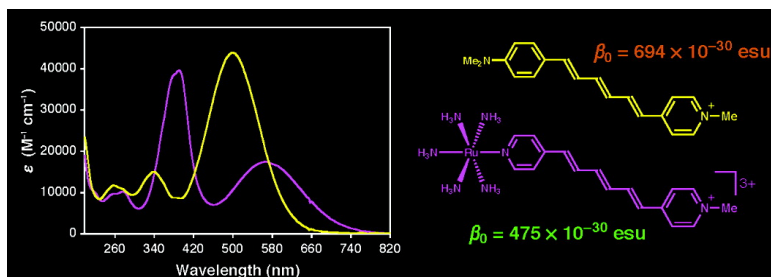


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Contrasting Linear and Quadratic Nonlinear Optical Behavior of Dipolar Pyridinium Chromophores with 4-(Dimethylamino)phenyl or Ruthenium(II) Ammine Electron Donor Groups

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Abstract: In this article, we contrast the optical properties of dipolar chromophores having 4-(dimethylamino)-phenyl electron donor (D) and pyridinium acceptor (A) groups with those of closely related cations having pyridyl-coordinated Ru^{II} donors. A range of physical data, including that from Stark (electroabsorption) spectroscopy, permits unprecedented quantitative comparisons, most notably regarding the effects of extension of bridging polyene chains. The purely organic compounds display normal optical properties in that their intense, visible $\pi \rightarrow \pi^*$ intramolecular charge-transfer (ICT) bands red-shift as the number of *E*-ethylene units (*n*) increases from 1 to 3 and the associated static first hyperpolarizabilities β_0 increase steadily with *n*. The related Ru^{II} complexes show intense, visible $d \rightarrow \pi^*$ metal-to-ligand charge-transfer (MLCT) bands, which are found to lower energy when compared with the ICT transitions of the corresponding organics. Abnormally, these MLCT bands blue-shift as *n* increases, and β_0 maximizes at *n* = 2. Time-dependent density-functional theory and finite field calculations verify these empirical trends for both types of compound, which can be rationalized as arising from the differing orbital structures of the chromophores and the associated degrees of D–A electronic coupling.

Introduction

Molecular organic materials with nonlinear optical (NLO) properties continue to attract considerable research interest, largely because of their potential uses in novel optoelectronic/photonic devices.¹ Various organic salts have been studied in this context, especially stilbazolium-type compounds, such as *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST), which are particularly promising for device applications.² Molecules having large quadratic NLO activities typically contain electron donor (D) and acceptor (A) groups connected via polarizable π -systems,¹ with pyridinium rings acting as

powerful electron acceptors in stilbazolium and related species. The linear optical properties of such chromophores are characterized by intense $\pi(D) \rightarrow \pi^*(A)$ intramolecular charge-transfer (ICT) absorption bands. At the molecular level, quadratic NLO behavior is governed by first hyperpolarizabilities β , and static first hyperpolarizabilities β_0 are generally used for comparing active molecules. An important feature of organic salts is that counterion variations can be exploited as a means to modify crystal packing, potentially affording noncentrosymmetric macroscopic structures that are crucial for bulk quadratic NLO effects. Additional attractive features of crystalline salts are their inherently greater stabilities and higher chromophore number densities when compared with alternative NLO materials such as poled polymers.

Research in the NLO field has recently increasingly featured studies on organotransition metal complexes, which may offer improved scope for the creation of multifunctional materials when compared with purely organic compounds.³ Our contribu-

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tion to this area has involved systematic hyper-Rayleigh scattering (HRS)⁴ and Stark (electroabsorption)⁵ spectroscopic measurements on ruthenium(II) pyridyl ammine complexes of pyridinium-substituted ligands.⁶ Such chromophores can exhibit very large β_0 responses, which are associated with intense, low energy $d(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{pyridinium})$ metal-to-ligand charge-transfer (MLCT) transitions.⁶ These MLCT absorption and NLO properties are highly tunable, according to the widely used two-state model,⁷ and can also be readily and reversibly switched by exploiting $\text{Ru}^{\text{III/II}}$ redox.⁸ We have also carried out HRS, Stark spectroscopic, and second harmonic generation (SHG) studies on stilbazolium-type chromophores with *N*-arylpyridinium groups,⁹ and we have published a preliminary report contrasting the optical properties of a few of these compounds with those of their Ru^{II} pentaammine analogues.¹⁰ Electrochemical and UV-visible spectroscopic studies show that a pyridyl-coordinated $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ center is rather more electron-rich than a $-\text{C}_6\text{H}_4-4\text{-NMe}_2$ group, and some evidence was found that the complexes have larger β_0 values than their purely organic counterparts.¹⁰

Despite the fact that very many reports of purely organic and organotransition metal NLO compounds have appeared,^{1,3} quantitative, systematic comparisons of these two types of chromophore are extremely scarce. Indeed, prior to our recent communication,¹⁰ the only such reported study appeared to be a ZINDO-based analysis of β values, which indicated that the ferrocenyl and 4-(methoxy)phenyl D groups are essentially interchangeable.¹¹ The benchmark NLO compound 4,4'-dimethyl-

aminonitrostilbene has also been compared with a related molybdenum mononitrosyl complex by using ab initio methods.¹² It is clearly important to develop a fuller knowledge and understanding of the similarities and differences between the available types of chromophores that may compete for NLO device applications. In particular, the question as to whether incorporating transition metal centers into NLO chromophores is beneficial remains largely unanswered. To this end, we have amassed a considerable body of data that allows ample opportunities for further comparisons, especially concerning the effects of conjugation extension on linear and NLO properties. Because the HRS data for the organics and the Ru^{II} complexes were obtained under different conditions and are inevitably subject to complications due to resonance effects, only the Stark-derived data and theoretically calculated parameters are considered here.

