BACKGROUND/CONTEXT

Recent years have witnessed great interest in molecular materials which display non-linear optical (NLO) behaviour, due to their potential for applications in nascent optoelectronic and photonic technologies. The majority of such materials consist of purely organic compounds, but various organotransition metal complexes are also known to possess NLO properties. The incorporation of metal centres into highly polarizable molecular frameworks can lead to large NLO responses, and offers a versatility of structure and function (e.g. redox or magnetic properties) beyond that available with traditional organic materials. Ruthenium complexes have been especially well studied for their quadratic (second-order) NLO properties, and our contribution to this field has focused on Ru ammine complexes of coumarin or pyridinium ligands.

Molecules having large quadratic NLO activities contain electron donor and acceptor groups connected via polarisable π-systems. At the molecular level, quadratic NLO behaviour is governed by first hyperpolarizabilities which are generally measured by using the electric-field-induced second harmonic generation (EFISHG) or hyper-Rayleigh scattering (HRS) techniques. The HRS method has the important advantage over the more traditional EFISHG approach in being applicable to charged compounds, such as complex salts. Static (off-resonance) β₀ values, obtained by application of the two-state model for dipolar chromophores, are most relevant to practical applications and are generally used for comparison purposes. The creation of new materials for quadratic NLO applications begins with the design of chromophores possessing large β₀ values. Detailed β₀ structure-activity relationships for purely organic compounds are established, but comparable understanding for organotransition metal complexes is less well-developed.

Our systematic studies with Ru ammine/pyridinium complexes, using HRS measurements, have led to the following conclusions: (i) such complexes possess unusually large β₀ values; (ii) their intense, low energy metal-to-ligand charge-transfer (MLCT) absorptions and β₀ values can be finely tuned by ligand-based changes and β₀ correlates well with 1/(Eₘₚₓₚ₂) in accord with the two-state model; (iii) the MLCT absorption and β₀ responses of {Ru(NH₃)₅}²⁺ complexes can be reversibly and very effectively switched by Ru redox. It is worth noting that since our discovery of redox-switching of β responses, other research groups have also reported similar effects in different metal complexes.

KEY ADVANCES AND SUPPORTING METHODOLOGY

(i) Stark Spectroscopic Studies

Our studies prior to the commencement of this grant had relied solely on the HRS technique to extract β₀ values. In order to obtain further insights into the electronic structures of our complexes,
and also to verify their large HRS $\beta_0$ values, we decided to extend our studies to include Stark (electroabsorption) spectroscopic measurements. Stark spectroscopy\textsuperscript{20} has recently been applied to a small number of compounds having quadratic NLO properties such as donor-acceptor polyenes,\textsuperscript{21} porphyrins,\textsuperscript{22} metalloacenyl derivatives\textsuperscript{23} and Ru\textsuperscript{II} complexes.\textsuperscript{24} The Stark technique involves analysing the effect of an applied electric field on absorption bands and allows measurement of the dipole moment change on CT excitation $\Delta \mu_{12}$. According to the two-state model, $\beta_0 = 3\Delta \mu_{12}(\mu_{12})^2/(E_{\text{max}})^2$,\textsuperscript{14} where $\mu_{12}$ is the transition dipole moment which is derived from the oscillator strength. If $\Delta \mu_{12}$ and $\mu_{12}$ values are derived, then various other molecular electronic parameters can also be calculated, e.g. diabatic dipole moment changes $\Delta \mu_{\text{ab}}$, mixing coefficients $c_{b2}$ and electronic coupling matrix elements $H_{ab}$ for the diabatic states. Stark spectroscopy is hence a powerful technique which can provide extensive information concerning molecular electronic structures. Stark measurements have been carried out on a large number of complex salts available from our previous synthetic studies,\textsuperscript{10b–e} and selected data are shown in Table 1 below.

<table>
<thead>
<tr>
<th>L</th>
<th>L'</th>
<th>$E_{\text{max}}$/eV</th>
<th>$\Delta \mu_{12}$/D</th>
<th>$\mu_{12}$/D</th>
<th>$\beta_0$[HRS] $\times 10^{30}$ esu</th>
<th>$\beta_0$[Stark] $\times 10^{30}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>MeO$^+$</td>
<td>3.08</td>
<td>13.8</td>
<td>5.2</td>
<td>123</td>
<td>120</td>
</tr>
<tr>
<td>Mebpe$^+$</td>
<td>2.92</td>
<td>16.2</td>
<td>5.5</td>
<td>142</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>PhQ$^+$</td>
<td>2.85</td>
<td>15.3</td>
<td>5.7</td>
<td>220</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>Phbpe$^+$</td>
<td>2.79</td>
<td>19.5</td>
<td>5.7</td>
<td>192</td>
<td>249</td>
<td></td>
</tr>
<tr>
<td>mim</td>
<td>2-PymQ$^+$</td>
<td>2.53</td>
<td>16.8</td>
<td>6.4</td>
<td>336</td>
<td>323</td>
</tr>
<tr>
<td>dmap</td>
<td>4-AcPhQ$^+$</td>
<td>2.71</td>
<td>20.3</td>
<td>6.8</td>
<td>410</td>
<td>388</td>
</tr>
</tbody>
</table>

