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A comparison of the pentaammine(pyridyl)ruthenium(II) and 4-(dimethylamino)phenyl groups as electron donors for quadratic non-linear optics

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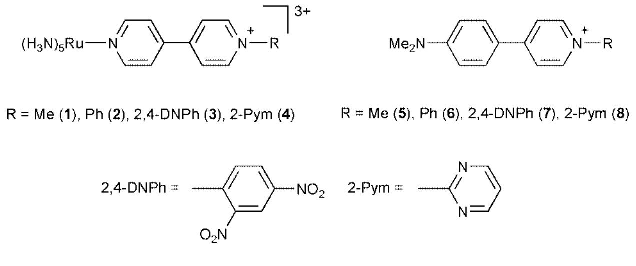
Hyper-Rayleigh scattering and Stark spectroscopic studies show that the complex salts [1–4]PF_6 have larger static first hyperpolarizabilities β_0 than [5–8]PF_6, because the higher HOMO energy of a $\{Ru^{II}(NH_3)_5\}^{2+}$ centre more than offsets the superior π-orbital overlap in the purely organic chromophores.

Recent years have witnessed great interest in molecular materials having non-linear optical (NLO) properties, due to their potential for applications in nascent optoelectronic/photonic technologies.[1] Most such materials are purely organic, but organotransition metal complexes also exhibit NLO effects.[2] Our contribution to this field has focused on the quadratic NLO properties of dipolar Ru^{II} ammine complexes.[3]

Molecules with large quadratic NLO activities contain electron donor and acceptor groups connected via polarisable π-systems. Molecular quadratic NLO behaviour arises from first hyperpolarizabilities β, and static first hyperpolarizabilities β_0 are used for comparison purposes. Perhaps surprisingly, quantitative, systematic comparisons of the electron donor/acceptor properties of metal centres with those of more traditional organic groups are very scarce. Indeed, the only such study appears to be a ZINDO analysis of β values which showed that the ferrocenyl and 4-(methoxy)phenyl donor groups are essentially interchangeable.[4] Here we report an experimental study of the complex salts [**1**–**4**]PF_6 and the organics [**5**–**8**]PF_6 which allows a comparison of the $\{Ru^{II}(NH_3)_5(py)\}^{2+}$ (py = pyridyl) and 4-(dimethylamino)phenyl π-electron donors.



[**1**–**4**]PF_6[3b,c] and [**5**–**7**]Cl[5] were synthesized as described previously, and [**5**–**7**]Cl were metathesised to [**5**–**7**]PF_6 by precipitation from H_2O–NH_4PF_6.† [**8**]PF_6 was prepared from 4-(dimethylaminophenyl)pyridine[6] and 2-chloropyrimidine, followed by precipitation from H_2O–NH_4PF_6.†

Selected spectroscopic and electrochemical data for [**1**–**8**]PF_6 are given in Table 1. The visible absorptions of [**1**–**4**]PF_6 are due to $d_\pi(Ru^{II}) \rightarrow p_{\pi*}$(pyridinium) charge-transfer (CT) excitations,[3b,c] whilst those of [**5**-**8**]PF_6 arise from $p_\pi(NMe_2) \rightarrow p_{\pi*}$(pyridinium) CTs. The CT energies E_{max} of [**5**–**8**]PF_6 are higher than those of [**1**–**4**]PF_6, but the organic *vs.* complex energy difference decreases from 0.85 to 0.72 eV as R changes in the order Me > Ph > 2,4-DNPh > 2-Pym. Also, the molar extinction coefficients of the CT bands of [**5**–**8**]PF_6 are *ca.* 2–3 times larger than those of [**1**–**4**]PF_6. Within both series, E_{max} decreases as R changes in the order Me > Ph > 2,4-DNPh > 2-Pym, the differences between the extremes being 0.26 eV for [**1**–**4**]PF_6 and 0.39 eV for [**5**–**8**]PF_6.

