Determination of the molecular quadratic non-linear optical responses of V-shaped metallochromophores by using Stark spectroscopy †

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The static molecular first hyperpolarizabilities β_0 of a series of V-shaped Ru^{II} chromophores with two overlapping visible metal-to-ligand charge-transfer absorptions have been determined by using data obtained from Stark spectroscopy.

Molecular non-linear optical (NLO) materials hold great promise for applications in optical data processing,[1] and organotransition metal complexes have recently formed an increasingly important component of research in this area.[2] Quadratic NLO properties derive at the molecular level from first hyperpolarizabilities β. Most of the chromophores studied to date contain an electron donor group (D) connected to an electron acceptor (A) *via* a π-conjugated bridge. The optical non-linearities of such simple dipolar species are largely one-dimensional (1D), *i.e.* dominated by one β tensor component. Introducing multiple D and/or A groups renders β multi-dimensional (MD). Organic MD NLO compounds have recently emerged as candidates for quadratic NLO applications,[3] offering potential advantages over 1D chromophores such as increased β responses without undesirable loss of visible transparency. Dipolar 2D C_{2v} molecules with large off-diagonal β components also offer new possibilities for phase-matching second harmonic generation.[3d,f] Some neutral dipolar 2D metal complexes have been studied,[4] but none of these are closely similar to the V-shaped species reported here.

R = Me (**1**), Ph (**2**), (**3**), (**4**)
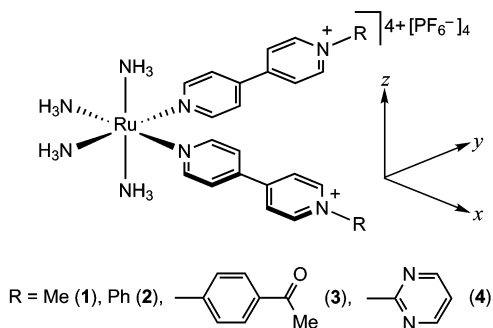
We have previously described studies on 1D ruthenium ammine complex salts with very large β responses that are tunable by ligand-based changes,[5] and also reversibly switchable *via* $Ru^{III/II}$ redox.[6] We now employ similar design strategies for the creation of the series of novel dipolar 2D C_{2v} chromophores in **1**–**4**, each of which features a Ru^{II} D centre connected to two pyridinium A groups. **1**–**4** were synthesized by reactions of *cis*-[$Ru^{II}(NH_3)_4(H_2O)_2$]$^{2+}$, generated *in situ* by Zn(Hg)

reduction of *cis*-[$Ru^{III}(NH_3)_4Cl_2$]Cl,[7] with known pro-ligand salts.[5a–c] Full synthetic details are reported as ESI. †§

As found in other related complexes such as *cis*-[Ru^{II}-$(NH_3)_4L_2$]$^{2+}$ (L = pyridine, isonicotinamide),[8] **1**–**4** each shows two very close visible absorption bands (Table 1, Fig. 1) arising from dπ(Ru^{II}) → π*(L) metal-to-ligand charge-transfer (MLCT) transitions. A simple MO analysis has attributed these bands to orthogonally polarized excitations from the primarily $4d_{xy}$ Ru-based HOMO into two L-based LUMOs which are combinations of π* MOs of the individual pyridyl ligands.[8b] For **1**–**4**, the lower energy absorption (MLCT-1) is more intense than the higher energy band (MLCT-2) in all cases, and the energy gap between these bands is constant at *ca.* 0.3 eV. As observed previously in related 1D complexes,[5c] the E_{max} values for both MLCT bands decrease as L changes in the order MeQ$^+$ > PhQ$^+$ > 4-AcPhQ$^+$ > 2-PymQ$^+$, due to the steadily increasing acceptor strength of the pyridinium groups. Also, in similar fashion to the 1D complexes,[5c] the $Ru^{III/II}$ $E_{1/2}$ values (Table 1) are essentially independent of L, but the L$^{+/0}$ potentials become less negative in the order MeQ$^+$ < PhQ$^+$ < 4-AcPhQ$^+$ < 2-PymQ$^+$, as L becomes a stronger electron acceptor. Two close L$^{0/-}$ reduction waves are also observed for **1** and **2** (Table 1), indicating that the one-electron reduced neutral radical ligands L$^\bullet$ are electronically coupled.
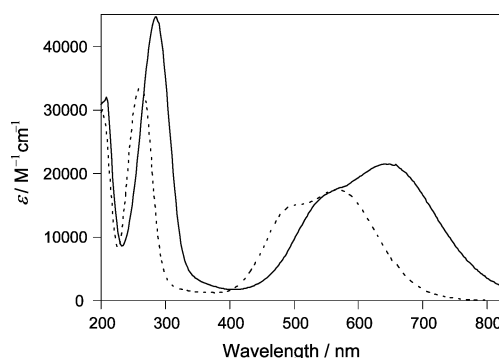