Table 1. Stark spectroscopic and HRS data for salts trans-[Ru$^{\text{II}}$(NH$_3$)$_5$L(L')]$[PF_6]$$_3$

[mim = N-methylimidazole; dmap = 4-(dimethylamino)pyridine; MeO$^+$ = N-methyl-4,4'-bipyridinium; Mebpe$^+$ = N-methyl-4-(trans-2-(4-pyridyl)ethenyl)pyridinium; PhQ$^+$ = N-phenyl-4,4'-bipyridinium; Phbpe$^+$ = N-phenyl-4-(trans-2-(4-pyridyl)ethenyl)pyridinium, 4-AcPhQ$^+$ = N-(4-acetylphenyl)-4,4'-bipyridinium; 2-PymQ$^+$ = N-(2-pyrimidyl)-4,4'-bipyridinium]. $E_{\text{max}}$ and Stark data at 77 K in PrCN; HRS data at 298 K in MeCN.

In general, the $\beta_0$[Stark] values agree well with $\beta_0$[HRS]. The Stark results hence confirm that the two-state model is valid for our Ru\textsuperscript{II} complexes, verify their large magnitudes of $\beta_0$ and also reinforce our earlier conclusion that N-arylation enhances $\beta_0$,\textsuperscript{10c–e} the latter effect being most significant in the 4,4'-bipyridinium-based complexes. Increases in $\beta_0$ are generally associated with decreases in $E_{\text{max}}$ and increases in both $\mu_{12}$ and $\Delta \mu_{12}$, and insertion of a trans-CH=CH bridge into the 4,4'-bipyridinium unit of L' enhances $\beta_0$ by ca 35–50%. A detailed account of these studies will soon be published.\textsuperscript{25}

We have also used our Stark results and HRS data to allow a comparison of the relative merits of the 4-dimethylaminophenyl and pentaammine(pyridyl)ruthenium(II) groups as electron donors for NLO effects. Perhaps surprisingly, quantitative, systematic comparisons of the electron donor/acceptor properties of metal centres with those of more traditional organic groups are very scarce. Our studies show that the complex salts [3–6]PF$_6$ have larger $\beta_0$ values than the compounds [7–10]PF$_6$, because the higher HOMO energy of a {Ru$^{\text{II}}$(NH$_3$)$_5$}$^{2+}$ centre more than offsets the superior $\pi$-orbital overlap in the purely organic chromophores.\textsuperscript{26} Representative data are as follows: for 4, $\beta_0$[HRS] = 220 $\times 10^{-30}$ esu; $\beta_0$[Stark] = 186 $\times 10^{-30}$ esu. For 8, $\beta_0$[HRS] = 23 $\times 10^{-30}$ esu; $\beta_0$[Stark] = 150 $\times 10^{-30}$ esu.
(ii) Complexes with Anionic Trans Ligands

Because our dipolar RuII complexes follow the two-state model, $\beta_0$ increases as the MLCT absorption red-shifts. The MLCT energy can be decreased, and hence $\beta_0$ enhanced, by increasing the electron donor strength of the RuII centre and/or by increasing the electron acceptor strength of the pyridinium unit. As noted in the original proposal, one strategy for increasing the electron donor strength of a trans-{RuII(NH$_3$)$_4$}$_2^{2+}$ centre is to incorporate trans ligands which are more basic than those studied previously (e.g. NH$_3$ or dmap). We have therefore attempted to prepare trans-{RuII(NH$_3$)$_4$}$_2^{2+}$ complexes with a variety of different anionic trans ligands including thiocyanate (NCS$^-$), cyanate (NCO$^-$) and azide (N$_3$). Unfortunately, coordination of such ligands under the normal aqueous reaction conditions has proven challenging (most likely due to solvation effects) and the only ligand from which we have been able to isolate pure products is NCS$^-$. Hence, the series of complexes trans-[RuII(NCS)(NH$_3$)$_4$L]$^{2+}$ ($L' = \text{MeQ}^+$ 11, PhQ$^+$ 12, 4-AcPhQ$^+$ 13, 2-PymQ$^+$ 14, Mebpe$^+$ 15) has been prepared. Evidence that the RuII centres in 11–15 are stronger electron donors than their {RuII(NH$_3$)$_5$}$_2^{2+}$ counterparts is found in the MLCT spectra and cyclic voltammetric Ru$^{III/II}$ $E_{1/2}$ values. For example, the data for the 4,4$'${bipyridinium-based complexes are shown in Table 2 below.

