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Tuning of charge-transfer absorption and molecular quadratic non-linear optical properties in ruthenium(II) ammine complexes †

Benjamin J. Coe,*[a] James A. Harris,[a] Inge Asselberghs,[b] André Persoons,[b,c] John C. Jeffery,[d] Leigh H. Rees,[d] Thomas Gelbrich[e] and Michael B. Hursthouse[e]

[a] *Department of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: b.coe@man.ac.uk*
[b] *Laboratory of Chemical and Biological Dynamics, Center for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*
[c] *Optical Sciences Center, University of Arizona, Tucson, Arizona, AZ 85721, USA*
[d] *Department of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*
[e] *EPSRC X-ray Crystallography Service, Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

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The ligands *N*-methyl-2,7-diazapyrenium (Medap$^+$), *N*-(2-pyrimidyl)-4,4′-bipyridinium (PymQ$^+$), *N*-methyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Mebpe$^+$) and *N*-phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Phbpe$^+$) have been used to prepare a series of complex salts *trans*-[$Ru^{II}(NH_3)_4(L^D)(L^A)$][$PF_6$]$_3$ [L^D = NH_3 and L^A = Medap$^+$ **1**, PymQ$^+$ **2**, Mebpe$^+$ **3** or Phbpe$^+$ **4**; L^D = pyridine (py) and L^A = Medap$^+$ **8**, PymQ$^+$ **9**, Mebpe$^+$ **10** or Phbpe$^+$ **11**; L^D = 1-methylimidazole (mim) and L^A = Medap$^+$ **12**, PymQ$^+$ **13**, Mebpe$^+$ **14** or Phbpe$^+$ **15**]. The salt *trans*-[$Ru^{II}(NH_3)_4$(py)(4,4′-bpy)][PF_6]$_2$ (4,4′-bpy = 4,4′-bipyridine) **16** has also been prepared. The dipolar complexes in **1**–**4** and **8**–**15** exhibit intense $d_\pi(Ru^{II})\rightarrow\pi^*(L^A)$ metal-to-ligand charge-transfer (MLCT) absorptions in the region 560–700 nm. For a given L^A, the MLCT energy decreases as the donor strength of L^D increases, in the order py < NH_3 < mim. Within the pairs of Medap$^+$/PymQ$^+$ complexes, the energy of the Ru-based HOMO is constant and the MLCT energy decreases by *ca*. 0.3 eV as the acceptor strength of L^A increases on going from Medap$^+$ to PymQ$^+$. The complexes of Mebpe$^+$ or Phbpe$^+$ also have similar HOMO energies which are lower than those of their Medap$^+$/PymQ$^+$ counterparts due to the increased basicity of L^A. Replacement of Mebpe$^+$ by Phbpe$^+$ decreases the MLCT energy by *ca.* 0.1 eV due to the greater electron-withdrawing ability of Phbpe$^+$. Single-crystal structures of **8**·4MeCN and **16**·2MeCN have been determined. Molecular first hyperpolarizabilities β of **1**–**4** and **8**–**15**, obtained from hyper-Rayleigh scattering measurements at 1064 nm, are in the range (579–1068) × 10^{-30} esu. Static hyperpolarizabilities β_0 derived by using the two-level model are also very large, with **13** having the largest at 336 × 10^{-30} esu. In general, β_0 increases as the absorption energy decreases, in keeping with the two-level model.

Introduction

Molecular materials possessing non-linear optical (NLO) properties are of great interest for applications in optoelectronic and photonic devices of the 21st century.[1] Organotransition metal complexes form an important sub-class of NLO materials which have recently attracted increasing attention.[2] Such compounds are promising because polarizable d electrons can contribute to enhanced NLO responses, and redox activity provides extensive opportunities for modulation of NLO properties. The creation of materials for quadratic (second order) NLO applications begins with the molecular engineering of chromophores possessing large first hyperpolarizabilities, β. Detailed structure–activity relationships for β of purely organic compounds are well established,[1] but comparable understanding for organotransition metal complexes is poorly developed.[2] Systematic investigations into the quadratic NLO activity of metal complexes are hence timely.

The quadratic NLO properties of ruthenium complexes have proven an especially popular research topic, and large β responses have been reported.[3–8] Most of these studies have involved organometallic σ-acetylide or allenylidene complexes with $\{Ru^{II}(\eta^5\text{-}L')L_2\}^+$ [L′ = cyclopentadienyl or indenyl; L_2 = mono- or bi-dentate phosphine ligand(s)] or *trans*-$\{Ru^{II}Cl(dppm)_2\}^+$ [dppm = bis(diphenylphosphino)methane] electron donor groups.[5–8] We are investigating the quadratic NLO behaviour of ruthenium ammines which combine synthetic accessibility with especially well understood redox and spectroscopic properties. Initial studies have shown that $\{Ru^{II}(NH_3)_5\}^{2+}$ or *trans*-$\{Ru^{II}(NH_3)_4L\}^{2+}$ (L = 4-dimethylaminopyridine or 1-methylimidazole) complexes of *N*-methyl/aryl-4,4′-bipyridinium ligands possess very large β values.[9] In such dipolar molecules the d^6 ruthenium(II) centre acts as a powerful π donor whilst the pyridinium ring is an acceptor. These complexes hence exhibit intense, low energy metal-to-ligand charge-transfer (MLCT) absorptions, and a good correlation exists between β_0 (the static first hyperpolarizability) and $1/E^2$ where E is the MLCT energy.[9c] This is in accord with the two-level model which is often used to relate charge-transfer absorption and NLO properties in classical dipolar organic chromophores.[10] Furthermore, the NLO responses of the $\{Ru^{II}(NH_3)_5\}^{2+}$ complexes can be reversibly and very effectively switched *via* $Ru^{III/II}$ redox.[11]

We have begun to develop a versatile family of complexes, the MLCT absorptions and quadratic NLO responses of which are readily controlled. The subject of this report is the further tuning of these properties in ruthenium(II) ammine complexes,

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3617/

principally by changing the structure of the acceptor-substituted ligand. Previous work with NLO-active transition metal complexes has often borrowed "molecular engineering" concepts from purely organic molecules,[2] for example by simply replacing an amino donor with an electron-rich metal centre. We are seeking to develop novel approaches towards modifying the properties of MLCT chromophores which have no existing counterparts in simple organics. The results of these studies are of direct relevance to the design of other transition metal-based NLO compounds and also related organic chromophores.

Experimental

Materials and procedures

The compound $RuCl_3 \cdot 2H_2O$ was supplied by Johnson Matthey plc. The salts $[Ru^{II}(NH_3)_5(H_2O)][PF_6]_2$,[12] *trans*-$[Ru^{II}Cl(NH_3)_4(SO_2)]Cl$,[12] *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$,[12] *N*-methyl-2,7-diazapyrenium chloride ([Medap$^+$]Cl)[13] and *N*-methyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium iodide ([Mebpe$^+$]I)[14] were prepared according to published procedures. The latter two salts were metathesized to [Medap$^+$]PF_6 and [Mebpe$^+$]PF_6, respectively, by precipitation from water–aqueous NH_4PF_6. 2,7-Diazapyrene was prepared by using a combination of published procedures,[15,16] with one simple modification: in the synthesis of the intermediate 1,3,6,8-tetrahydro-2,7-dimethyldiazapyrene we found that extraction into boiling methanol affords a higher yield of a purer product compared with the published THF extraction method.[16] All other reagents were obtained commercially and used as supplied. Products were dried overnight at room temperature in a vacuum desiccator ($CaSO_4$) prior to characterization.

Physical measurements

Proton NMR spectra were recorded on a Varian Gemini 200 spectrometer and all shifts are referenced to $SiMe_4$. The fine splitting of pyridyl or phenyl ring AA′BB′ patterns is ignored and the signals are reported as simple doublets, with *J* values referring to the two most intense peaks. Solvents of crystallization were detected as singlets at δ 2.86 (water) or 2.09 (acetone) in acetone-d_6 solutions. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester and UV/VIS spectra were obtained by using a Varian Cary 1E spectrophotometer.

Cyclic voltammetric measurements were carried out by using an EG&G PAR model 173 potentiostat/galvanostat with a model 175 universal programmer. A single-compartment cell was used with the saturated calomel reference electrode (SCE) separated by a salt bridge from the platinum-bead working electrode and platinum-wire auxiliary electrode. Acetonitrile (HPLC grade) was used as received and tetra-*n*-butylammonium hexafluorophosphate, twice recrystallized from ethanol and dried *in vacuo*, as supporting electrolyte. Solutions containing *ca.* 10^{-3} mol dm^{-3} analyte (0.1 mol dm^{-3} electrolyte) were deaerated by purging with N_2. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 200 mV s^{-1}.