The cyclic voltammetric data show that the $\{Ru^{II}(NH_3)_5\}^{2+}$ moiety is much easier to oxidise than the $-NMe_2$ group, and the pyridinium groups in the complexes are easier to reduce than those in the organics. These observations are consistent with the lower E_{max} values, due to smaller HOMO–LUMO gaps, for [**1**–**4**]PF_6 compared with [**5**–**8**]PF_6. Furthermore, the E_{red} values show that the $-C_6H_4NMe_2$-4 group exerts a greater electron-donating influence on the acceptors than does the $\{Ru^{II}(NH_3)_5(py)\}^{2+}$ moiety, despite the fact that the $\{Ru^{II}(NH_3)_5\}^{2+}$ centre is more electron-rich than the $-NMe_2$ group. E_{ox} does not change greatly within each series, but E_{red} becomes less negative as R changes in the order Me < Ph < 2-Pym < 2,4-DNPh. This trend almost parallels the decreasing CT energies and reflects the increasing electron-deficiency of the acceptor group. The NMR data show that the protons *ortho* to the pyridinium N atoms are more shielded in [**5**–**8**]PF_6, consistent with the greater net electron-donating effect of the $-C_6H_4NMe_2$-4 group *vs.* $\{Ru^{II}(NH_3)_5(py)\}^{2+}$.

The greater electron-donating influence of a $-C_6H_4NMe_2$-4 group compared with $\{Ru^{II}(NH_3)_5(py)\}^{2+}$ can be traced to two

Table 1 Visible absorption, cyclic voltammetric and proton NMR data for salts [**1**–**8**]PF_6

Salt	E_{max}/eV[a] (ε/dm^3 mol^{-1} cm^{-1})	E/V (*vs.* Ag–AgCl)[b] E_{ox}[d]	E_{red}[e]	δ/ppm[c] py-H[f]
[**1**]PF_6[g]	2.10 (15 800)	0.48	−0.89	9.15
[**2**]PF_6[g]	1.97 (19 300)	0.48	−0.73	9.33
[**3**]PF_6[g]	1.88 (16 900)	0.48	−0.38	9.37
[**4**]PF_6[h]	1.84 (18 000)	0.51	−0.43	10.17
[**5**]PF_6	2.95 (40 200)	1.14	−1.35	8.76
[**6**]PF_6	2.77 (50 100)	1.18	−1.11	9.01
[**7**]PF_6	2.64 (45 300)	1.27	−0.55	9.23
[**8**]PF_6	2.56 (55 600)	1.22	−0.81	9.78

[a] Using acetonitrile solutions (*ca.* 10^{-5} mol dm^{-3}). [b] Measured in acetonitrile solutions *ca.* 10^{-3} mol dm^{-3} in analyte and 0.1 mol dm^{-3} in $NBu^n_4PF_6$ at a platinum-bead/disc working electrode with a scan rate of 200 mV s^{-1}. $E_{1/2}$ values are given for [1]PF_6, [2]PF_6 and [4]PF_6; E_{pa} or E_{pc} values are given for [3]PF_6 and [5–8]PF_6 (return waves are also observed in some cases). Ferrocene internal reference $E_{1/2}$ = 0.43 V. [c] Chemical shift at 200 MHz with respect to $SiMe_4$ in CD_3COCD_3. [d] Potential for first oxidation of HOMO. [e] Potential for first reduction of LUMO. [f] Doublet signal for protons *ortho* to pyridinium N atom. [g] Ref. 3(*b*). [h] Ref. 3(*c*).

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Table 2 Visible absorption, Stark and HRS data for salts [**1**–**8**]PF_6

Salt	E_{max}/eV[a]	f_{os}[b]	$\lvert\mu_{12}\rvert$/D	$\lvert\Delta\mu_{12}\rvert$/D	$\Delta\mu_{ab}$/D	c_b^2	$H_{ab}/10^3$ cm^{-1}	$\beta_0/10^{-30}$ esu[c]	$\beta/10^{-30}$ esu[d]	$\beta_0/10^{-30}$ esu[e]
[**1**]PF_6	1.92	0.20	5.2	13.8	17.3	0.10	4.7	60	750[f]	123[f]
[**2**]PF_6	1.78	0.22	5.7	15.3	19.1	0.10	4.3	93	858[f]	220[f]
[**3**]PF_6	1.70	0.22	5.8	16.3	20.0	0.09	4.0	113	871[f]	289[f]
[**4**]PF_6	1.64	0.28	6.7						640[g]	230[g]
[**5**]PF_6	2.93	0.66	7.7	13.2	20.3	0.17	9.0	54		
[**6**]PF_6	2.74	0.79	8.7	12.7	21.6	0.21	8.9	75	50	23
[**7**]PF_6	2.64	0.66	8.1						70	29
[**8**]PF_6	2.52	0.88	9.6	12.4	22.9	0.23	8.5	106	75	29