Experimental Section

Materials and Procedures. The compounds *N*-methyl-4-picolinium hexafluorophosphate [mepic^+] PF_6^- and 5-(4-dimethylaminophenyl)penta-2,4-dienal¹³ were prepared according to published procedures. 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. ¹H NMR spectra were recorded on a Varian Gemini 200 spectrometer, and all shifts are referenced to TMS. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester and UV/Vis/NIR spectra were obtained by using a Hewlett-Packard 8452A diode array or a Varian Cary IE spectrophotometer. Mass spectra were recorded via +electrospray on a Micromass Platform spectrometer (cone voltage 80 V). Cyclic voltammetry was carried out with an EG&G PAR model 283 potentiostat/galvanostat. A single-compartment cell was used with a Ag-AgCl reference electrode, a Pt disk working electrode, and a Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH_2), and $\text{NBu}^+_4\text{-PF}_6^-$, twice recrystallized from ethanol and dried in vacuo, was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M analyte (0.1 M electrolyte) were deaerated by purging with N_2 . All $E_{1/2}$ values were calculated from $(E_{\text{pa}} + E_{\text{pc}})/2$ at a scan rate of 200 mV s⁻¹.

Synthesis of *E,E,E*-*N*-Methyl-4-[6-(4-dimethylaminophenyl)hexa-1,3,5-trienyl]pyridinium Hexafluorophosphate (4). The cation in this salt has previously been isolated with tosylate,^{2b,c} iodide,¹⁴ or a range of benzenesulfonate anions,¹⁴ but **4** is apparently a new compound. A solution of [mepic^+] PF_6^- (254 mg, 1.00 mmol), 5-(4-dimethylaminophenyl)penta-2,4-dienal (201 mg, 1.00 mmol) and piperidine (2 drops) in methanol (100 mL) was heated under reflux for 4 h in the dark. The reaction mixture was allowed to cool slowly to room temperature, and the dark purple microcrystalline solid was filtered off, washed with methanol, and dried: 323 mg, 74%; δ_{H} (CD_3CN) 8.31 (2 H, d, $J = 6.5$ Hz, $\text{C}_5\text{H}_4\text{N}$), 7.81 (2 H, d, $J = 6.2$ Hz, $\text{C}_5\text{H}_4\text{N}$), 7.58 (1 H, dd, $J = 15.3, 11.2$ Hz, CH), 7.41 (2 H, d, $J = 9.0$ Hz, C_6H_4), 7.02–6.53 (7 H, m, 5CH and C_6H_4), 4.14 (3 H, s, N^+-Me), 3.00 (6 H, s, NMe_2). Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{F}_6\text{N}_2\text{P}$: C, 55.05; H, 5.31; N, 6.42. Found: C, 55.00; H, 5.39; N, 6.44. $[\text{M} - \text{PF}_6^-]^+ = 291$.

Stark Spectroscopy. The apparatus, experimental methods, and data analysis procedure were as previously reported,^{6e,15} with a xenon arc lamp used as the light source in place of a tungsten filament bulb. Butyronitrile ($n\text{-C}_3\text{H}_7\text{CN}$) was used as the glassing medium, for which

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the local field correction f_{lm} is estimated as 1.33.^{6e,15} The Stark spectrum for **4** was measured three times using different field strengths, and the signal was always found to be quadratic in the applied field. Analysis of the Stark spectrum in terms of the Liptay treatment^{5a} afforded the dipole moment difference $\Delta\mu_{12}$. A two-state analysis¹⁵ of the ICT transition gives

$$\Delta\mu_{\text{ab}}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2 \quad (1)$$

where $\Delta\mu_{\text{ab}}$ is the dipole moment difference between the diabatic states, $\Delta\mu_{12}$ is the observed (adiabatic) dipole moment difference, and μ_{12} is the transition dipole moment. The latter can be determined from the oscillator strength f_{os} of the transition by

$$|\mu_{12}| = [f_{\text{os}} / (1.08 \times 10^{-5} (E_{\text{max}}))]^{1/2} \quad (2)$$

where E_{max} is the energy of the ICT maximum (in wavenumbers). The degree of delocalization c_{b}^2 and electronic coupling matrix element H_{ab} for the diabatic states are given by

$$c_{\text{b}}^2 = \frac{1}{2} \left[1 - \left(\frac{\Delta\mu_{12}^2}{\Delta\mu_{12}^2 + 4\mu_{12}^2} \right)^{1/2} \right] \quad (3)$$

$$|H_{\text{ab}}| = \left| \frac{E_{\text{max}}(\mu_{12})}{\Delta\mu_{\text{ab}}} \right| \quad (4)$$

If the polarizability change $\Delta\alpha$ and hyperpolarizability β_0 tensors have only nonzero elements along the ICT direction, then these quantities are given by

$$\Delta\alpha = -4 \frac{(\mu_{12})^2}{E_{\text{max}}} \quad (5)$$

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{(E_{\text{max}})^2} \quad (6)$$

A relative error of $\pm 20\%$ is estimated for the β_0 values derived from the Stark data and using eq 6.

Computational Procedures. All theoretical calculations were performed by using the Gaussian 98¹⁶ program. Molecular geometries were optimized assuming C_s symmetry using the hybrid functional B3P86¹⁷ and the LanL2DZ¹⁸ basis set. The same model chemistry was used for properties calculations. Electronic transitions were calculated by means of the TD-DFT method, and the excited-state dipole moments were calculated by using the one particle RhoCI density. The default Gaussian 98 parameters were used in every case.

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X-ray Crystallography. Suitable crystals of **4** were grown by slow evaporation of an acetonitrile solution, and a crystal of approximate dimensions $1.00 \times 0.75 \times 0.04$ mm³ was chosen for diffraction study. Data were collected on a Nonius Kappa CCD area-detector diffractometer controlled by the Collect software package.¹⁹ The data were processed by Denzo²⁰ and corrected for absorption by using the empirical method employed in Sortav²¹ from within the MaXus suite of programs.²² The structure was solved by direct methods and refined by full-matrix least-squares on all F_o^2 data using SHELXS-97²³ and SHELXL-97.²⁴ The quality of the structure is relatively poor because of low diffraction angles, but is nevertheless of use for the purposes of the present study. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in idealized positions with thermal parameters riding on those of the parent atom. The asymmetric unit contains two $C_{20}H_{23}N_2^+$ positions and two PF_6^- positions. Crystallographic data and refinement details are presented in Table 4.

Results and Discussion

Linear Optical, Electrochemical, and ¹H NMR Studies.