Syntheses

4-Methyl-*N*-phenylpyridinium chloride, [Phpic$^+$]Cl. A solution of 4-methylpyridine (2.4 cm^3, 25 mmol) and chloro-2,4-dinitrobenzene (5 g, 25 mmol) in ethanol (25 cm^3) was heated at reflux for 2 h. After cooling to room temperature, diethyl ether was added and the black precipitate filtered off, washed with diethyl ether and dried. The crude product was purified by precipitation from boiling ethanol–diethyl ether to afford a grey solid which was filtered off, washed with diethyl ether and dried: 3.68 g. $\delta_H(D_2O)$ 9.31 (1 H, d, *J* 2.5 Hz, H^3), 8.89–8.83 (3 H, m, H^5 + C_5H_4N), 8.19–8.06 (3 H, m, H^6 + C_5H_4N) and 2.79 (3 H, s, Me). This material was dissolved in boiling ethanol (30 cm^3), aniline (5.6 cm^3, 61 mmol) was added and the resulting solution heated at reflux for 3 h. The solution was cooled to room temperature and reduced to half volume *in vacuo*. On addition of water a green material precipitated which was filtered off, washed with water and discarded. The filtrate was reduced to dryness and dissolved in ethanol. The addition of diethyl ether afforded a golden-brown precipitate which was filtered off, washed with diethyl ether and dried: yield 2.24 g (39%). $\delta_H(D_2O)$ 8.85 (2 H, d, *J* 6.6, C_5H_4N), 7.99 (2 H, d, *J* 6.9 Hz, C_5H_4N), 7.67 (5 H, s, Ph) and 2.71 (3 H, s, Me) (Found: C, 63.30; H, 6.06; N, 6.23. Calc. for $C_{12}H_{12}ClN \cdot 1.25H_2O$: C, 63.16; H, 6.40; N, 6.14%).

***N*-Phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium chloride, [Phbpe$^+$]Cl.** A mixture of [Phpic$^+$]Cl·1.25H_2O (3.08 g, 13.5 mmol), pyridine-4-carbaldehyde (1.5 cm^3, 15.8 mmol) and piperidine (0.4 cm^3) in ethanol (3 cm^3) was heated at reflux for 15 min. The resulting solution was cooled in an ice-bath, causing formation of a solid mass. A black liquid was decanted off and the residue dissolved in ethanol and precipitated by addition of diethyl ether. The pink solid was filtered off, washed with diethyl ether and dried: yield 1.04 g (23%). $\delta_H(D_2O)$ 8.94 (2 H, d, *J* 6.8, C_5H_4N), 8.48 (2 H, d, *J* 5.9, C_5H_4N), 8.19 (2 H, d, *J* 6.7, C_5H_4N), 7.71 (1 H, d, *J* 16.4, CH), 7.69 (5 H, s, Ph), 7.59 (2 H, d, *J* 6.2, C_5H_4N) and 7.51 (1 H, d, *J* 16.4 Hz, CH) (Found: C, 64.19; H, 5.38; N, 8.06. Calc. for $C_{18}H_{15}ClN_2 \cdot 2.25H_2O$: C, 64.48; H, 5.86; N, 8.35%).

***N*-Phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium hexafluorophosphate, [Phbpe$^+$]PF_6.** The salt [Phbpe$^+$]Cl·2.25H_2O (200 mg, 0.596 mmol) was dissolved in the minimum volume of water and aqueous NH_4PF_6 added dropwise. The white precipitate was filtered off, washed with water and dried: yield 210 mg (87%). $\delta_H(CD_3COCD_3)$ 9.31 (2 H, d, *J* 6.8, C_5H_4N), 8.71 (2 H, d, *J* 6.1, C_5H_4N), 8.57 (2 H, d, *J* 6.8, C_5H_4N), 8.16 (1 H, d, *J* 16.4, CH), 8.00–7.95 (2 H, m, Ph), 7.94 (1 H, d, *J* 16.4, CH), 7.82–7.78 (3 H, m, Ph) and 7.72 (2 H, d, *J* 6.0 Hz, C_5H_4N) (Found: C, 53.56; H, 3.77; N, 6.72. Calc. for $C_{18}H_{15}F_6N_2P$: C, 53.48; H, 3.74; N, 6.93%).

***N*-(2-Pyrimidyl)-4,4′-bipyridinium chloride, [PymQ$^+$]Cl.** A mixture of 4,4′-bipyridine (2.06 g, 13.2 mmol) and 2-chloropyrimidine (1.00 g, 8.73 mmol) was heated quickly to *ca.* 70 °C. Upon solidification, the green material was dissolved in ethanol (5 cm^3) and heated at reflux for 6 h. Addition of diethyl ether afforded a green precipitate which was filtered off, washed with diethyl ether and dried: yield 1.30 g (55%). $\delta_H(D_2O)$ 10.08 (2 H, d, *J* 7.3, C_5H_4N), 9.10 (2 H, d, *J* 4.9, $C_4H_3N_2$), 8.74 (2 H, d, *J* 6.1, C_5H_4N), 8.61 (2 H, d, *J* 7.3, C_5H_4N), 7.96 (2 H, d, *J* 6.3, C_5H_4N) and 7.85 (1 H, t, *J* 5.0 Hz, $C_4H_3N_2$) (Found: C, 61.94; H, 4.42; N, 20.39. Calc. for $C_{14}H_{11}ClN_4$: C, 62.11; H, 4.10; N, 20.70%).

***N*-(2-Pyrimidyl)-4,4′-bipyridinium hexafluorophosphate, [PymQ$^+$]PF_6.** The salt [PymQ$^+$]Cl (500 mg, 1.85 mmol) was dissolved in the minimum volume of water and aqueous NH_4PF_6 added dropwise. The white precipitate was filtered off, washed with water and dried: yield 665 mg (95%). $\delta_H(CD_3COCD_3)$ 10.36 (2 H, d, *J* 7.4, C_5H_4N), 9.29 (2 H, d, *J* 4.8, $C_4H_3N_2$), 8.96–8.91 (4 H, m, C_5H_4N), 8.14 (2 H, d, *J* 6.3, C_5H_4N) and 8.04 (1 H, t, *J* 4.8 Hz, $C_4H_3N_2$) (Found: C, 44.36; H, 2.93; N, 14.88. Calc. for $C_{14}H_{11}F_6N_4P$: C, 44.22; H, 2.92; N, 14.73%).

$[Ru^{II}(NH_3)_5(Medap^+)][PF_6]_3$ 1. A solution of $[Ru^{II}(NH_3)_5(H_2O)][PF_6]_2$ (250 mg, 0.505 mmol) and [Medap$^+$]PF_6 (188 mg, 0.516 mmol) in Ar-degassed acetone (5 cm^3) was stirred at room temperature under Ar for 2 h. The addition of diethyl ether afforded a dark precipitate which was filtered off, washed with diethyl ether and dried. Purification was effected by

precipitations from acetone–aqueous NH_4PF_6 and then from acetone–diethyl ether to afford a dark purple solid: yield 137 mg (32%). $\delta_H(CD_3COCD_3)$ 10.05 (2 H, s, $C_{14}H_8N_2$), 9.83 (2 H, s, $C_{14}H_8N_2$), 8.54 (2 H, d, *J* 9.2, $C_{14}H_8N_2$), 8.48 (2 H, d, *J* 9.2 Hz, $C_{14}H_8N_2$), 4.89 (3 H, s, Me), 3.59 (3 H, s, *trans*-NH_3) and 2.81 (12 H, s, 4 × *cis*-NH_3) (Found: C, 21.10; H, 3.08; N, 11.49. Calc. for $C_{15}H_{26}F_{18}N_7P_3Ru$: C, 21.44; H, 3.12; N, 11.67%).

$[Ru^{II}(NH_3)_5(PymQ^+)][PF_6]_3$ 2. This was prepared in identical manner to salt **1** by using $[Ru^{II}(NH_3)_5(H_2O)][PF_6]_2$ (100 mg, 0.202 mmol) and $[PymQ^+]PF_6$ (77 mg, 0.203 mmol) in place of $[Medap^+]PF_6$. Purification was effected by several precipitations from acetone–diethyl ether to afford a dark blue solid: yield 75 mg (42%). $\delta_H(CD_3COCD_3)$ 10.17 (2 H, d, *J* 7.5, C_5H_4N), 9.28–9.22 (4 H, m, $C_5H_4N + C_4H_3N_2$), 8.94 (2 H, d, *J* 7.5 Hz, C_5H_4N), 8.03–7.96 (3 H, m, $C_5H_4N + C_4H_3N_2$), 3.75 (3 H, s, *trans*-NH_3) and 2.74 (12 H, s, 4 × *cis*-NH_3) (Found: C, 19.15; H, 3.14; N, 13.76. Calc. for $C_{14}H_{26}F_{18}N_9P_3Ru{\cdot}2H_2O$: C, 18.84; H, 3.39; N, 14.13%).

