] The d^6 Ru^{II} centres behave as
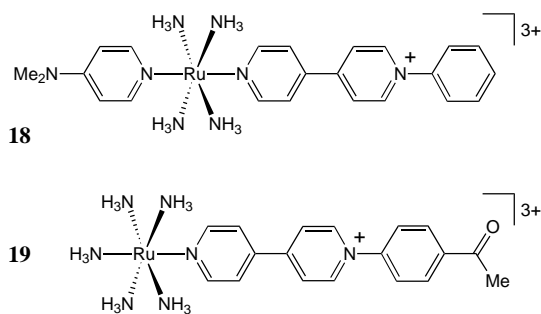
powerful π-donors and are readily oxidized to their electron-deficient Ru^{III} analogues either electrochemically or chemically. It has been found that both the visible absorptions and HRS signals from such complexes featuring $\{\text{Ru}^{II}(\text{NH}_3)_5\}^{2+}$ donors are dramatically attenuated upon oxidation with 1:1 30% aqueous $H_2O_2/2$ M HCl, and are restored to their original magnitudes by re-reduction with 62% $N_2H_4 \cdot H_2O$ solution.[32] A completely reversible switching (Scheme 9) of the molecular NLO responses is thus achieved, the difference in β between **19** and **19^{ox}** being approximately 10–20-fold. This constitutes the only documented case in which β switching has been achieved through the redox reaction of a D group (type I, Scheme 1), and such an approach has obvious potential for extension to the switching of bulk NLO effects in electrode-deposited films.
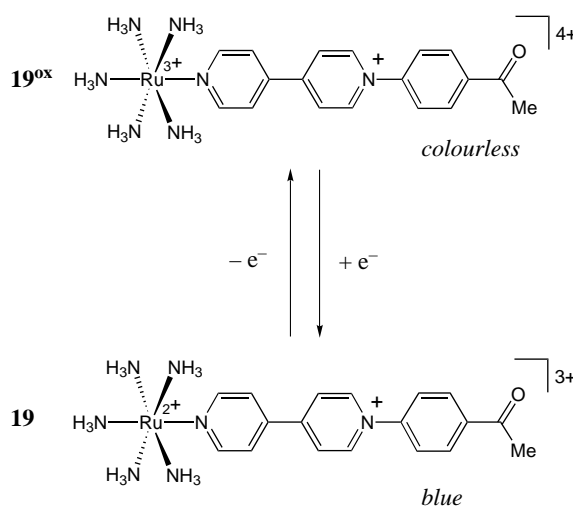
Scheme 9. Redox reactions of complex **19**.

Summary and Conclusions

The studies discussed herein illustrate a variety of approaches to the switching of quadratic NLO properties in a diverse range of materials. For purposes of comparison, selected details [except for the nitrobenzylpyridines for which an actual switching has not yet been demonstrated (see section on nitrobenzylpyridines above)] are summarised in Table 3.

With the exceptions of the studies with **9**, **17** and **19**, all have employed photoexcitation to stimulate some form of molecular structural change. If the macroscopic consequences of such a change are minor, then switching can be achieved in the solid-state (e.g., **16**). In principle, owing to the strong correlation between optical absorption and NLO properties, any material that is markedly photochromic (or thermochromic) can be expected to also possess photoswitchable NLO responses. Flavylium compounds, which can exist in several different states, are a particularly attractive example.[33] In the case of **17** photoexcitation was also used, but produced a transient excited state with an essentially unchanged molecular structure. The study with **9** is unusual in being the only example to feature manipulation of macroscopic alignment. The use of redox-switching with **19** is also unique. Transition

Table 3. Summary of data for switching of quadratic NLO responses in molecular materials.

Material (form)[a]	β data[b]	Switching stimulus	Property switched (direction)[c]	Extent of switching (%)[d]	Timescale	Source of effect	Type[e]	Ref(s).
bR (susp)	HRS $\beta_{1064} = 2100$	570 nm excitation	532 nm SHG ($\downarrow$)	60–90	μs	formation of M state	II + III	[17, 19]
7 (PMMA matrix)	MO $\beta_0 = 44.6$ (7) $\beta_0 = 8.4$ (*cis*-7)	488 nm excitation	532 nm SHG ($\downarrow$)	30	s	*trans* →*cis* isomerization	III	[20]
9 (solid)	–	electric poling	532 nm SHG ($\uparrow$)	80	s	dipole alignment	–	[21]
10 (soln)	SHG $\mu\beta_0 = 127$ (10) $\mu\beta_0 = 620$ (10c)	365 nm excitation	532 nm EFISHG ($\uparrow$)	75	30 s/5 min	photocyclization	III	[23]
16 (crystal)	MO $\beta_0 = 2.3$ (16) $\beta_0 = 1.3$ (16pt)	365 nm excitation	532 nm SHG ($\downarrow$) 953 nm SHG ($\downarrow$)	60 10	30 s	tautomerization	III	[26]
17 (LB film)	SHG $\beta_{1064} \approx 70$	378 nm excitation 355 nm excitation	295 nm SHG ($\downarrow$) 532 nm SHG ($\downarrow$)	30	ps	MLCT excitation	I + II	[29, 30]
19 (soln)	HRS $\beta_0 = 354$	chemical oxidation	532 nm HRS ($\downarrow$)	(β) 90–95	< s	oxidation of D	I	[31, 32]

[a] susp = suspension; soln = solution. [b] All β values $\times 10^{30}$ esu; $\mu\beta \times 10^{48}$ esu. [c] $\uparrow$ denotes an increased NLO response, $\downarrow$ a decrease. [d] Decrease with respect to maximum response. [e] According to Scheme 1.

metal complexes are ideally suited towards the latter type of switching, but large effects can only be expected with strongly electrochromic materials. A further possibility for controlling the extent of D–A π-conjugation, which has not yet been exploited as a mechanism for β switching, is inter-ring twisting in polyaryl chromophores. Recent theoretical work has shown that such conformational effects can cause large changes in NLO reponses.[34]

In conclusion, several demonstrations of switching of quadratic NLO responses have recently been reported that exploit the diverse, tailorable properties of molecular materials. Given the wealth of NLO-active molecules now available, many exciting developments in this field can be anticipated and these will further increase the potential of molecular materials for future applications in NLO technologies.

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