Figure 1 shows the chemical structures of the investigated salts. The electronic absorption spectra of salts **1–7** show intense ICT bands, while complex salts **8–26** all display intense MLCT bands in the visible region, together with $\pi \rightarrow \pi^*$ intraligand charge-transfer (ILCT) transitions in the UV. For **8–26**, cyclic voltammetric studies reveal reversible or quasi-reversible Ru^{III/II} oxidation waves, together with pyridinium ligand first reduction processes that are reversible only for $n = 0$, even up to scan rates as high as 200 V s⁻¹. In contrast, the purely organic salts **1–7** show only irreversible redox processes at all available scan rates, both for oxidation of the $-NMe_2$ groups and for reduction of the pyridinium units. All of the salts **1–26** show well-defined ¹H NMR spectra, in which the lowest field doublet signals are assigned as arising from the protons *ortho* to the pyridinium N atom. Selected ICT/MLCT absorption, electrochemical, and ¹H NMR data for salts **1–26** are presented in Table 1, with the data arranged such that the entries for each of the organic compounds **1–7** are immediately followed by those for the complexes with the same pyridinium group and conjugated bridge. Representative UV–visible absorption spectra of the purely organic $n = 1$ or 3 salts (**1** and **4**, respectively) and of their {Ru^{II}(NH₃)₅}²⁺ analogues (**8** and **11**, respectively) are shown in Figure 2.

The ICT energies E_{max} of **1–7** are higher in every case than the MLCT energies of their Ru^{II} counterparts, but the organic vs metal complex energy difference varies between ca. 0.9 and 0.2 eV, being largest when $n = 0$ and smallest when $n = 3$. Hence, the effect of changing the electronic nature of the D group becomes less significant as the conjugated system is extended. Also, the molar extinction coefficients ϵ of the ICT bands of **1–7** are ca. 2–3 times larger than those of the MLCT bands of the related complexes. For the purely organic compounds **1–4** and **5/6**, E_{max} decreases as n increases, in

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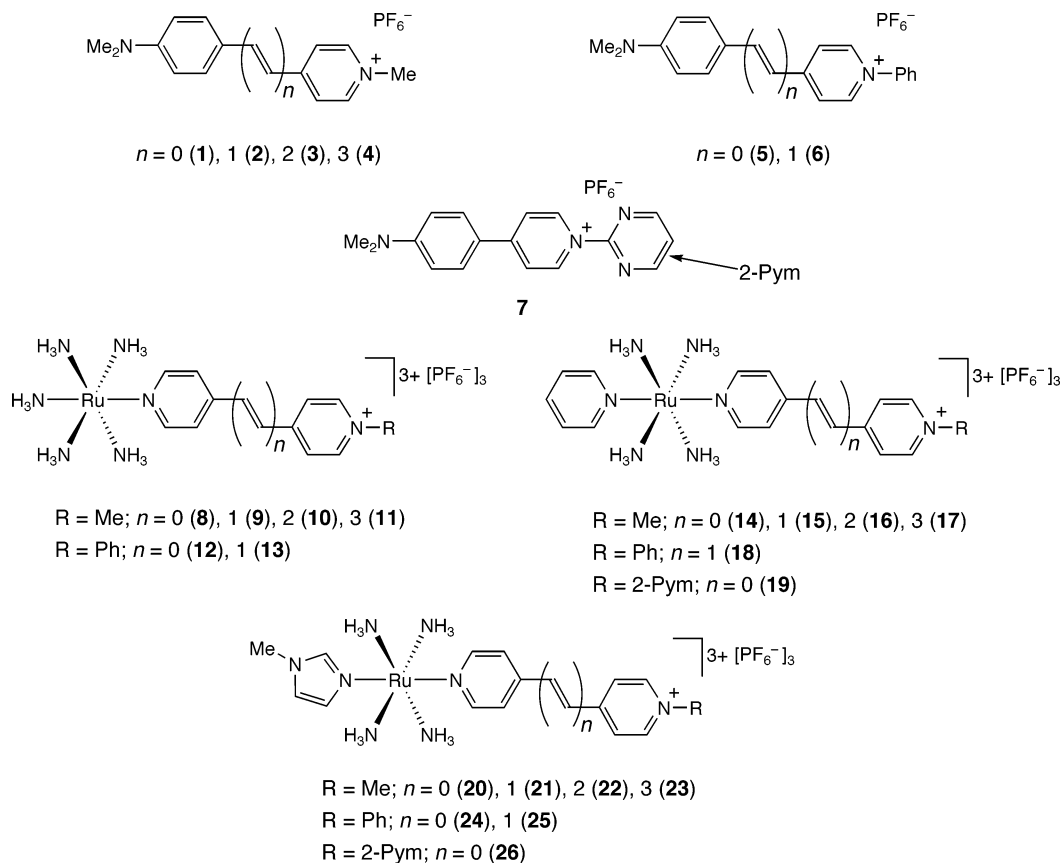


Figure 1. Chemical structures of the salts investigated.

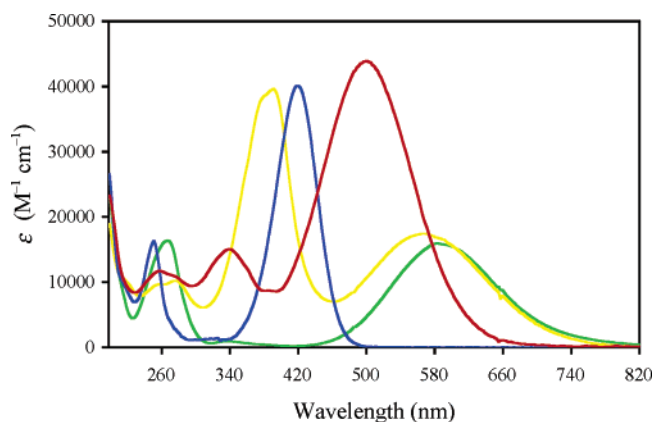


Figure 2. UV–visible absorption spectra of salts **1** (blue), **4** (red), **8** (green), and **11** (yellow) at 298 K in acetonitrile.

keeping with well-established principles for D- π -A chromophores.¹ In marked contrast, the MLCT E_{max} values increase steadily on moving from $n = 1$ to 3 within each of the complex series **8–11**, **14–17**, and **20–23**. We have previously discussed this highly unusual behavior,^{6f,i} which has been observed in only one other type of D-A polyenes that contain tetrathiafulvalenyl D groups.²⁵ Although the ICT ϵ values remain constant within the organic series **1–4**, the ILCT bands for each of the complex series **8–11**, **14–17**, and **20–23** gain intensity steadily as n increases. The latter absorptions also show the normal trend of red-shifting with increasing conjugation path length.