$[Ru^{II}(NH_3)_5(Mebpe^+)][PF_6]_3$ 3. This was prepared in similar manner to salt **2** by using $[Mebpe^+]I$ (79 mg, 0.244 mmol) in place of $[PymQ^+]PF_6$ and 1:1 water–acetone (5 cm^3) in place of acetone. The addition of aqueous NH_4PF_6 afforded a dark precipitate which was filtered off, washed with water and dried. Purification was effected by precipitations from acetone–diethyl ether, acetone–NBu^n_4Cl and finally water–aqueous NH_4PF_6 to afford a dark purple solid: yield 58 mg (35%). $\delta_H(CD_3COCD_3)$ 8.94 (4 H, d, *J* 6.9, C_5H_4N), 8.33 (2 H, d, *J* 7.0, C_5H_4N), 8.02 (1 H, d, *J* 16.4, CH), 7.89 (1 H, d, *J* 16.4, CH), 7.54 (2 H, d, *J* 6.8 Hz, C_5H_4N), 4.49 (3 H, s, Me), 3.41 (3 H, s, *trans*-NH_3) and 2.65 (12 H, s, 4 × *cis*-NH_3) (Found: C, 19.28; H, 3.18; N, 11.68. Calc. for $C_{13}H_{28}F_{18}N_7P_3Ru$: C, 19.08; H, 3.45; N, 11.98%).

$[Ru^{II}(NH_3)_5(Phbpe^+)][PF_6]_3$ 4. This was prepared in identical manner to salt **2** by using $[Phbpe^+]PF_6$ (83 mg, 0.205 mmol) in place of $[PymQ^+]PF_6$. The product was purified as for **3** with one further precipitation from acetone–diethyl ether to afford a dark blue solid: yield 113 mg (62%). $\delta_H(CD_3COCD_3)$ 9.25 (2 H, d, *J* 7.0, C_5H_4N), 8.97 (2 H, d, *J* 6.3, C_5H_4N), 8.51 (2 H, d, *J* 6.9, C_5H_4N), 8.18 (1 H, d, *J* 16.2, CH), 8.04 (1 H, d, *J* 16.2, CH), 7.99–7.94 (2 H, m, Ph), 7.81–7.77 (3 H, m, Ph), 7.58 (2 H, d, *J* 6.9 Hz, C_5H_4N), 3.44 (3 H, s, *trans*-NH_3) and 2.65 (12 H, s, 4 × *cis*-NH_3) (Found: C, 25.28; H, 3.52; N, 10.51. Calc. for $C_{18}H_{30}F_{18}N_7P_3Ru{\cdot}0.3C_3H_6O$: C, 25.28; H, 3.57; N, 10.92%).

***trans*-$[Ru^{III}(SO_4)(NH_3)_4(mim)]Cl$ 5.** A mixture of *trans*-$[Ru^{II}Cl(NH_3)_4(SO_2)]Cl$ (100 mg, 0.329 mmol) and 1-methylimidazole (mim, 0.2 cm^3, 2.51 mmol) was dissolved in water (5 cm^3) and heated at *ca.* 45 °C under Ar for 30 min. Acetone (100 cm^3) was added to the brown solution and a white precipitate filtered off, washed with acetone and dried to afford crude *trans*-$[Ru^{II}(NH_3)_4(mim)(SO_2)]Cl_2$ (124 mg, 98%). This material was dissolved in water (5 cm^3) and oxidized by the addition of a 1:1 mixture of 30% aqueous H_2O_2–2 M HCl (2 cm^3). After 5 min at room temperature, acetone (200 cm^3) was added and the golden precipitate filtered off, washed with acetone and dried: crude yield 111 mg (88%).

***trans*-$[Ru^{III}(SO_4)(NH_3)_4(Medap^+)]Cl_2$ 6.** This salt was prepared in identical manner to that of **5** by using $[Medap^+]Cl$ (167 mg, 0.656 mmol) in place of mim. The addition of acetone (30 cm^3) to the brown solution afforded a mauve precipitate which was filtered off, washed with acetone and dried to yield crude *trans*-$[Ru^{II}(NH_3)_4(Medap^+)(SO_2)]Cl_3$ (151 mg, 82%). The oxidation was carried out by using water (10 cm^3) to dissolve the SO_2 salt and acetone (100 cm^3) to precipitate the golden product: crude yield: 108 mg (59%).

***trans*-$[Ru^{III}(SO_4)(NH_3)_4(Mebpe^+)]Cl_2$ 7.** This was prepared in identical manner to that of salt **6** by using $[Mebpe^+]I$ (214 mg, 0.660 mmol) in place of $[Medap^+]Cl$ to afford a golden solid: crude yield 135 mg (77%).

***trans*-$[Ru^{II}(NH_3)_4(py)(Medap^+)][PF_6]_3$ 8.** A solution of *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$ (108 mg, 0.284 mmol) in water (5 cm^3) was reduced over zinc amalgam (5 lumps) with argon agitation for 15 min. This was filtered under Ar into a flask containing $[Medap^+]Cl$ (360 mg, 1.41 mmol) and the solution was stirred at room temperature in the dark under Ar for 6 h. The addition of acetone (100 cm^3) to the deep blue solution gave a dark precipitate which was filtered off, washed with acetone and dried (crude *trans*-$[Ru^{II}(NH_3)_4(py)(Medap^+)]Cl_3$). This material was purified by precipitation from water–acetone and then metathesized to its PF_6^- salt by precipitation from water–aqueous NH_4PF_6. Further purification was effected by several precipitations from acetone–diethyl ether to afford a dark blue solid: yield 99 mg (39%). $\delta_H(CD_3COCD_3)$ 10.15 (2 H, s, $C_{14}H_8N_2$), 9.99 (2 H, s, $C_{14}H_8N_2$), 9.00 (2 H, d, $H^{2,6}$), 9.12 (2 H, d, *J* 9.1, $C_{14}H_8N_2$), 8.63 (2 H, d, *J* 9.2 Hz, $C_{14}H_8N_2$), 8.03 (1 H, t, H^4), 7.65 (2 H, t, $H^{3,5}$), 5.01 (3 H, s, Me) and 2.83 (12 H, s, $4NH_3$) (Found: C, 26.78; H, 3.09; N, 10.61. Calc. for $C_{20}H_{28}F_{18}N_7P_3Ru$: C, 26.62; H, 3.13; N, 10.86%).

***trans*-$[Ru^{II}(NH_3)_4(py)(PymQ^+)][PF_6]_3$ 9.** This was prepared in identical manner to that of salt **8** by using *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$ (103 mg, 0.271 mmol) and $[PymQ^+]Cl$ (367 mg, 1.36 mmol) in place of $[Medap^+]Cl$. Purification was effected by precipitation from acetone–diethyl ether to afford a dark blue solid: yield: 172 mg (69%). $\delta_H(CD_3COCD_3)$ 10.28 (2 H, d, *J* 7.4, C_5H_4N), 9.27 (2 H, d, *J* 4.9, $C_4H_3N_2$), 9.26 (2 H, d, *J* 7.0, C_5H_4N), 8.99–8.93 (4 H, m, $C_5H_4N + H^{2,6}$), 8.19 (2 H, d, *J* 7.0 Hz, C_5H_4N), 8.06–7.98 (2 H, m, $H^4 + C_4H_3N_2$), 7.63 (2 H, t, $H^{3,5}$) and 2.88 (12 H, s, $4NH_3$) (Found: C, 25.16; H, 3.10; N, 13.32. Calc. for $C_{19}H_{28}F_{18}N_9P_3Ru$: C, 24.85; H, 3.07; N, 13.73%).

