

Highly Unusual Effects of π -Conjugation Extension on the Molecular Linear and Quadratic Nonlinear Optical Properties of Ruthenium(II) Ammine Complexes

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Molecular nonlinear optical (NLO) materials are of great current interest for potential applications in emerging optoelectronic/photonic technologies.¹ Organotransition metal complexes offer many exciting possibilities for combining NLO effects with other molecular electronic properties (e.g., redox or magnetic behavior) to afford novel multifunctional materials.² Regarding quadratic (second-order) NLO effects, which are governed at the molecular level by first hyperpolarizabilities β , molecular engineering guidelines for purely organic chromophores are now well established.¹ However, comparable knowledge and understanding relating to metal complexes is currently somewhat less substantial.²

Most molecules with large β values comprise conjugated π -systems bearing electron donor (D) and acceptor (A) groups, and their linear optical properties are hence dominated by intense D(π) \rightarrow A(π^*) charge-transfer (CT) transitions. According to a widely used two-state model (TSM) for such dipolar species,³ the static first hyperpolarizability β_0 (the intrinsic, off-resonant β) is given by $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{\max})^2$ (eq 1), where μ_{12} is the transition dipole moment, $\Delta\mu_{12}$ is the dipole moment change, and E_{\max} is the maximal energy of the CT absorption.⁴ One of the principal strategies for increasing β_0 in dipolar organics is simply to extend the conjugation length, because this generally increases $\Delta\mu_{12}$ and decreases E_{\max} .¹ Hence, D–A polyenes have attracted considerable attention⁵ and have been found to display some of the largest β_0 values known.⁶ Most such studies have involved purely organic D/A groups, but those describing metal complexes (often with ferrocenyl D groups) also show that polyene chain extension leads to the expected trends in the optical properties.⁷

We have recently used the hyper-Rayleigh scattering (HRS) technique⁸ and Stark (electroabsorption) spectroscopy⁹ to study the quadratic NLO properties of ruthenium pyridyl ammine complexes; such chromophores can display very large β_0 values which are associated with intense, low energy metal-to-ligand CT (MLCT) transitions.¹⁰ The MLCT absorption and NLO properties of these complexes are highly tunable, in accord with the TSM, and can also be reversibly switched via Ru^{III/II} redox.¹¹ Kanis et al. have used ZINDO calculations on the hypothetical series Cr(CO)₅-{NC₃H₄-4-(CH=CH)_n-C₆H₄-4-CHO} to predict that β_{vec} (the vector component of β along the dipole axis) maximizes at $n = 1$, and then decreases sharply up to $n = 3$.¹² This behavior is clearly very different from that of purely organic polyenes and was rationalized on the basis of the fact that a pyridyl-coordinated metal center is

both a π -donor and a σ -acceptor, and the primary acceptor of charge from the metal d-orbitals is actually the pyridyl ring, and not the remote formyl group.¹² Perhaps surprisingly, no other theoretical or empirical studies have since tested this conclusion. We have hence carried out HRS and Stark experiments on the two series of complex salts **1–4** and **5–8** to directly probe the effects of conjugation extension on the linear and NLO properties.

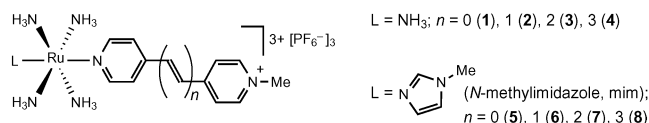


Table 1. Visible Absorption and Cyclic Voltammetric Data

salt	E_{\max}^a (eV)	ϵ_{\max}^a (M ⁻¹ cm ⁻¹)	μ_{12}^a (D)	E, V vs Ag–AgCl ($\Delta E_p, \text{mV}$) ^b	
				$E_{1/2}[\text{Ru}^{\text{III/II}}]$	$E_{1/2}[\text{L}^{\text{+0}}]$ or E_{pc}^c
1^d	2.10	15 800	6.0	0.51 (75)	–0.86 (70)
2^e	2.08	16 100	6.2	0.46 (70)	–0.80
3	2.12	18 700	6.8	0.45 (85)	–0.79
4	2.18	17 500	6.7	0.45 (75)	–0.77
5^f	2.06	16 200	6.2	0.52 (75)	–0.83 (70)
6^e	2.05	16 200	6.4	0.47 (80)	–0.81
7	2.09	21 400	7.4	0.44 (85)	–0.77
8	2.18	21 900	7.8	0.45 (100)	–0.75

^a Measured in MeCN at 298 K; $\mu_{12} = [f_{os}/(1.08 \times 10^{-5} E_{\max})]^{1/2}$, where f_{os} is the oscillator strength determined by numerical integration of the digitized spectra. ^b Measured with solutions in (freshly distilled from CaH₂) MeCN ca. 10⁻³ M in analyte and 0.1 M in [N⁺(Bu)₄]PF₆ at a Pt bead/disk working electrode with a scan rate of 200 mV s⁻¹. Ferrocene internal reference $E_{1/2} = 0.46$ V, $\Delta E_p = 70$ mV. ^c For an irreversible reduction process. ^d Reference 10b. ^e Reference 10c. ^f Reference 10a.

1,^{10b} **2**,^{10c} **5**,^{10a} and **6**^{10c} were prepared as previously described, and **3**, **4**, **7**, and **8** were obtained via established methods.^{10a–c} The pyridyl polyene ligands in the latter were synthesized via stepwise oxopropenylations of pyridine-4-carboxaldehyde, followed by condensations with *N*-methyl-4-picolinium iodide. Full synthetic details will be published elsewhere.