Although the data for the organic compounds are irreversible, the cyclic voltammetric studies clearly show that the Ru^{II} ammine moieties are much easier to oxidize than the $-\text{C}_6\text{H}_4-4\text{-NMe}_2$ units, with a given A group and conjugated bridge.

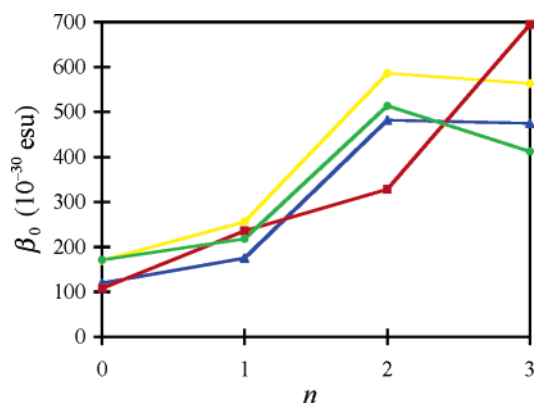


Figure 3. Stark-derived β_0 values as a function of n (only dominant MLCT transitions considered for complexes). Red = organic series (**1–4**). Blue = *trans*-NH₃ complex series (**8–11**). Green = *trans*-py complex series (**14–17**). Yellow = *trans*-mim complex series (**20–23**).

Also, the pyridinium groups in the complexes are considerably easier to reduce than those in the organics. These observations are consistent with the higher E_{max} values, because of larger HOMO–LUMO gaps, for **1–7** when compared with those of the MLCT bands of their Ru^{II} counterparts. Furthermore, the more negative pyridinium reduction potentials for the organic

(25) (a) González, M.; Martín, N.; Segura, J. L.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1998**, *39*, 3269–3272. (b) Garín, J.; Orduna, J.; Rupérez, J. I.; Alcalá, R.; Villacampa, B.; Sánchez, C.; Martín, N.; Segura, J. L.; González, M. *Tetrahedron Lett.* **1998**, *39*, 3577–3580. (c) González, M.; Martín, N.; Segura, J. L.; Seoane, C.; Garín, J.; Orduna, J.; Alcalá, R.; Sánchez, C.; Villacampa, B. *Tetrahedron Lett.* **1999**, *40*, 8599–8602. (d) González, M.; Segura, J. L.; Seoane, C.; Martín, N.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B.; Hernández, V.; López Navarrette, J. T. *J. Org. Chem.* **2001**, *66*, 8872–8882. (e) Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron* **2001**, *57*, 7883–7892.

Table 1. Selected Charge-Transfer Absorption, Electrochemical, and ^1H NMR Data for Salts **1–26**

salt	n	$\lambda_{\text{max}}^{a,b}$ (nm)	$E_{\text{max}}^{a,b}$ (eV)	$\epsilon_{\text{max}}^{a,b}$ ($\text{M}^{-1}\text{cm}^{-1}$)	(V vs Ag–AgCl) ^{a,e}		$\delta[\text{py-H}]^g$ (ppm) ^g
					$E_{1/2}[\text{Ru}^{\text{III/II}}]$ or E_{pa}^c	$E_{1/2}[\text{L}^{+/0}]$ or E_{pc}^d	
1^h	0	420	2.95	40 200	1.14 ^c	−1.35 ^d	8.76
8^j	0	590	2.10	15 800	0.50	−0.87	9.15
		268	4.63	16 300			
14^k	0	566	2.19	17 200	0.68	−0.82	9.19
		254	4.88	17 700			
20^l	0	602	2.06	16 200	0.51	−0.84	9.15
		268	4.63	18 100			
2ⁱ	1	470	2.64	42 800	0.94 ^c	−1.11 ^d	8.70
9^m	1	595	2.08	16 100	0.45	−0.81 ^d	8.94
		312	3.97	23 800			
15^m	1	563	2.20	14 800	0.64	−0.76 ^d	8.95
		311	3.99	23 800			
21^m	1	604	2.05	16 200	0.46	−0.82 ^d	8.94
		310	4.00	23 000			
3^h	2	487	2.55	38 700	0.95 ^c	−1.15 ^d	8.75
10^k	2	584	2.12	18 700	0.44	−0.80 ^d	8.94
		354	3.50	32 600			
16^k	2	552	2.25	19 800	0.63	−0.76 ^d	8.93
		356	3.48	35 800			
22^k	2	592	2.09	21 400	0.43	−0.78 ^d	8.96
		352	3.52	40 200			
4	3	500	2.48	43 800	0.71 ^c	−0.94 ^d	8.76
11^k	3	568	2.18	17 500	0.44	−0.78 ^d	8.91
		392	3.16	39 700			
17^k	3	542	2.29	24 900	0.61	−0.77 ^d	8.93
		392	3.16	51 100			
23^k	3	570	2.18	21 900	0.44	−0.76 ^d	8.91
		392	3.16	52 500			
5^h	0	448	2.77	50 100	1.18 ^c	−1.11 ^d	9.01
12^j	0	628	1.97	19 300	0.50	−0.71	9.33
		280	4.43	18 500			
24^{i,m}	0	642	1.93	21 500	0.50	−0.69	9.38
		280	4.43	21 400			
6ⁱ	1	504	2.46	51 400	0.93 ^c	−0.88 ^d	8.96
13^m	1	628	1.97	17 200	0.46	−0.60 ^d	9.25
		329	3.77	25 800			
18^m	1	591	2.10	17 100	0.65	−0.60 ^d	9.30
		328	3.78	30 000			
25^m	1	638	1.93	17 600	0.47	−0.60 ^d	9.26
		329	3.77	28 400			
7^h	0	485	2.56	55 600	1.12 ^c	−0.81 ^d	9.78
19^m	0	644	1.93	16 800	0.71	−0.37	10.28
		283	4.38	24 500			
26^m	0	698	1.78	18 700	0.56	−0.37	10.22
		285	4.35	24 300			

^a In acetonitrile solutions at 293 K. ^b Solutions ca. 10^{-5} M. ^c Peak potential for first irreversible oxidation (of HOMO, localized on $-\text{C}_6\text{H}_4-4\text{-NMe}_2$ group); smaller return wave also observed in some cases. ^d Peak potential for first irreversible reduction (of LUMO, localized on pyridinium group); smaller return wave also observed in some cases. ^e Solutions ca. 10^{-3} M in analyte and 0.1 M in NBu_4PF_6 at a platinum bead/disk working electrode with a scan rate of 200 mV s^{-1} . Ferrocene internal reference $E_{1/2} = 0.45\text{ V}$, $\text{L} = 4,4'$ -bipyridinium. ^f Doublet signal for protons ortho to pyridinium N atom. ^g Chemical shift at 200 MHz with respect to TMS in CD_3COCD_3 . ^h Data taken in part from ref 9c. ⁱ Data taken in part from ref 9a. ^j Data taken from ref 6c. ^k Data taken from ref 6i. ^l Data taken from ref 6a. ^m Data taken from ref 6d.