![Complexes diagram](image)

Table 2. MLCT and cyclic voltammetric data for salts trans-[RuII(NH$_3$)$_4$L(L')]$_2$[PF$_6$]$_n$

<table>
<thead>
<tr>
<th>L</th>
<th>L'</th>
<th>n</th>
<th>$E_{max}$/eV</th>
<th>$E_{1/2}$/V</th>
</tr>
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<tbody>
<tr>
<td>NH$_3$</td>
<td>MeQ$^+$</td>
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<td>2.10</td>
<td>0.48</td>
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<td>MeQ$^+$</td>
<td>2</td>
<td>1.99</td>
<td>0.38</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>PhQ$^+$</td>
<td>3</td>
<td>1.97</td>
<td>0.48</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>PhQ$^+$</td>
<td>2</td>
<td>1.84</td>
<td>0.40</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4-AcPhQ$^+$</td>
<td>3</td>
<td>1.90</td>
<td>0.49</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>4-AcPhQ$^+$</td>
<td>2</td>
<td>1.79</td>
<td>0.41</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>2-PymQ$^+$</td>
<td>3</td>
<td>1.84</td>
<td>0.51</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>2-PymQ$^+$</td>
<td>2</td>
<td>1.67</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Data at 298 K in MeCN. $E_{1/2}$ values quoted with respect to Ag-AgCl reference electrode.

As expected, the MLCT bands for 11–14 shift to lower energies as the electron accepting strength of L' increases in the order R = Me > Ph > 4-AcPh > 2-Pym. Replacement of a trans NH$_3$ by a SCN$^-$ ligand red-shifts the MLCT bands by 0.11–0.17 eV and decreases the Ru$^{III/II}$ potentials by 80–100 mV. It can hence be anticipated that complexes 11–15 will possess larger $\beta_0$ values than their pentaammine analogues. The salts [11–15]PF$_6$ will soon be investigated by using both HRS and Stark spectroscopic measurements.

(iii) Complexes of Pyridyl Polyene Ligands
Donor/acceptor-substituted polyenes have been studied in some detail for their NLO properties and have proven to be a useful probe for the structure-activity relationships that control $\beta$ in organic chromophores.\textsuperscript{27} Indeed, the quadratic NLO responses of compounds such as 16 containing powerful, heterocyclic electron acceptor groups are amongst the largest of any known molecules.\textsuperscript{28} A small number of organotransition metal complexes of polyene ligands have also been studied,\textsuperscript{29} most of which contain ferrocenyl donor groups (e.g. 17; $\mu =$ dipole moment; $\mu \beta$ for DANS $\approx 500 \times 10^{-48}$ esu)\textsuperscript{29a} and (E,E)-1,3-butadienyl linkages. The only related complex of Ru$^{II}$ is the $\sigma$-acetylide 18 (but note that $\beta_0$ is severely underestimated in this case due to limitations of the two-state model).\textsuperscript{6} Polyene complexes containing Ru$^{II}$ ammine electron donor groups can be expected to possess very large $\beta_0$ values.

Our initial studies focused on the syntheses of potential ligands bearing 1,3-diethyl-2-thiobarbituric acid acceptor groups (as found in 17). Unfortunately, these experiments proved unsuccessful, so we subsequently turned our attention to the syntheses of polyene species containing pyridinium groups. The pyridyl polyenal compounds 19–21 were prepared via stepwise elongations of pyridine-4-carboxaldehyde with (1,3-dioxolan-2-yl-methyl)tributyl phosphonium bromide\textsuperscript{28,30} and used to synthesize the pyridyl ligands 22–24 (Scheme 1). Compounds 19–21 have previously been prepared via different routes,\textsuperscript{31} but 22–24 are new. The ligands 22 and 23 have been used to synthesize the pyridyl polyene complexes 25–30, but complexes of 24 have not yet been isolated. The MLCT absorption data for 25–30, together with those for some previously reported complexes are given in Table 3.