***trans*-$[Ru^{II}(NH_3)_4(py)(Mebpe^+)][PF_6]_3$ 10.** This was prepared in similar manner to that of salt **8** by using **7** (135 mg, 0.253 mmol) in place of *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$ and pyridine (0.1 cm^3, 1.24 mmol) in place of $[Medap^+]Cl$. The solution was stirred for 3 h in the dark and addition of aqueous NH_4PF_6 gave a dark precipitate which was filtered off, washed with water and dried. Purification was effected by precipitation from acetone–diethyl ether to afford a dark blue solid: yield 81 mg (36%). $\delta_H(CD_3COCD_3)$ 8.98–8.92 (4 H, m, $C_5H_4N + H^{2,6}$), 8.88 (2 H, d, *J* 6.5, C_5H_4N), 8.36 (2 H, d, *J* 6.9, C_5H_4N), 8.09 (1 H, d, *J* 16.5, CH), 7.95 (1 H, t, H^4), 7.93 (1 H, d, *J* 16.4, CH), 7.74 (2 H, d, *J* 6.8 Hz, C_5H_4N), 7.56 (2 H, t, $H^{3,5}$), 4.53 (3 H, s, Me) and 2.78 (12 H, s, $4NH_3$) (Found: C, 24.72; H, 3.50; N, 10.85. Calc. for $C_{18}H_{30}F_{18}N_7P_3Ru$: C, 24.56; H, 3.43; N, 11.14%).

***trans*-$[Ru^{II}(NH_3)_4(py)(Phbpe^+)][PF_6]_3$ 11.** This was prepared in identical manner to that of salt **8** by using *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$ (109 mg, 0.287 mmol) and $[Phbpe^+]Cl{\cdot}2.25H_2O$ (424 mg, 1.26 mmol) instead of $[Medap^+]Cl$. Purification was effected by precipitation from acetone–diethyl ether to afford a dark blue solid: yield 163 mg (58%). $\delta_H(CD_3COCD_3)$ 9.30 (2 H, d, *J* 6.9, C_5H_4N), 8.98 (2 H, d, *J* 6.6, C_5H_4N), 8.90 (2 H, d, $H^{2,6}$), 8.55 (2 H, d, *J* 7.0, C_5H_4N), 8.25 (1 H, d, *J* 16.2, CH), 8.07 (1 H, d, *J* 16.2 Hz, CH), 8.00–7.93 (3 H, m, Ph + H^4), 7.82–7.78 (5 H, m, Ph + C_5H_4N), 6.90 (2 H, t, $H^{3,5}$) and 2.81 (12 H, s, $4NH_3$) (Found: C, 30.18; H, 3.39; N, 9.64. Calc. for $C_{23}H_{32}F_{18}N_7P_3Ru{\cdot}0.5C_3H_6O$: C, 30.29; H, 3.63; N, 10.09%).

***trans*-$[Ru^{II}(NH_3)_4(mim)(Medap^+)][PF_6]_3$ 12.** This was prepared in similar manner to that of salt **8** by using **6** (108 mg, 0.194 mmol) in place of *trans*-$[Ru^{III}(SO_4)(NH_3)_4(py)]Cl$ and mim (0.2 cm^3, 2.51 mmol) in place of $[Medap^+]Cl$. The solution

was stirred for 3 h in the dark and addition of aqueous NH_4PF_6 afforded a dark precipitate which was filtered off, washed with water and dried. Purification was effected by sequential precipitations from acetone–NBu^n_4Cl, water–aqueous NH_4PF_6 and finally from acetone–diethyl ether: yield 69 mg (39%). $\delta_H(CD_3COCD_3)$ 10.10 (2 H, s, $C_{14}H_8N_2$), 9.88 (2 H, s, $C_{14}H_8N_2$), 8.59 (2 H, d, *J* 8.8, $C_{14}H_8N_2$), 8.53 (2 H, d, *J* 9.2 Hz, $C_{14}H_8N_2$), 8.31 (1 H, s, $C_3N_2H_3$), 7.51 (1 H, s, $C_3N_2H_3$), 7.47 (1 H, s, $C_3N_2H_3$), 4.93 (3 H, s, $C_{14}H_8N_2$-*Me*), 3.95 (3 H, s, $C_3N_2H_3$-*Me*) and 2.85 (s, 12 H, $4NH_3$) (Found: C, 26.02; H, 3.20; N, 11.98. Calc. for $C_{19}H_{29}F_{18}N_8P_3Ru\cdot0.3C_3H_6O$: C, 25.90; H, 3.36; N, 12.14%).

***trans*-[$Ru^{II}(NH_3)_4$(mim)(PymQ$^+$)][PF_6]$_3$ 13.** This salt was prepared and purified in identical manner to that of **12** by using **5** (109 mg, 0.285 mmol) in place of **6** and [PymQ$^+$]Cl (385 mg, 1.42 mmol) in place of mim. A dark blue solid was obtained: yield 76 mg (28%). $\delta_H(CD_3COCD_3)$ 10.22 (2 H, d, *J* 7.5, C_5H_4N), 9.27–9.24 (4 H, m, C_5H_4N + $C_4H_3N_2$), 8.95 (2 H, d, *J* 7.4, C_5H_4N), 8.28 (1 H, s, $C_3N_2H_3$), 8.08 (2 H, d, *J* 6.6, C_5H_4N), 8.03 (1 H, t, *J* 4.1 Hz, $C_4H_3N_2$), 7.50 (1 H, s, $C_3N_2H_3$), 7.44 (1 H, s, $C_3N_2H_3$), 3.95 (3 H, s, Me) and 2.78 (12 H, s, $4NH_3$) (Found: C, 24.03; H, 3.46; N, 14.68. Calc. for $C_{18}H_{29}F_{18}N_{10}P_3Ru\cdot0.3C_3H_6O$: C, 24.18; H, 3.31; N, 14.92%).

***trans*-[$Ru^{II}(NH_3)_4$(mim)(Mebpe$^+$)][PF_6]$_3$ 14.** This salt was prepared and purified in identical manner to that of **12** by using **7** (104 mg, 0.195 mmol) in place of **6**. A dark purple solid was obtained: yield 64 mg (37%). $\delta_H(CD_3COCD_3)$ 8.94 (4 H, d, *J* 5.1, C_5H_4N), 8.35 (2 H, d, *J* 6.5, C_5H_4N), 8.18 (1 H, s, $C_3N_2H_3$), 8.06 (1 H, d, *J* 16.4, CH), 7.91 (1 H, d, *J* 16.5, CH), 7.62 (2 H, d, *J* 6.6 Hz, C_5H_4N), 7.45 (1 H, s, $C_3N_2H_3$), 7.37 (1 H, s, $C_3N_2H_3$), 4.51 (3 H, s, C_5H_4N-*Me*), 3.91 (3 H, s, $C_3N_2H_3$-*Me*) and 2.65 (12 H, s, $4NH_3$) (Found: C, 23.44; H, 3.56; N, 12.41. Calc. for $C_{17}H_{31}F_{18}N_8P_3Ru$: C, 23.11; H, 3.54; N, 12.68%).

***trans*-[$Ru^{II}(NH_3)_4$(mim)(Phbpe$^+$)][PF_6]$_3$ 15.** This salt was prepared in identical manner to that of **12** by using **5** (115 mg, 0.300 mmol) in place of **6** and [Phbpe$^+$]Cl·2.25H_2O (445 mg, 1.33 mmol) in place of mim. Purification was effected by precipitation from acetone–diethyl ether to give a dark blue solid: yield 97 mg (34%). $\delta_H(CD_3COCD_3)$ 9.26 (2 H, d, *J* 6.9, C_5H_4N), 8.96 (2 H, d, *J* 5.6, C_5H_4N), 8.52 (2 H, d, *J* 6.9, C_5H_4N), 8.23 (1 H, d, *J* 16.2, CH), 8.18 (1 H, s, $C_3N_2H_3$), 8.04 (1 H, d, *J* 16.2, CH), 8.00–7.96 (2 H, m, Ph), 7.81–7.78 (3 H, m, Ph), 7.68 (2 H, d, *J* 5.9 Hz, C_5H_4N), 7.45 (1 H, s, $C_3N_2H_3$), 7.39 (1 H, s, $C_3N_2H_3$), 3.94 (3 H, s, Me) and 2.67 (12 H, s, $4NH_3$) (Found: C, 28.51; H, 3.94; N, 11.08. Calc. for $C_{22}H_{33}F_{18}N_8P_3Ru\cdot0.3C_3H_6O$: C, 28.56; H, 3.64; N, 11.64%).