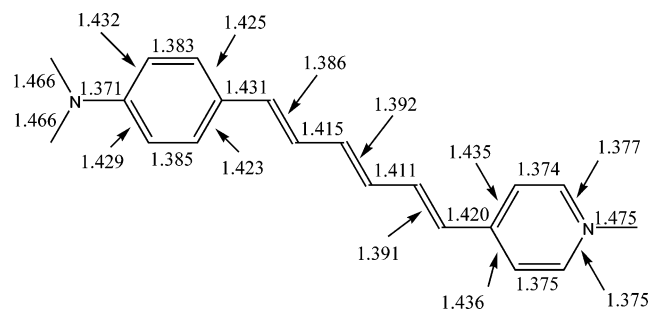


Figure 4. Bond distances (\AA) calculated using the B3P86/LanL2DZ model chemistry for the gas-phase geometry of salt **4**.

compounds show that the $-\text{C}_6\text{H}_4-4\text{-NMe}_2$ group exerts a greater electron-donating influence on the acceptors than do the Ru^{II} pyridyl ammine moieties, despite the fact that the Ru^{II} centers

are more electron-rich than the amino groups. This result is attributable to less effective π -orbital overlap between the Ru^{II} d-orbitals and pyridyl N p-orbitals than between the p-orbitals of the N atoms of the $-\text{NMe}_2$ groups and those of the C atoms of the adjacent phenyl rings. The NMR data show that the protons ortho to the pyridinium N atoms are more shielded in **1–7** (by ca. 0.2–0.5 ppm) than in their Ru^{II} analogues. This difference in shielding is also consistent with the greater net electron-donating effect of the $-\text{C}_6\text{H}_4-4\text{-NMe}_2$ group when compared with a Ru^{II} pyridyl ammine center because of increased π -orbital overlap. Furthermore, the organic vs metal complex chemical shift difference is largest when $n = 0$ and smallest when $n = 3$, showing that the effect of varying the electronic properties of the D group becomes less significant as n increases, as also observed in the ICT/MLCT data (see above).

Table 2. Selected Optical Absorption and Stark Spectroscopic Data for Salts 1–26

salt	<i>n</i>	λ_{\max}^a (nm)	E_{\max}^a (eV)	f_{os}	$\mu_{12}^{2,b}$ (D)	$\Delta\mu_{12}^c$ (D)	$\Delta\mu_{\text{ab}}^d$ (D)	r_{12}^e (Å)	r_{ab}^f (Å)	$c_0^{2,g}$	H_{ab}^h (cm ⁻¹)	$\Delta\alpha^i$ (10 ⁻³⁹ C m ² V ⁻¹)	β_0^j (10 ⁻³⁰ esu)	$\beta_0[\Sigma]^k$ (10 ⁻³⁰ esu)
1 ^l	0	423	2.93	0.66	7.7	13.2	20.3	2.7	4.2	0.17	9000	35.9	108	
8 ^m	0	645	1.92	0.20	5.2	13.8	17.3	2.9	3.6	0.10	4700	3.8	120	
14 ⁿ	0	611	2.03	0.29	6.1	16.2	20.3	3.4	4.2	0.10	4900	35.8	171	
20 ^m	0	658	1.88	0.22	5.5	17.1	20.3	3.6	4.2	0.08	4100	6.5	170	
2 ^l	1	480	2.58	0.80	9.1	16.3	24.4	3.4	5.1	0.17	7700	71.0	236	
9 ^m	1	681	1.82	0.23	5.5	16.2	19.6	3.4	4.1	0.09	4100	6.0	175	
15 ^m	1	638	1.94	0.25	6.0	19.3	22.7	4.0	4.7	0.08	4100	4.7	218	
21 ^m	1	687	1.80	0.26	6.3	18.0	22.0	3.7	4.6	0.09	4200	6.0	256	
3 ^l	2	503	2.47	0.78	9.1	20.4	27.4	4.2	5.7	0.13	6600	72.3	328	
10 ⁿ	2	675	1.84	0.43	7.9	22.4	27.4	4.7	5.7	0.09	4300	105.0	482	546
		377	3.29	0.58	6.8	12.7	18.6	2.6	3.9	0.16	9700	-50.2	64	
16 ⁿ	2	631	1.97	0.50	8.2	25.1	30.0	5.2	6.2	0.08	4300	68.3	514	565
		370	3.35	0.52	6.5	11.7	17.4	2.4	3.6	0.16	10 000	-3.51	51	
22 ⁿ	2	684	1.81	0.48	8.4	23.3	28.7	4.9	6.0	0.09	4300	101.0	586	645
		374	3.32	0.42	5.8	16.4	20.1	3.4	4.2	0.09	7700	-37.5	59	
4	3	523	2.37	1.25	11.8	24.0	33.7	5.0	7.0	0.14	6700	70.4	694	
11 ⁿ	3	669	1.85	0.36	7.2	27.1	30.6	5.6	6.4	0.06	3500	131.0	475	576
		408	3.04	0.63	7.4	14.5	20.8	3.0	4.3	0.15	8700	-9.4	101	
17 ⁿ	3	625	1.98	0.36	7.0	28.6	31.8	6.0	6.6	0.05	3500	64.9	412	546
		404	3.07	1.00	9.3	12.5	22.4	2.6	4.7	0.22	10 300	-2.5	134	
23 ⁿ	3	678	1.83	0.42	7.8	26.7	30.9	5.6	6.4	0.07	3700	136.0	563	658
		408	3.04	0.66	7.6	13.0	20.0	2.7	4.2	0.18	9300	-5.8	95	
5 ^l	0	452	2.74	0.79	8.7	12.7	21.6	2.6	4.5	0.21	8900	22.8	150	
12 ^m	0	696	1.78	0.22	5.7	15.3	19.1	3.2	4.0	0.10	4300	5.0	186	
24 ^m	0	708	1.75	0.27	6.2	17.4	21.4	3.6	4.5	0.09	4100	6.3	258	
6 ^l	1	514	2.41	0.80	9.4	16.3	24.8	3.4	5.2	0.17	7300	69.1	288	
13 ^m	1	714	1.74	0.21	5.7	19.5	22.6	4.1	4.7	0.07	3500	8.0	249	
18 ^m	1	672	1.85	0.26	6.2	20.6	24.0	4.3	5.0	0.07	3800	6.3	269	
25 ^m	1	741	1.67	0.26	6.5	20.2	24.0	4.2	5.0	0.08	3600	8.5	352	
7 ^l	0	492	2.52	0.88	9.6	12.4	22.9	2.6	4.8	0.23	8500	20.8	212	
19 ^m	0	711	1.74	0.29	6.5	12.4	18.0	2.6	3.7	0.15	5100	3.1	200	
26 ^m	0	784	1.58	0.24	6.4	16.8	21.1	3.5	4.4	0.10	3900	5.6	323	