Fig. 1 Electronic absorption spectra of **1** (- - -) and **4** (—) in MeCN.

Measurement of the molecular NLO responses of chromophores such as **1**–**4** is challenging. Resonance-enhanced β values for ionic chromophores are generally obtained *via* hyper-Rayleigh scattering (HRS) experiments,[9] and can be corrected for dispersion by using a simple two-state model[10] if a single charge-transfer (CT) process dominates β. However, such an approach to deriving static first hyperpolarizabilities β_0 is not feasible for chromophores with strongly overlapping low-energy CT bands. We have found that Stark spectroscopy is valuable for probing the NLO and related properties of 1D dipolar Ru^{II} ammines,[5d,e] and have now also applied this technique to **1**–**4**. Stark data have previously been used to assess the NLO responses of neutral, purely organic dipolar 2D chromophores, but with resolved CT bands.[3d]

Table 1 MLCT absorption and electrochemical data for **1**–**4** in MeCN

Salt	λ_{max}/nm, E_{max}/eV (ε/dm^3 mol^{-1} cm^{-1})[a]		$E_{1/2}$/V vs. Ag–AgCl (ΔE_p/mV)[b]		
	MLCT-1	MLCT-2	Ru$^{III/II}$	L$^{+/0}$	L$^{0/-}$
1	570, 2.18 (17 500)	502, 2.47 (15 100)	0.79 (85)	−0.81 (110)	−1.42 (65) −1.55 (70)
2	606, 2.05 (20 400)	528, 2.35 (16 500)	0.79 (70)	−0.66 (110)	−1.26 (70) −1.38 (65)
3	620, 2.00 (22 600)	536, 2.31 (17 500)	0.80 (70)	−0.55 (120)	−1.09 (290)[c]
4	644, 1.93 (21 500)	558, 2.22 (17 200)	0.82 (100)	−0.42[d]	

[a] Solutions *ca.* 5×10^{-5} mol dm^{-3}. [b] Solutions *ca.* 10^{-3} mol dm^{-3} in analyte and 0.1 mol dm^{-3} in NBu$^n_4$PF$_6$ at a platinum-disc working electrode; scan rate = 200 mV s^{-1}; ferrocene internal reference $E_{1/2}$ = 0.44 V, ΔE_p = 70 mV. [c] Shoulders evident. [d] E_{pc} for an irreversible reduction process.

Table 2 Modelled MLCT absorption, Stark spectroscopic and static first hyperpolarizability data for **1**–**4** in PrCN at 77 K

Salt	λ_{max}/nm[a]	E_{max}/eV[a]	μ_{12}/D[a,b]	θ/°[c]	μ_{12*}/D[d]	$\Delta\mu_{12}$/D[a]	β_0/$\times 10^{30}$ esu[e]
1	628	1.98	6.7	51.4	4.2	10.1	53
	518	2.39	5.2	32.0	4.4	11.3	45
2	632	1.96	7.4	33.0	6.2	13.8	163
	512	2.42	4.6	21.6	4.3	9.9	37
3	684	1.81	7.6	51.0	4.8	12.1	98
	558	2.22	5.6	25.5	5.0	13.0	78
4	731	1.97	7.9	51.0	5.0	11.7	119
	589	2.10	5.9	29.1	5.1	12.3	84

[a] For the two fitted Gaussian components. [b] Derived from $\mu_{12} = [f_{os}/(1.08 \times 10^{-5} E_{max})]^{1/2}$ where f_{os} is the oscillator strength. [c] Angle between $\Delta\mu_{12}$ and m$\Delta\mu_{12}$ (m = unit transition dipole moment, $\mu_{12}/|\mu_{12}|$); therefore angle between $\Delta\mu_{12}$ and μ_{12}. [d] Magnitude of μ_{12} in direction of $\Delta\mu_{12}$ ($\mu_{12} \times \cos\theta$). [e] Derived from $\beta_0 = 3\Delta\mu_{12}(\mu_{12*})^2/(E_{max})^2$ (relative error *ca.* ±20%).