<table>
<thead>
<tr>
<th>$n$</th>
<th>L = NH$_3$</th>
<th>L = mim</th>
<th>L = py</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>590$^{10d}$</td>
<td>602$^{10b}$</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
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<td>604$^{10e}$</td>
<td>563$^{10e}$</td>
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<td>2</td>
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<td>3</td>
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<td>529</td>
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</table>

Data at 298 K in MeCN.

The primary conclusion to emerge from the above data is that the MLCT absorption maxima shift to high energy as the polyene chain is extended. This is an unprecedented result because CT bands normally red-shift on polyene chain elongation; see for example the data for the organic series 31–34 (in MeCN).\textsuperscript{32} Similar trends have also been observed in organotransition metal polyene complexes such as 35–38 (in CH$_2$Cl$_2$).\textsuperscript{29f} The results of pending HRS and Stark spectroscopic studies on our Ru$^{II}$ pyridyl polyene complexes are certain to be interesting. The dependance of $\beta_0$ on the chain length is difficult to predict; both $\beta_0$ and $\Delta \mu_{12}$ are expected to increase as $n$ increases, but these changes are normally accompanied by decreasing CT energies. A decrease in $\beta_0$ with increasing $n$ would be most unusual behaviour.
PROJECT PLAN REVIEW

The original objectives of this project were changed somewhat, due to a regrettably long delay in the appointment of a research worker. The original grant included a 3 year PhD studentship. Since a suitable student was not forthcoming, the plan was then changed to allow for a 2 year PDRA, a position which was advertised twice before an appointment was made. The grant necessarily commenced about 1 year after its announcement, but the PDRA (Dr L A Jones) did not begin work until over 2 years had elapsed. By this time, many of the original objectives of the project had already been fulfilled. In particular, we had achieved substantial advances in tuning of molecular quadratic NLO responses (original objective 1), and had also demonstrated the redox-switching of $\beta_0$ responses in Ru$^{II}$ ammine complexes (original objective 3). Preliminary experiments with bimetallic complexes did not give encouraging results, so the original objective 2 was abandoned in favour of other more promising avenues of investigation. The Stark spectroscopic studies were carried out by an EPSRC quota student (J A Harris) whose visit to Brookhaven National Laboratory (BNL) was financed out of this grant.

RESEARCH IMPACT AND BENEFITS TO SOCIETY

Although our demonstration of redox-switching of $\beta_0$ responses has already inspired other academic researchers, it is not yet possible to assess the impact of the studies supported by this grant because most of the results have yet to be published (see below). The grant has certainly provided valuable training and experience for Dr Jones and also for (now) Dr Harris. The broader benefits to society of fundamental research into novel NLO materials can be expected to become apparent as the technologies for device fabrication and exploitation mature.

EXPLANATION OF EXPENDITURE

Overall spending was within budget. However, as noted above, the grant was used to support a 2 year PDRA rather than the originally intended 3 year PhD studentship. This change was agreed with EPSRC before an appointment was made. The visit to BNL was also not in the original plans. However, the new collaboration which this has initiated (with Dr B S Brunschwig) is ongoing and expected to make significant novel contributions to the study of metal complexes with NLO activity.

FURTHER RESEARCH OR DISSEMINATION ACTIVITIES

None of the synthetic results obtained by Dr Jones have yet been published because the HRS and Stark spectroscopic data are to be obtained. When these data are available, then the results will form at least 2 further full papers in internationally reknowned academic chemistry journals (1 on the SCN$^-$ complexes and 1 on the polyene complexes). The necessary research visits to BNL and Leuven are scheduled to occur in early 2002. Further EPSRC funding has been obtained (1 year) to allow Dr Jones to continue his studies which are to include complexes of pyridyl polyyne ligands and also novel species containing {$\text{Fe}^{II}(\text{CN})_3$}$^3^-$ electron donor groups.
SUMMARY

This grant has allowed us to make considerable progress in our studies of the NLO properties of transition metal complexes. A number of novel ligands and complexes have been prepared and a new international collaboration to obtain Stark spectroscopic data has been initiated, building on the successes of our previous studies. Published output from this grant is expected to include at least 4 papers in peer-reviewed academic journals. Continuation funding has been secured from EPSRC and future significant developments from these investigations can be anticipated.


(6) S. Houbrechts et al., Organometallics, 1996, 15, 5266; V. Cadierno et al., Organometallics, 1999, 18, 582.


(8) I.-Y. Wu et al., Organometallics, 1997, 16, 2038; I.-Y. Wu et al., Organometallics, 1998, 17, 2188.


(17) T. Weyland et al., Organometallics, 2000, 19, 5235.


(32) B. J. Coe et al., unpublished results.