^a In butyronitrile glasses at 77 K. ^b Transition dipole moment derived from eq 2. ^c Dipole moment change calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^d Diabatic dipole moment change calculated from eq 1. ^e Delocalized electron-transfer distance calculated from $\Delta\mu_{12}/e$. ^f Effective (localized) electron-transfer distance calculated from $\Delta\mu_{\text{ab}}/e$. ^g Degree of delocalization calculated from eq 3. ^h Electronic coupling matrix element calculated from eq 4. ⁱ Polarizability change calculated from eq 5. ^j Static first hyperpolarizability calculated from eq 6. ^k Sum of the β_0 values for the two absorption bands (where present) for the complex chromophores, i.e., $\beta_0[\text{ILCT}] + \beta_0[\text{MLCT}]$. ^l Data taken in part from ref 9c. ^m Data taken from ref 6e. ⁿ Data taken in part from ref 6i.

Table 3. Results of B3P86/LanL2DZ Calculations on the Cations in Salts 1–4, 8–11, and 14–17

parent salt	<i>n</i>	E_{\max}^a (eV)	f_{os}^a	μ_{12}^a (D)	$\Delta\mu_{12}^a$ (D)	transition	β_0^b (10 ⁻³⁰ esu)	β_0^c (10 ⁻³⁰ esu)
1	0	3.01	0.89	8.85	13.03	HOMO → LUMO	131	74
2	1	2.65	1.32	11.46	13.94	HOMO → LUMO	305	150
3	2	2.38	1.73	13.84	15.95	HOMO → LUMO	628	269
4	3	2.17	2.15	16.14	17.70	HOMO → LUMO	1141	609
8 ^d	0	2.57	0.37	6.19	21.17	HOMO → LUMO	144	112
		4.86	0.51	5.25	1.13	HOMO-3 → LUMO	2	
9 ^d	1	2.56	0.48	6.99	26.07	HOMO → LUMO	225	112
		3.84	0.43	5.45	16.72	HOMO → LUMO + 1	39	
		4.01	0.49	5.69	6.22	HOMO-3 → LUMO	15	
10 ^d	2	2.62	0.79	8.90	27.94	HOMO → LUMO	376	156
		3.39	1.06	9.10	3.48	HOMO-3 → LUMO	29	
11 ^d	3	2.60	1.74	13.27	18.81	HOMO → LUMO	571	134
		3.07	0.57	6.99	10.94	HOMO-3 → LUMO	66	
14 ^d	0	2.34	0.50	7.50	21.71	HOMO → LUMO	260	192
		3.80	0.17	3.40	1.76	HOMO → LUMO + 2	2	
		4.87	0.50	5.19	5.56	HOMO-6 → LUMO	7	
15 ^d	1	2.34	0.58	8.07	26.97	HOMO → LUMO	373	259
		3.57	0.34	4.98	10.10	HOMO → LUMO + 1	23	
		3.99	0.73	6.96	4.41	HOMO-3 → LUMO	16	
16 ^d	2	2.42	0.83	9.52	29.77	HOMO → LUMO	535	271
		3.31	1.14	9.95	6.57	HOMO-3 → LUMO	69	
		3.54	0.13	3.14	1.53	HOMO → LUMO + 1	1	
17 ^d	3	2.46	1.58	13.01	25.03	HOMO → LUMO	819	212
		3.00	0.96	9.19	7.78	HOMO-1 → LUMO	85	
		3.34	0.01	1.05	9.04	HOMO → LUMO + 1	1	

^a Calculated in the gas phase by using TD-DFT at the optimized B3P86/LanL2DZ geometry. ^b Calculated from the TD-DFT results by using eq 6. ^c Calculated by using the FF method. ^d Data taken in part from ref 6i.

Stark Spectroscopic Studies. The results of Stark spectroscopic studies with salts 1–26 in butyronitrile glasses at 77 K are collected in Table 2. These experiments afford dipole moment changes $\Delta\mu_{12}$ for the ICT/MLCT/ILCT transitions,

which can be used to calculate β_0 values according to the two-state eq 6. Although we have also reported HRS data for salts 1–26, these were obtained under different conditions (800- or 1300-nm femtosecond lasers with high-frequency demodulation