[a] Butyronitrile glasses at 77 K (*ca*). 10^{-5} mol dm^{-3}). [b] Oscillator strength determined by numerical integration of the digitized absorption spectra. [c] Static first hyperpolarizability calculated from eqn. (1). [d] First hyperpolarizability measured in acetonitrile at 298 K using a ns 1064 nm laser for [**1**–**4**]PF_6 and a fs 1300 nm laser for [**5**–**8**]PF_6. [e] Static first hyperpolarizability estimated from β *via* the two-state model.[9] [f] Ref. 3(*b*). [g] Ref. 3(*c*).

factors. Firstly, the latter is a σ-electron acceptor, as well as a π-donor, whilst the former is only a π-donor. The second, and perhaps more important, factor is more effective p(N)–p(C) compared with p(N)–d(Ru) π-orbital overlap. Such an effect also explains differences between mixed-valence ions containing $-C_6H_4NMe_2$-4 or $\{Ru^{II}(NH_3)_5(py)\}^{2+}$ groups.[7]

We have obtained β values for [**1**–**8**]PF_6 by using hyper-Rayleigh scattering (HRS) studies;[8] β_0 values were derived *via* the two-state model[9] and results are shown in Table 2. The previously reported β_0 values of [**1-4**]PF_6 were derived from nanosecond 1064 nm HRS,[3*b,c*] whilst [**5-8**]PF_6 were studied using femtosecond 1300 nm HRS,[10] incorporating fluorescence demodulation.[11] Unfortunately, the 650 nm HRS signal from [**5**]PF_6 was too weak to allow determination of β. Two conclusions can be drawn from the HRS data: *(i)* the β_0 values of the complexes appear to be much larger than those of their organic counterparts (but note that comparison of HRS β_0 values obtained under different experimental conditions may be of limited validity),[12] and (*ii*) decreasing E_{max} generally corresponds with increasing β_0 within both series.

Stark spectroscopy affords dipole moment changes upon CT excitation $\Delta\mu_{12}$.[13] According to the two-state model, $\Delta\mu_{12}$ can be used to calculate β_0 by using eqn. (1)[9]

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{2(E_{max})^2} \tag{1}$$

where μ_{12} is the transition dipole moment. The results of Stark studies on [**1**–**8**]PF_6, carried out at 77 K as previously described,[14] are given in Table 2. Unfortunately, the data fits for [**4**]PF_6 and [**7**]PF_6 were unsatisfactory. The μ_{12} values, diabatic dipole moment changes $\Delta\mu_{ab}$, mixing coefficients c_b^2 and electronic coupling matrix elements H_{ab} for the diabatic states were calculated as previously described.[14]

The CT f_{os} and μ_{12} values of [**5**–**8**]PF_6 are larger than those of [**1**–**4**]PF_6. Furthermore, μ_{12} generally increases as E_{max} decreases within each series. [**1**–**8**]PF_6 show relatively large $\Delta\mu_{12}$ values, with [**1**]PF_6 and [**2**]PF_6 having larger values than [**5**]PF_6 and [**6**]PF_6, respectively. For the complexes, $\Delta\mu_{12}$ increases as R changes in the order Me < Ph < 2,4-DNPh, but a similar trend is not shown by the organics. The values of c_b^2 and H_{ab} for the organics are about twice those for the complexes, consistent with the less effective d(Ru)–p(N) *vs.* p(N)–p(C) π-orbital overlap indicated by the electrochemical and NMR data. The β_0 values derived from eqn. (1) are in agreement with the HRS results in as much as they increase as E_{max} decreases within each series. However, in contrast with HRS, the Stark data indicate that the β_0 values of [**1**]PF_6 and [**2**]PF_6 are only slightly larger than those of their organic counterparts. This is because the β_0-enhancing effects of decreasing E_{max} and increasing $\Delta\mu_{12}$ are largely offset by decreasing μ_{12} when moving from organic to complex.

In conclusion, a $\{Ru^{II}(NH_3)_5(py)\}^{2+}$ centre is more electron-rich than a $-C_6H_4NMe_2$-4 group, but the latter exerts a greater electron-donating effect on pyridinium units due in part to more effective π-orbital overlap. HRS data show that [**1**–**4**]PF_6 have much larger β_0 values than their organic counterparts, but Stark spectroscopy indicates that the increase in β_0 between the complexes and organics is much smaller. Nevertheless, the complexes do have the added attraction that their CT absorption and NLO responses are redox-switchable.[15]

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† [**5**–**8**]PF_6 were characterised by C,H,N analyses and proton NMR spectroscopy.

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