***trans*-[$Ru^{II}(NH_3)_4$(py)(4,4′-bpy)][PF_6]$_2$ 16.** This salt was prepared in similar manner to that of **8** by using *trans*-[$Ru^{III}(SO_4)(NH_3)_4$(py)]Cl (200 mg, 0.527 mmol) and 4,4′-bipyridine (2.06 g, 13.2 mmol) in acetone (10 cm^3) in place of [Medap$^+$]Cl. The crude product was precipitated by addition of aqueous NH_4PF_6/Na_2CO_3, followed by removal of the acetone *in vacuo*. Two reprecipitations from acetone–diethyl ether afforded a red, microcrystalline solid: yield 215 mg (59%). $\delta_H(CD_3COCD_3)$ 9.00 (2 H, d, *J* 6.8, C_5H_4N), 8.88 (2 H, d, $H^{2,6}$), 8.74 (2 H, d, *J* 6.1 Hz, C_5H_4N), 7.95–7.84 (5 H, c m, $2C_5H_4N$ and H^4), 7.55 (2 H, t, $H^{3,5}$) and 2.81 (12 H, s, $4NH_3$) (Found: C, 25.95; H, 3.69; N, 13.94. Calc. for $C_{15}H_{25}F_{12}N_7P_2Ru$: C, 25.95; H, 3.63; N, 14.12%).

Hyper-Rayleigh scattering

Details of the hyper-Rayleigh scattering (HRS) experiment have been discussed elsewhere,[17] and the experimental procedure used was as described previously.[18] β Values were determined by using the electric-field-induced second harmonic generation β_{1064} for *p*-nitroaniline (29.2×10^{-30} esu in acetonitrile)[19] as an external reference. All measurements were performed by using the 1064 nm fundamental wavelength of an injection-seeded, Q-switched Nd-YAG laser (Quanta-Ray GCR-5, 8 ns pulses, 7 mJ, 10 Hz). The use of dilute acetonitrile solutions (10^{-5}–10^{-6} mol dm^{-3}) ensured a linear dependence of $I_{2\omega}/I_\omega^2$ upon solute concentration, precluding the need for Lambert–Beer correction factors. Samples were passed through a 0.45 μm filter (Millipore), and checked for fluorescence.[20,21] One-dimensional hyperpolarizability is assumed, *i.e.* $\beta_{1064} = \beta_{333}$, and a relative error of ±15% is estimated.

Crystal structure determinations

Crystals of salts **8**·4MeCN and **16**·2MeCN were obtained by slow diffusion of diethyl ether vapour into acetonitrile solutions. A red-brown crystal of **8**·4MeCN of approximate dimensions 0.1 × 0.1 × 0.15 mm and a red-orange crystal of **16**·2MeCN with dimensions 0.2 × 0.1 × 0.05 mm were chosen for diffraction studies.

Data collection details are as follows: for **8**·4MeCN, data were collected on a Nonius Kappa CCD area-detector diffractometer controlled by the COLLECT software package.[22] Images were processed by DENZO[23] and the data corrected for absorption by using the empirical method employed in SORTAV[24] from within the MAXUS suite of programs.[25] For **16**·2MeCN, data were collected on a Siemens SMART CCD area-detector diffractometer. An empirical absorption correction was applied and the data frames were integrated using SAINT.[26] The structure of **8**·4MeCN was solved by direct methods and refined by full-matrix least squares on all F_o^2 data using SHELXS 97[27] and SHELXL 97.[28] The same approach was used for **16**·2MeCN, but using Siemens SHELXTL 5.03.[26] In both cases, all non-hydrogen atoms, including those of the PF_6^- anions and the acetonitrile molecules of crystallization, were refined anisotropically. Crystallographic data and refinement details are presented in Table 3.

CCDC reference number 186/1638.

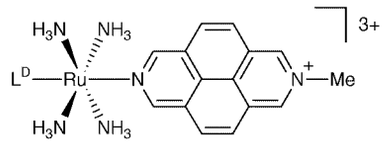
See http://www.rsc.org/suppdata/dt/1999/3617/ for crystallographic files in .cif format.

Results and discussion

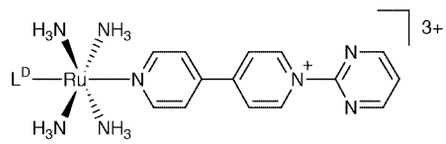
Molecular design and synthesis

This report constitutes an extension of our previous studies in which we have found that complexes *trans*-[$Ru^{II}(NH_3)_4(L^D)$-(L^A)]$^{3+}$ in which L^A is a *N*-R-4,4′-bipyridinium ligand exhibit large β_0 responses which increase in the order R = Me < Ph < 4-MeCOPh.[9c] The new complexes in the salts **1**–**4** and **8**–**15** were designed to probe the effects of several further molecular structural changes on the electronic absorption and quadratic NLO properties. These changes can be summarized as follows. *(i)* The complexes of *N*-methyl-2,7-diazapyrenium (Medap$^+$) in **1**, **8** and **12** feature fixed, coplanar L^A rings and 4 additional π electrons when compared with their 4,4′-bipyridinium analogues. *(ii)* The 2-pyrimidyl ring in the complexes of *N*-(2-pyrimidyl)-4,4′-bipyridinium (PymQ$^+$) in **2**, **9** and **13** is considerably more electron deficient than the *N*-aryl substituents used previously. *(iii)* The complexes of *N*-methyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Mebpe$^+$) and *N*-phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Phbpe$^+$) (in **3**, **4**, **10**, **11**, **14**, **15**) are similar to their predecessors containing *N*-methyl-4,4′-bipyridinium (MeQ$^+$) or *N*-phenyl-4,4′-bipyridinium (PhQ$^+$), but have planar and extended conjugated systems. The salt **16** is included in this report primarily to allow crystal structural comparisons (see later).

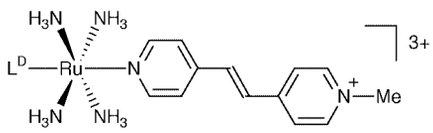
The salt [PymQ$^+$]Cl has been reported previously, but without details.[29] This compound is prepared by nucleophilic attack of 4,4′-bipyridine upon 2-chloropyrimidine, and it was found that initial melt reactions improve the yields of subsequent reactions in refluxing ethanol. The ion Phbpe$^+$ was obtained



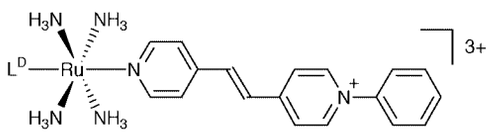
L^D = NH_3 **1**, py **8**, mim **12**



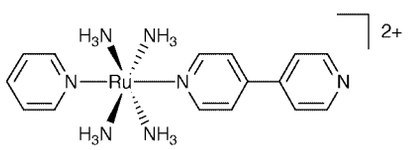
L^D = NH_3 **2**, py **9**, mim **13**



L^D = NH_3 **3**, py **10**, mim **14**



L^D = NH_3 **4**, py **11**, mim **15**



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from the condensation of 4-methyl-*N*-phenylpyridinium chloride with pyridine-4-carbaldehyde using piperidine as a base catalyst. The yield of this reaction diminishes with increasing reflux times, in similar fashion to the related, published preparation of $Mebpe^+$.[30] The new complex salts were synthesized and purified by using previously described procedures,[9] with some minor modifications. In the syntheses of the salts **8**–**16** the sequences of ligand complexations described are those which give the optimum product yields and purities.

Electronic spectroscopy studies

Electronic absorption spectra for all of the new complex salts, except for the sulfatoruthenium(III) intermediates **5**–**7**, were recorded in acetonitrile and results are presented in Table 1. Complexes **1**–**4** and **8**–**15** show intense, broad $d_\pi(Ru^{II})\rightarrow\pi^*(L^A)$ (L^A = pyridinium-substituted ligand) MLCT bands in the region 560–700 nm, the energies of which depend on the relative energies of the Ru-based HOMO and of the L^A-based LUMO.[31] The MLCT band of **16** is found at considerably higher energy due to the weaker electron-accepting nature of 4,4′-bpy compared with the pyridinium ligands. The pyridine complexes in **8**–**11** and **16** also show less intense, high energy, $d_\pi(Ru^{II})\rightarrow\pi^*$(py) MLCT bands at *ca.* 385 nm, although this absorption is obscured by a more intense UV band for **8** and overlaps with the $d_\pi(Ru^{II})\rightarrow\pi^*$(4,4′-bpy) band for **16**. All of the complexes also show one or more intense UV absorptions due to intraligand $\pi\longrightarrow\pi^*$ excitations. Data for the visible MLCT bands of **1**–**4** and **8**–**15** are collected in Table 2, together with those for the related salts of the ligands MeQ^+, PhQ^+, *N*-(4-acetylphenyl)-4,4′-bipyridinium (4-$AcPhQ^+$) and *N*-(2,4-dinitrophenyl)-4,4′-bipyridinium (2,4-$DNPhQ^+$) for purposes of comparison.[9b,c]