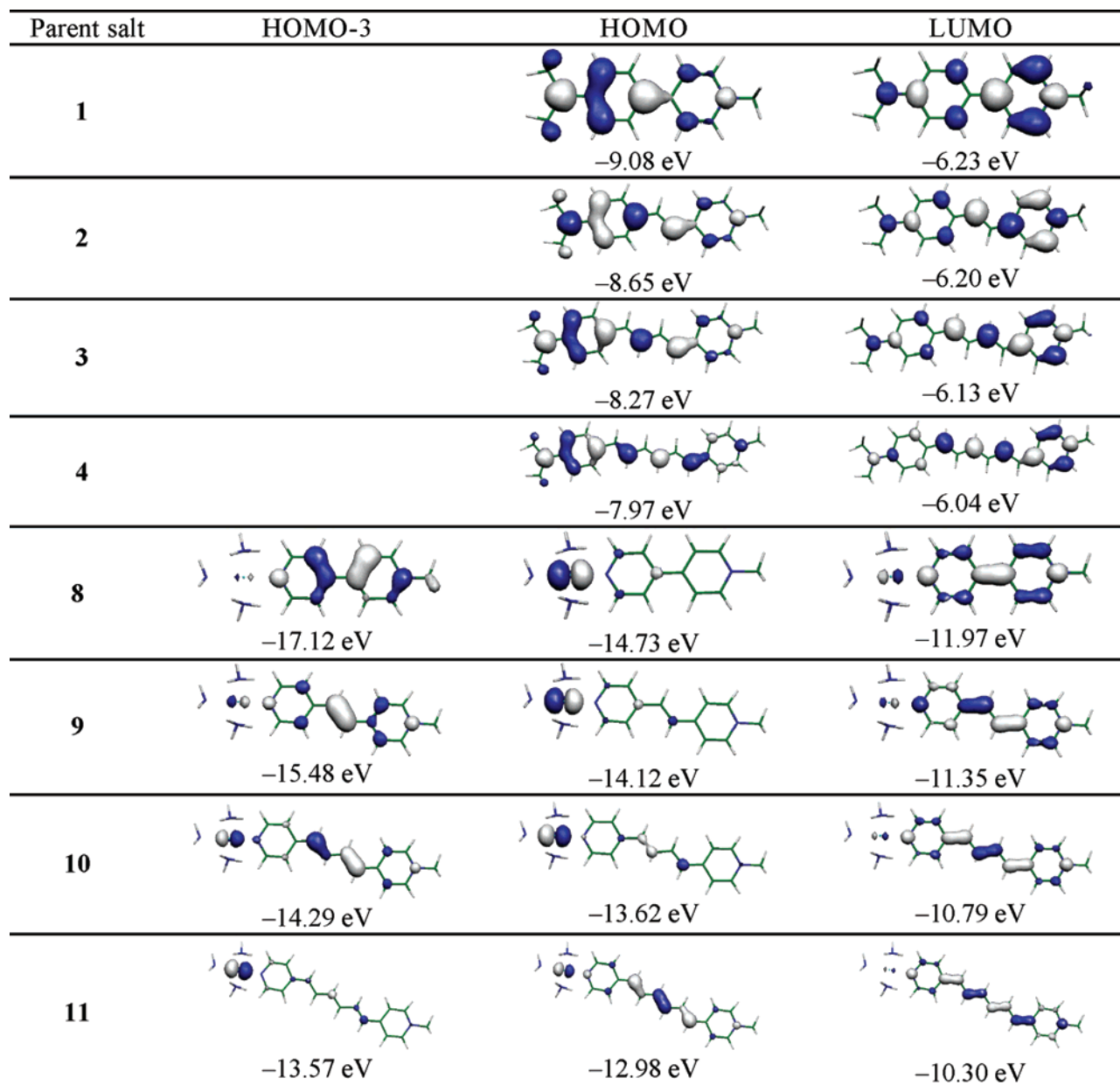


Figure 5. Illustrations of the 0.04 contour surface diagrams of the MOs involved in the ICT transitions of the cations **1–4** and in the MLCT and ILCT transitions of the complex cations in **8–11**, calculated from TD-DFT. The entries for **8–11** were taken from ref 6i, in which the corresponding illustrations for the complex cations in **14–17** can also be found.

of multiphoton fluorescence for **1–7**;⁹ 1064 nm nanosecond laser for **8–26**),^{6a–d,f,i} and they are inevitably subject to complications arising from resonance effects. The utility of such data for comparing the β_0 responses of the organics with those of the related Ru^{II} complexes is hence rather limited. In contrast, the Stark measurements were all carried out by using exactly the same experimental procedure and therefore provide data that may be compared directly with confidence.

The E_{\max} values generally decrease on moving from solution to glass (Tables 1 and 2), but the differences are larger for the MLCT bands of the complex salts (0.16–0.35 eV) than for the ICT bands of their purely organic counterparts (0.02–0.11 eV). The ILCT absorptions of the complexes show intermediate-sized shifts. The intensities of the MLCT bands in the complex salts, as indicated by their f_{os} and μ_{12} values, are lower than those of the ICT bands in the corresponding organic chromophores.

However, while the ϵ_{\max} values at room temperature and f_{os} values at 77 K are 2–3 times larger for the ICT bands, the μ_{12} values of these bands are only ca. 40% larger because of their higher energies when compared with the MLCT bands. Within the organic polyene series **1–4**, μ_{12} is largest for $n = 3$, while μ_{12} maximizes at $n = 2$ within each of the three complex series **8–11**, **14–17**, and **20–23**. Within a given polyene series, $\Delta\mu_{12}$ increases substantially as the conjugation path length is extended, in keeping with normal expectations for dipolar molecules.¹ The $\Delta\mu_{12}$ values for the ICT bands of the organics are of similar magnitude or a little smaller than those of the MLCT bands of the analogous complex chromophores, while the ILCT transitions have $\Delta\mu_{12}$ values that are only about half as large as those for the MLCT absorptions. In contrast, the ICT bands have $\Delta\mu_{ab}$ values that are generally larger than those of either the MLCT or ILCT transitions.

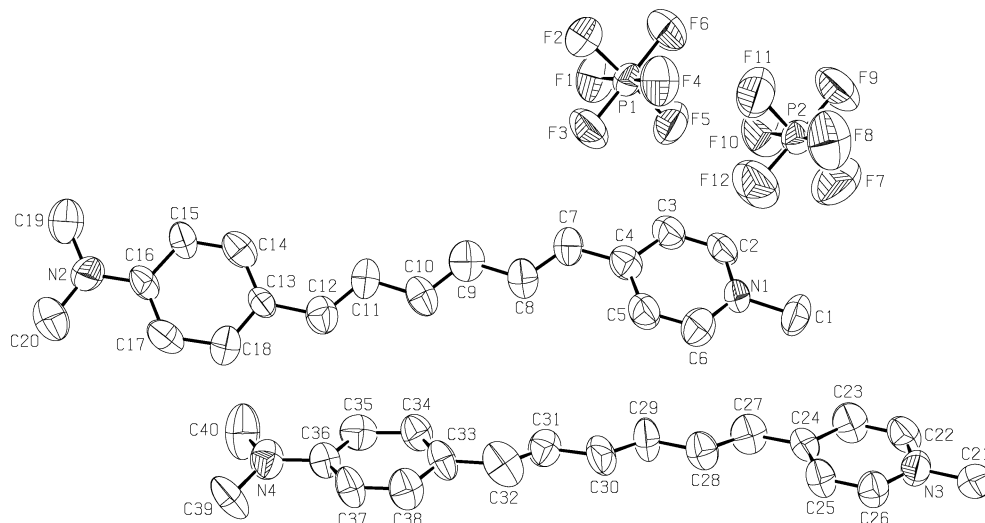


Figure 6. Representation of the molecular structure of the salt **4**.