For each of **1**–**4**, the visible absorption spectrum was fit to the sum of two or three Gaussian curves, two of which were dominant. The 1st and 2nd derivatives of the latter were then used to model the Stark spectrum (*e.g.* Fig. 2). Such a fitting procedure has previously been adopted in Stark analyses of purely organic[11] and metal-containing chromophores,[12] but has only once been used to derive NLO responses.[13] As expected for 2D chromophores, the dipole moment change $\Delta\mu_{12}$ and transition dipole moment μ_{12} vectors are offset by *ca.* 20–50°, so the components of μ_{12} along the $\Delta\mu_{12}$ directions μ_{12*} were derived and used in the two-state equation $\beta_0 = 3\Delta\mu_{12}(\mu_{12*})^2/(E_{max})^2$ to determine the magnitudes of the two orthogonal β_0 components (Table 2). The β responses of **1**–**4** are evidently

highly 2D. Comparison of the results with the available data for the related complexes [Ru^{II}(NH$_3$)$_5$L]$^{3+}$ [L($\beta_0 \times 10^{30}$ esu): MeQ$^+$ (120); PhQ$^+$ (186); 4-AcPhQ$^+$ (229)][5d] affords the following general conclusions: (*i*) the β_0 values for both types of chromophore are similarly large and (*ii*) *N*-arylation causes substantial increases in β_0 when compared with the MeQ$^+$ complexes in both 1D and 2D cases (except for the value from the MLCT-2 band of **2**). A factor which limits the β responses of **1**–**4** is the decreased electron-donating strength of the Ru^{II} centres, as evidenced by their Ru$^{III/II}$ $E_{1/2}$ values of *ca.* 0.80 V *vs.* Ag–AgCl, which are *ca.* 300 mV higher than those of their [Ru^{II}-(NH$_3$)$_5$L]$^{3+}$ analogues.[5b]

In summary, we report novel V-shaped chromophores and the first instance in which Stark spectroscopy with Gaussian-fitting has been used to assess molecular quadratic NLO responses arising from MLCT transitions. The treatment is approximate, but the results are reasonable when compared with 1D systems, and the approach adopted should also be applicable to other 2D dipolar chromophores with overlapping CT bands.
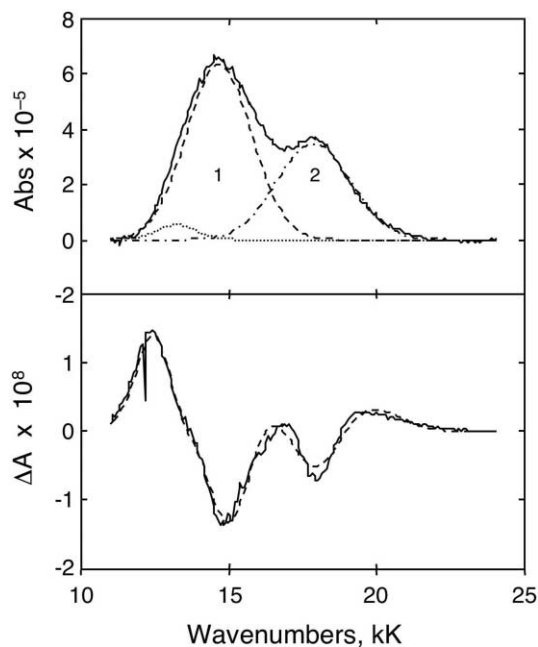
Fig. 2 Stark spectrum and calculated fit for **3** in an external electric field of 2.80×10^7 V m^{-1}. Top panel: absorption spectrum with fitting (numbers signify dominant Gaussian curves, the data for which are reported); bottom panel: Stark spectrum, experimental (—) and fit (- - -).

Notes and references

§ **1**–**4** were characterised by proton NMR spectroscopy and satisfactory CHN analyses.

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