The MLCT band maxima of the $Medap^+$ complexes in **1** and **12** are blue-shifted by 0.03 eV with respect to those of their MeQ^+ counterparts.[9] The maxima of the $PymQ^+$ complexes in **2** and **13** are red-shifted by *ca.* 0.3 eV with respect to those of their $Medap^+$ analogues and red-shifted by 0.06–0.08 eV with respect to those of their 4-$AcPhQ^+$ analogues.[9c] Given an almost constant HOMO energy (see later), this shows that $PymQ^+$ has the lowest LUMO energy of the 4,4′-bipyridinium ligands studied, in keeping with the highly electron-deficient nature of the 2-pyrimidyl group. The acceptor strength of L^A hence increases in the order $MeQ^+ < PhQ^+ < 4\text{-}AcPhQ^+ < 2,4\text{-}DNPhQ^+ < PymQ^+$. The MLCT energies of the complexes of $Mebpe^+$ (in **3** and **14**) and $Phbpe^+$ (in **4** and **15**) are very similar to those of their analogues featuring MeQ^+ or PhQ^+, respectively.[9]

Comparison of the MLCT data for the pairs **3/4**, **10/11** and **14/15** reveals shifts of *ca.* −0.1 eV on replacing an N–Me with an N–Ph substituent. This shows that $Phbpe^+$ is a considerably stronger acceptor than $Mebpe^+$, in keeping with the previously noted difference between PhQ^+ and MeQ^+.[9c] With a given L^A, the MLCT energy decreases as the net donor strength of L^D increases, in the order py < NH_3 < mim, reflecting a progressive destabilization of the Ru-based HOMO.

Electrochemical studies

All of the new complex salts, except for **5**–**7**, were studied by cyclic voltammetry in acetonitrile and results are presented in Table 1. All exhibit reversible or quasi-reversible $Ru^{III/II}$ oxidation waves, together with generally irreversible ligand-based reduction processes. By contrast, the related complexes of MeQ^+, PhQ^+ or 4-$AcPhQ^+$ each show two reversible or quasi-reversible ligand reduction waves.[9a,c] Selected electrochemical data for **1**–**4** and **8**–**15** and for previously reported complex salts are included in Table 2.

The $Ru^{III/II}$ $E_{1/2}$ values for **1** and **12** are shifted by *ca.* +40 mV with respect to those of their MeQ^+ analogues,[9] due to the lower basicity of $Medap^+$ caused by increased delocalization. The accompanying blue shifts in the MLCT bands (see earlier) can hence be attributed largely to a slight stabilization of the Ru-based HOMOs in the $Medap^+$ complexes. By contrast, the $Ru^{III/II}$ $E_{1/2}$ values for **3**, **4**, **14** and **15** are shifted by *ca.* −40 mV with respect to those of their MeQ^+ or PhQ^+ analogues,[9] due to the mildly electron-donating character of the ethylene units. Comparison of the $Ru^{III/II}$ $E_{1/2}$ values for the pairs **3/4**, **10/11** and **14/15** reveals negligible shifts on replacing an N–Me with an N–Ph substituent, whilst the ligand E_{pc} values show large positive shifts. The corresponding red shifts in the MLCT bands (see earlier) are hence purely a result of stabilization of the ligand-based LUMOs. With a given L^A, the $Ru^{III/II}$ $E_{1/2}$ values become less positive as the donor strength of L^D increases, in the order py < mim ≈ NH_3, reflecting the HOMO destabilization indicated by the MLCT data (see earlier).

Comparison of the ligand reduction potentials for **2** and **13** with those of the previously reported complexes confirms that the $PymQ^+$ ligand is a considerably stronger electron acceptor than MeQ^+, PhQ^+ or 4-$AcPhQ^+$, in keeping with the MLCT data (see earlier). The accompanying variations in the $Ru^{III/II}$ $E_{1/2}$ values are only small, showing that the HOMO energy is relatively insensitive to changes in the substituent at N. Complex **9** also exhibits a relatively anodic reduction wave attributed to the $PymQ^+$ ligand.

Crystallographic studies

Single crystal structures were obtained for salts **8**·4MeCN and **16**·2MeCN, and representations of the molecular struc-

Table 1 Electrochemical and UV/VIS data for complex salts in acetonitrile

Complex salt	$E_{1/2}$/V *vs.* SCE (ΔE_p/mV)[a]		λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})[b]	Assignment
	$Ru^{III/II}$	Ligand waves		
1 $[Ru^{II}(NH_3)_5(Medap^+)][PF_6]_3$	0.50 (70)	−0.98[c]	581 (14 800)	$d_\pi \longrightarrow \pi^*(Medap^+)$
			397 (10 900)	$\pi \longrightarrow \pi^*$
			376 (7800)	$\pi \longrightarrow \pi^*$
			335 (24 900)	$\pi \longrightarrow \pi^*$
			241 (37 200)	$\pi \longrightarrow \pi^*$
2 $[Ru^{II}(NH_3)_5(PymQ^+)][PF_6]_3$	0.49 (100)	−0.45 (200)[d]	673 (18 000)	$d_\pi \longrightarrow \pi^*(PymQ^+)$
			285 (21 500)	$\pi \longrightarrow \pi^*$
3 $[Ru^{II}(NH_3)_5(Mebpe^+)][PF_6]_3$	0.41 (70)	−0.85[c]	595 (16 100)	$d_\pi \longrightarrow \pi^*(Mebpe^+)$
			312 (23 800)	$\pi \longrightarrow \pi^*$
4 $[Ru^{II}(NH_3)_5(Phbpe^+)][PF_6]_3$	0.42 (90)	−0.66[c]	628 (17 200)	$d_\pi \longrightarrow \pi^*(Phbpe^+)$
			329 (25 800)	$\pi \longrightarrow \pi^*$
8 *trans*-$[Ru^{II}(NH_3)_4(py)(Medap^+)][PF_6]_3$	0.65 (75)	−0.95[c]	564 (12 300)	$d_\pi \longrightarrow \pi^*(Medap^+)$
			397 (11 300)	$\pi \longrightarrow \pi^*$
			378 (10 900)	$\pi \longrightarrow \pi^*$
			334 (19 100)	$\pi \longrightarrow \pi^*$
			242 (33 100)	$\pi \longrightarrow \pi^*$
9 *trans*-$[Ru^{II}(NH_3)_4(py)(PymQ^+)][PF_6]_3$	0.67 (80)	−0.41 (90)[d]	644 (16 800)	$d_\pi \longrightarrow \pi^*(PymQ^+)$
		−1.10 (100)[d]	385 (5800)	$d_\pi \longrightarrow \pi^*(py)$
			283 (24 500)	$\pi \longrightarrow \pi^*$
10 *trans*-$[Ru^{II}(NH_3)_4(py)(Mebpe^+)][PF_6]_3$	0.60 (70)	−0.75 (150)[d]	563 (14 800)	$d_\pi \longrightarrow \pi^*(Mebpe^+)$
			386 (5900)	$d_\pi \longrightarrow \pi^*(py)$
			311 (23 800)	$\pi \longrightarrow \pi^*$
11 *trans*-$[Ru^{II}(NH_3)_4(py)(Phbpe^+)][PF_6]_3$	0.61 (90)	−0.64[c]	591 (17 100)	$d_\pi \longrightarrow \pi^*(Phbpe^+)$
			387 (sh) (6900)	$d_\pi \longrightarrow \pi^*(py)$
			328 (30 000)	$\pi \longrightarrow \pi^*$
12 *trans*-$[Ru^{II}(NH_3)_4(mim)(Medap^+)][PF_6]_3$	0.51 (70)	−0.97[c]	593 (16 700)	$d_\pi \longrightarrow \pi^*(Medap^+)$
			398 (12 000)	$\pi \longrightarrow \pi^*$
			377 (9300)	$\pi \longrightarrow \pi^*$
			337 (27 600)	$\pi \longrightarrow \pi^*$
			242 (33 100)	$\pi \longrightarrow \pi^*$
13 *trans*-$[Ru^{II}(NH_3)_4(mim)(pymQ^+)][PF_6]_3$	0.52 (90)	−0.41 (120)[d]	698 (18 700)	$d_\pi \longrightarrow \pi^*(PymQ^+)$
		−1.17 (100)[d]	285 (24 300)	$\pi \longrightarrow \pi^*$
14 *trans*-$[Ru^{II}(NH_3)_4(mim)(Mebpe^+)][PF_6]_3$	0.42 (80)	−0.86[a]	604 (16 200)	$d_\pi \longrightarrow \pi^*(Mebpe^+)$
			310 (23 000)	$\pi \longrightarrow \pi^*$
15 *trans*-$[Ru^{II}(NH_3)_4(mim)(Phbpe^+)][PF_6]_3$	0.43 (70)	−0.66[c]	638 (17 600)	$d_\pi \longrightarrow \pi^*(Phbpe^+)$
			329 (28 400)	$\pi \longrightarrow \pi^*$
16 *trans*-$[Ru^{II}(NH_3)_4(py)(4,4'\text{-bpy})][PF_6]_2$	0.60 (80)		464 (17 000)	$d_\pi \longrightarrow \pi^*(4,4'\text{-bpy})$
			378 (sh) (2800)	$d_\pi \longrightarrow \pi^*(py)$
			246 (17 600)	$\pi \longrightarrow \pi^*$

[a] Measured in solutions *ca.* 10^{-3} mol dm^{-3} in analyte and 0.1 mol dm^{-3} in $NBu^n_4PF_6$ at a platinum-bead working electrode with a scan rate of 200 mV s^{-1}. Ferrocene internal reference $E_{1/2}$ = 0.41 V, ΔE_p = 90 mV. [b] Solutions (5–7) × 10^{-5} mol dm^{-3}. [c] E_{pc} for an irreversible reduction process. [d] Irreversible process as evidenced by $i_{pc} \neq i_{pa}$.