The pro-ligand salts show pyridyl(π) \rightarrow pyridinium(π^*) CT transitions in the UV, the energies of which decrease steadily on conjugation extension,¹³ as is found with all other known D–A polyenes. The visible absorption spectra of **1–8** are dominated by broad MLCT bands (Table 1), which give rise to intense purple or blue colorations. Within both series, E_{\max} decreases slightly on moving from $n = 0$ to 1, but then increases as n increases further up to 3. Cyclic voltammetric data for **1–8** (Table 1) show that $E_{1/2}[\text{Ru}^{\text{III/II}}]$ decreases by 50 mV on moving from $n = 0$ to 1 (due to the mildly electron donating influence of the 4-vinyl groups),

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Table 2. Visible Absorption, Stark Spectroscopic, and HRS Data

salt	E_{\max}^a (eV)	μ_{12}^a (D)	$\Delta\mu_{12}^a$ (D)	$\beta_0[S]^b$ (10^{-30} esu)	β_{1064}^c (10^{-30} esu)	$\beta_0[H]^d$ (10^{-30} esu)
1 ^{e,f}	1.92	5.2	13.8	120	750	123
2 ^{e,g}	1.82	5.5	16.2	175	828	142
3	1.84	7.9	22.4	482	2593	372
4	1.85	7.2	27.1	475	1308	131
5 ^{e,h}	1.88	5.5	17.1	170	523	100
6 ^{e,g}	1.80	6.3	18.0	256	857	168
7	1.81	8.4	23.3	586	1440	237
8	1.83	7.8	26.7	563	1660	175

^a Measured in PrCN at 77 K. ^b Derived from eq 1. ^c Obtained from 1064 nm HRS in MeCN at 298 K. ^d Derived from β_{1064} by using the TSM.³ ^e Reference 10d. ^f Reference 10b. ^g Reference 10c. ^h Reference 10a.

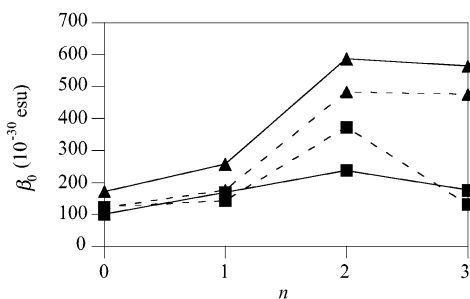


Figure 1. β_0 as a function of n . Dashed lines = NH_3 series (**1–4**); full lines = mim series (**5–8**); \blacktriangle = values calculated from Stark data; \blacksquare = values derived from HRS and corrected by using the TSM.

but further conjugation extension does not significantly affect $E_{1/2}[\text{Ru}^{\text{III}}]$. The pyridinium ligand first reduction waves are reversible only for $n = 0$, even up to scan rates of 200 V s^{-1} . Although correlation between the MLCT energies and the redox potentials is hence not possible, it can be concluded that variations in the ligand-based LUMO energies are primarily responsible for the observed changes in E_{\max} on moving from $n = 1$ to 3.

1–8 were studied via Stark spectroscopy in PrCN at 77 K. As observed previously with Ru amines,^{10d,14} the E_{\max} values decrease markedly on moving from solution to glass (Tables 1 and 2). Although the same general trend in the variation of E_{\max} with increasing n is found in either medium, the form of this trend varies. The $\Delta\mu_{12}$ values increase steadily with n , as is normal for D–A polyenes, while μ_{12} maximizes at $n = 2$ (Table 2). The $\beta_0[S]$ values, derived from eq 1, increase on moving from $n = 0$ to 2, and then decrease slightly (Table 2). HRS experiments in MeCN gave resonance enhanced β_{1064} values for **1–8** which were used to estimate β_0 by using the TSM³ ($\beta_0[H]$, Table 2). Within both series, $\beta_0[H]$ maximizes at $n = 2$, and the values for $n = 3$ or 1 are similar. The $\beta_0[H]$ values are mostly smaller than their $\beta_0[S]$ counterparts, consistent with the decreases in E_{\max} on moving from solution to glass. Also, the increase in $\beta_0[H]$ on moving from $n = 1$ to 2 is smaller than that observed in $\beta_0[S]$ for the mim complexes (in **6** and **7**).

The same conclusion clearly emerges from both the Stark and the HRS results; that is, β_0 in these complex chromophores is maximized at $n = 2$ (Figure 1). This agrees with the earlier theoretical predictions inasmuch as conjugation extension does not lead to continual increases in β_0 .¹² However, the prediction that β_0 falls off dramatically after only one CH=CH unit is at variance with our data. Also, the general form of the trend shown by our results differs from that predicted; that is, the β_0 drop-off after maximization is relatively gradual for three of the four sets of data obtained (Figure 1). These different conclusions may arise from limitations of the ZINDO model, but are more probably related to the obviously limited similarity between the $\text{Cr}(\text{CO})_5$ and $\text{trans}\{-\text{Ru}^{\text{II}}(\text{NH}_3)_4\text{L}\}^{2+}$

($\text{L} = \text{NH}_3$ or mim) centers, the latter being considerably stronger electron donors.

In summary, we have presented the first experimental study on the effects of polyene chain extension on the optical properties of metal pyridyl complexes. Neither blue-shifting of CT bands nor decreasing of β_0 with the addition of CH=CH units has ever been observed previously. It is hence apparent that the design criteria for metal-containing NLO chromophores can diverge dramatically from those for purely organic molecules. Further systematic studies may well uncover other interesting, and perhaps unexpected, differences.

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Supporting Information Available: Spectroscopic and analytical data for **3**, **4**, **7**, and **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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