Table 2 Electrochemical, visible MLCT absorption and HRS data for the salts *trans*-$[Ru^{II}(NH_3)_4(L^D)(L^A)][PF_6]_3$ in acetonitrile

Salt	L^D	L^A	$E_{1/2}$/V *vs.* SCE		λ_{max}[MLCT]/nm (ε/dm^3 mol^{-1} cm^{-1})	E_{max}[MLCT]/eV	β_{1064}[a]	β_0[a]
			$Ru^{III/II}$	$L^{A\ +/0}$				
1	NH_3	$Medap^+$	0.50		581 (14 800)	2.13	660	89
2	NH_3	$PymQ^+$	0.49	−0.45	673 (18 000)	1.84	640	230
3	NH_3	$Mebpe^+$	0.41		595 (16 100)	2.08	828	142
4	NH_3	$Phbpe^+$	0.42		628 (17 200)	1.97	751	192
[b]	NH_3	MeQ^+	0.46	−0.91	590 (15 800)	2.10	750	123
[b]	NH_3	PhQ^+	0.46	−0.75	628 (19 300)	1.97	858	220
[b]	NH_3	4-$AcPhQ^+$	0.47	−0.64	654 (18 000)	1.90	1112	354
[b]	NH_3	2,4-$DNPhQ^+$			660 (16 900)	1.88	871	289
8	py	$Medap^+$	0.65		564 (12 300)	2.20	579	51
9	py	$PymQ^+$	0.67	−0.41	644 (16 800)	1.93	774	228
10	py	$Mebpe^+$	0.60	−0.75	563 (14 800)	2.20	904	78
11	py	$Phbpe^+$	0.61		591 (17 100)	2.10	936	151
12	mim	$Medap^+$	0.51		593 (16 700)	2.09	756	126
13	mim	$PymQ^+$	0.52	−0.41	698 (18 700)	1.78	818	336
14	mim	$Mebpe^+$	0.42		604 (16 200)	2.05	857	168
15	mim	$Phbpe^+$	0.43		638 (17 600)	1.93	1068	310
[c]	mim	MeQ^+	0.47	−0.88	602 (16 200)	2.06	523	100
[b]	mim	PhQ^+	0.46	−0.73	642 (21 500)[d]	1.93	874	254
[b]	mim	4-$AcPhQ^+$	0.48	−0.63	666 (19 500)	1.86	962	332

[a] The value of β_{1064} (×10^{30} esu) is the uncorrected first hyperpolarizability measured using a 1064 nm Nd-YAG laser fundamental (15% error); β_0 is the static hyperpolarizability estimated by using the two-level model.[10] The quoted cgs units (esu) can be converted into SI units (C^3 m^3 J^{-2}) by dividing by a factor of 2.693 × 10^{20}. [b] Ref. 9(*c*). [c] Ref. 9(*a*). [d] λ_{max} slightly altered from value quoted in ref. 9(*c*).

Table 3 Crystallographic data and refinement details for complexes **8**·4MeCN and **16**·2MeCN

	8·4MeCN	**16**·2MeCN
Formula	$C_{28}H_{40}F_{18}N_{11}P_3Ru$	$C_{19}H_{31}F_{12}N_9P_2Ru$
M	1066.69	776.54
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$C2/c$
a/Å	12.8413(3)	16.296(4)
b/Å	23.9689(3)	22.383(3)
c/Å	14.0305(5)	8.683(1)
β/°	90	108.33(2)
U/Å^3	4318.47(19)	3006.4(10)
Z	4	4
T/K	150(2)	173(2)
μ/mm^{-1}	0.589	0.731
Reflections collected	45910	15164
Independent reflections (R_{int})	8434 (0.1226)	3458 (0.0215)
Final *R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0482, 0.0867	0.0324, 0.0914
(all data)	0.0972, 0.0979	0.0374, 0.0940

[a] Structures were refined on F_o^2 using all data; the value of *R*1 is given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$.

Table 4 Selected interatomic distances (Å) and angles (°) for salts **8**·4MeCN and **16**·2MeCN

8·4MeCN			
Ru1–N2	2.046(3)	Ru1–N5	2.138(5)
Ru1–N1	2.083(3)	Ru1–N7	2.147(5)
Ru1–N4	2.127(4)	Ru1–N6	2.154(4)
N2–Ru1–N1	177.2(2)	N4–Ru1–N7	90.72(19)
N2–Ru1–N4	91.18(16)	N5–Ru1–N7	179.4(2)
N1–Ru1–N4	87.37(16)	N2–Ru1–N6	90.85(15)
N2–Ru1–N5	87.9(2)	N1–Ru1–N6	90.68(16)
N1–Ru1–N5	89.7(2)	N4–Ru1–N6	177.21(19)
N4–Ru1–N5	88.8(2)	N5–Ru1–N6	93.18(19)
N2–Ru1–N7	91.7(2)	N7–Ru1–N6	87.30(19)
N1–Ru1–N7	90.6(2)		
16·2MeCN			
Ru(1)–N(11)	2.076(3)	Ru(1)–N(2)	2.140(2)
Ru(1)–N(21)	2.077(3)	Ru(1)–N(1^1)	2.149(2)
Ru(1)–N(2^1)	2.140(2)	Ru(1)–N(1)	2.149(2)
N(11)–Ru(1)–N(21)	180.0	N(2^1)–Ru(1)–N(1^1)	87.74(10)
N(11)–Ru(1)–N(2^1)	90.54(5)	N(2)–Ru(1)–N(1^1)	92.27(10)
N(21)–Ru(1)–N(2^1)	89.46(5)	N(11)–Ru(1)–N(1)	89.20(5)
N(11)–Ru(1)–N(2)	90.53(5)	N(21)–Ru(1)–N(1)	90.80(5)
N(21)–Ru(1)–N(2)	89.47(5)	N(2^1)–Ru(1)–N(1)	92.27(10)
N(2^1)–Ru(1)–N(2)	178.93(10)	N(2)–Ru(1)–N(1)	87.74(10)
N(11)–Ru(1)–N(1^1)	89.20(5)	N(1^1)–Ru(1)–N(1)	178.40(11)
N(21)–Ru(1)–N(1^1)	90.80(5)		

Symmetry transformation used to generate equivalent atoms: 1 1 − *x*, *y*, $-z + \frac{3}{2}$.

tures of the cations are shown in Figs. 1 and 2, bond lengths and angles in Table 4.

In salt **16**·2MeCN the torsion angle C(22)–N(21)–N(11)–C(12) between the py ligand and the co-ordinated pyridyl ring of the 4,4′-bpy is 12.2°, and the planes of the co-ordinated rings approximately bisect the H_3N–Ru–NH_3 angles. Similar arrangements have also been found in *trans*-[$Ru^{III}(NH_3)_4$(Him)(isn)][CF_3CO_2]$_3$·Pr^iOH (Him = imidazole, isn = isonicotinamide)[32] and *trans*-[$Ru^{III}(NH_3)_4(Him)_2$]Cl_3·H_2O,[33] and it has been suggested that the quasi-coplanarity of the *trans* rings may allow π coupling through the Ru.[32] As expected, steric repulsions between the 2,2′-hydrogens cause the 4,4′-bpy ligand in **16**·2MeCN to twist, with a C(32A)–C(31)–C(24)–C(23) torsion of 38.5°. This compares with torsion angles between the pyridyl rings of the 4,4′-bipyridinium ligands in *trans*-[$Ru^{II}(NH_3)_4(MeQ^+)$(PTZ)][PF_6]$_3$·Me_2CO[9a] (PTZ = phenothiazine) and *trans*-[$Ru^{II}(NH_3)_4(PhQ^+)$(PTZ)][PF_6]$_3$·Et_2O,[9c] of 9.6 and 2.6°, respectively. The marked contrast with **16**·2MeCN can be ascribed to increased delocalization in the latter two complexes due to the greater electron-withdrawing capabilities of MeQ^+ and PhQ^+ with respect to 4,4′-bpy. The bond distances Ru(1)–N(11) and Ru(1)–N(21) in **16**·2MeCN are equivalent and *ca.* 0.07 Å shorter than the average of the Ru–NH_3 distances.

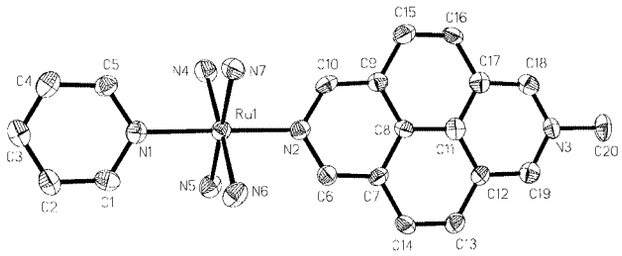

Fig. 1 Structural representation of the complex cation in the salt **8**·4MeCN (50% probability ellipsoids).

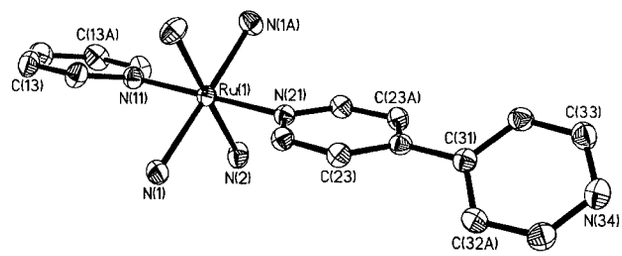

Fig. 2 Structural representation of the complex cation in the salt **16**·2MeCN (50% probability ellipsoids).

The structure of the cation in salt **8**·4MeCN resembles that in **16**·2MeCN in that the *trans* ligands are almost coplanar [C1–N1–N2–C6 9.8°], with the co-ordinated rings approximately bisecting the H_3N–Ru–NH_3 angles. However, in **8**·4MeCN the Ru1–N2 distance is *ca.* 0.05 Å shorter than Ru1–N1, indicating more extensive π-back bonding to $Medap^+$ than to the py ligand; Ru1–N2 is also *ca.* 0.03 Å shorter than the Ru1–N21 distance in **16**·2MeCN. These observations are in keeping with $Medap^+$ being a considerably stronger π acceptor than either py or 4,4′-bpy. The ammine ligands in **8**·4MeCN are hydrogen bonded to one PF_6^- anion and four acetonitrile molecules of crystallization.

Salt **16**·2MeCN adopts the centrosymmetric space group $C2/c$, whilst that of **8**·4MeCN ($Pna2_1$) is non-centrosymmetric. However, crystal packing diagrams of **8**·4MeCN reveal that the complex dipoles (as represented by the Ru(1)–N(3) vectors) are orientated almost completely antiparallel. This precludes the likelihood of this particular crystalline form of **8** exhibiting macroscopic quadratic NLO effects, in spite of the very large β_0 value determined in solution (see later).

Non-linear optical studies

The first hyperpolarizabilities β of the new complex salts **1**–**4** and **8**–**15** were measured in acetonitrile by using the HRS technique[17,18] with a 1064 nm Nd-YAG laser fundamental. Estimated static hyperpolarizabilities β_0 were obtained by application of the two-level model,[10] and results are presented in Table 2, together with data for a selection of previously reported complex salts.[9b,c] It should be noted that the utility of comparisons between these data is limited by the relatively large experimental errors in the HRS β values (±15%).

All of the new complexes show very large β and β_0 values which are comparable to those we have determined for related complexes,[9] and several of these values are amongst the largest found for metal-containing chromophores. Comparison of the data for the $Medap^+$ complexes in **1** and **12** with their MeQ^+

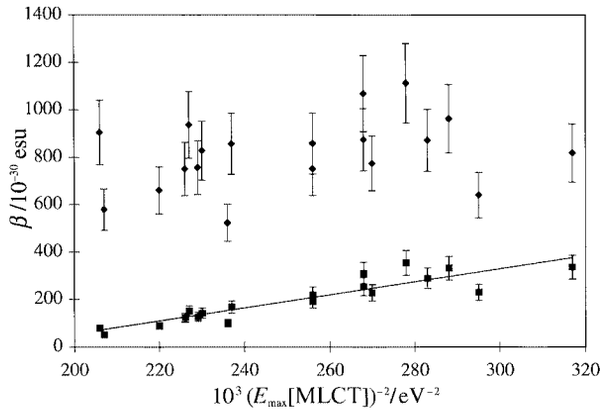

Fig. 3 Plot of the first hyperpolarizability against the inverse square of the MLCT energy for the salts **1**–**4**, **8**–**15** and other salts included in Table 2[9b,c] (◆ = β_{1064}; ■ = β_0).

analogues shows that for $L^D = NH_3$ the Medap$^+$ complex has a slightly smaller β_0, whilst when L^D = mim the reverse may be true. However, the differences are small and so it is reasonable to conclude that fixing the planarity of the 4,4′-bipyridinium rings does not greatly affect β_0. This is consistent with crystallographic studies which show that the MeQ$^+$ ligand adopts a quasi-planar configuration, and a similar situation is likely to pertain in solution due to strong donor–acceptor electronic coupling.[9a]

Although the visible absorption and electrochemical data clearly show that PymQ$^+$ is the strongest electron acceptor of the 4,4′-bipyridinium ligands studied (see earlier), this does not result in the anticipated increases in β_0 for the complexes where $L^D = NH_3$ (in **2**) or mim (in **13**). The β_0 values of **2** and **13** are, respectively, smaller than and equal to those of their 4-AcPhQ$^+$ analogues. At present, we cannot explain this apparent anomaly, but tentatively suggest that the β_0 values of the 4-AcPhQ$^+$ complexes are boosted by the presence of the acetyl groups. Clearly, further experiments are required in order to clarify this matter.

The complexes of Mebpe$^+$ and Phbpe$^+$, with the exception of **14**, have β_0 values indistinguishable from those of their 4,4′-bipyridinium analogues, providing little evidence for enhancement of the NLO response upon addition of a *trans*-ethylene unit. This contrasts with the situation in related organics where extension of conjugated bridges typically leads to increased first hyperpolarizabilites.[1] For example, the β_0 values determined *via* electric-field-induced second harmonic generation at 1907 nm for 4-(dimethylamino)-4′-nitrobiphenyl and *trans*-4-(dimethylamino)-4′-nitrostilbene are 40 and 55×10^{-30} esu, respectively.[34] However, in the latter case the addition of an ethylene unit also causes a 0.3 eV red shift in the intramolecular charge-transfer absorption band, whilst the same structural change does not significantly affect the MLCT maxima of the present complexes (see earlier).

The marked red-shifting of the MLCT bands due to the greater acceptor strength of Phbpe$^+$ with respect to Mebpe$^+$ (see earlier) also gives rise to increases in β_0 between the pairs **3/4**, **10/11** and **14/15**. This is in keeping with the previously noted difference between complexes of PhQ$^+$ and MeQ$^+$.[9c] For a given L^A, the MLCT energy increases in the order L^D = mim < NH_3 < py (see earlier), and the β_0 values broadly decrease in the opposite order.

According to the two-level model,[10] the dominant component of β is inversely proportional to E_{ge}^2 (the square of the energy gap between the ground state and first charge-transfer excited state). We have previously demonstrated a good linear correlation between β_0 and $1/E_{ge}^2$,[9c] and Fig. 3 shows that the data for the new complex salts fit reasonably well with this trend. Hence, decreasing the MLCT energy of these ruthenium(II) chromophores generally corresponds to an increase in the first hyperpolarizability. However, it should be noted that this correlation is only partial, and this may be explained by the fact that β_0 is also influenced by a number of other factors such as the oscillator strength of the charge-transfer transition.

Conclusion

The MLCT absorption properties of dipolar ruthenium(II) ammine complexes of pyridinium-substituted ligands show a fine degree of tunability. The associated large molecular first hyperpolarizabilities β_0 of these complexes are also tunable, although perhaps to a lesser extent. In general, β_0 increases as the MLCT absorption energy decreases, in keeping with the two-level model. Notably, extension of the conjugated bridge in these complexes neither significantly alters the MLCT energies nor leads to increases in β_0.

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