If it is assumed that one electronic charge is transferred in the various transitions, then the dipole moment changes can be used to calculate delocalized ($r_{12} = \Delta\mu_{12}/e$) and effective (localized, $r_{ab} = \Delta\mu_{ab}/e$) electron-transfer distances. The values of r_{12} for the complexes lie in the range ca. 2.5–6.0 Å and are larger than those of their organic counterparts. In contrast, the r_{ab} values of the organics (ca. 2.0–7.0 Å) are generally larger than those of the related complexes. As expected, the values of both r_{12} and r_{ab} for each of the polyene series increase with n . The calculated electron-transfer distances of 5.0 Å (r_{12}) and 7.0 Å (r_{ab}) for the cation in **4** are much smaller than the N–N distance obtained from the X-ray crystal structure (see later) of 15.5 Å and correspond approximately with the length of the hexa-1,3,5-trienyl bridge. Also as expected, the values of r_{12} and r_{ab} for the ILCT transitions in the complexes are ca. 40–70% smaller when compared with those of the corresponding MLCT processes.

The values of c_b^2 and H_{ab} for the ICT bands of the organics are in every case considerably larger than those for the MLCT bands of the complexes, indicating that for the ICT bands there is significant mixing between the donor and acceptor orbitals. These results are 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 ILCT bands of the complexes generally have larger c_b^2 and H_{ab} values than the ICT bands of the corresponding organics. Within the organic series **1–4**, β_0 increases steadily with n , as is normal for D–A polyene chromophores.¹ In contrast, within each of the three complex series **8–11**, **14–17**, and **20–23**, β_0 increases up to $n = 2$, but then begins to decrease if only the values derived from the MLCT data are considered. Even addition of the (smaller) β_0 values for the ILCT transitions of **8–11**, **14–17**, and **20–23** does not significantly alter the overall trend. It is hence clear that while continual extension of the polyene chain (at least up to $n = 3$) is a successful approach to enhancing the β_0 responses of purely organic pyridinium chromophores, similar benefits are not found in related Ru^{II} pyridyl compounds.

In a previous communication, we concluded that a {Ru^{II}–(NH₃)₅(pyridyl)}²⁺ center is a more effective π -electron donor (in terms of enhancing β_0) than a –C₆H₄–4–NMe₂ group, because the greater electron richness of the Ru^{II} center more than offsets the increased π -orbital overlap in related purely organic chro-

mophores.¹⁰ However, these studies involved only the $n = 0$ compounds **1**, **5**, **7**, **8**, and **12**, and the more extensive results analyzed here allow us to present a more complete comparison. Taken as a whole, the data in Table 2 confirm that pyridinium chromophores containing pyridyl-coordinated Ru^{II} ammine centers do in most cases have larger β_0 responses than closely related molecules with –C₆H₄–4–NMe₂ D groups. Although the estimated relative experimental error of $\pm 20\%$ on the β_0 values introduces a degree of uncertainty when making comparisons between a pair of compounds, the overall picture emerging from the collected data is clear. The greatest enhancements in β_0 are generally observed with *trans*-{Ru^{II}(NH₃)₄(mim)}²⁺ moieties (mim = *N*-methylimidazole; in salts **20–26**). However, the observation that unexpected blue-shifts and decreases in μ_{12} of the MLCT bands lead to decreasing β_0 values means that a –C₆H₄–4–NMe₂ group becomes the superior electron donor with the longest $n = 3$ polyene chain (Figure 3). Even the combined effects of the MLCT and ILCT transitions, which effectively correspond to co-directional transitions from two adjacent donor sites, in complex salts **11**, **17**, and **23** do not appear to compete with the very large β_0 response associated with the single ICT process in **4**. Nevertheless, such elongated Ru^{II} ammine pyridyl polyene complexes do have the added potential benefit over related organic systems of exhibiting redox-switchable NLO responses.⁸

Theoretical Studies. We have also carried out MO calculations on the chromophoric cations in the organic salts **1–4**, the results of which can be compared with those for the related complex cations in **8–11** and **14–17**.⁶ⁱ Molecular geometries were optimized at a planar C_s symmetry using the B3P86/LanL2DZ model chemistry; the reliability of this approach can be confirmed by comparison of the theoretical results with average bond distances from the X-ray crystal structure of salt **4** (see below). The calculated distances (Figure 4) are generally larger than those obtained from the crystallographic data. However, the mean absolute deviation is 0.032 Å, with a maximum deviation of 0.054 Å. The latter can be regarded as a reasonable result, given that solid-state geometries of salts are often very sensitive to the nature of the counterion and that the geometries of polar species are also affected by the polarity of the medium, an aspect which is not considered in gas-phase calculations.

Table 4. Crystallographic Data and Refinement Details for Salt 4

formula	C ₂₀ H ₂₃ F ₆ N ₂ P
M	436.37
crystal system	triclinic
space group	<i>P</i> 1
<i>a</i> /Å	10.5351(4)
<i>b</i> /Å	11.1979(5)
<i>c</i> /Å	19.6541(10)
α /deg	77.321(2)
β /deg	76.784(2)
γ /deg	68.538(3)
<i>U</i> /Å ³	2076.95(16)
<i>Z</i>	4
<i>T</i> /K	150(2)
μ /mm ⁻¹	0.193
reflections collected	13756
independent reflections (<i>R</i> _{int})	4216 (0.1497)
final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.1637, 0.4500
(all data)	0.1814, 0.4588

^a The structure was 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 $F_o > 4\sigma(F_o)$.

Excitation energies, transition dipole moments, and ground- and excited-state dipole moments were calculated by using the time-dependent density-functional theory (TD-DFT) approach. Although TD-DFT is known to yield a poor description of charge-transfer excitations,²⁶ it is the most accurate method that can be used on large molecules at an affordable computational cost. β_0 values have been calculated by the finite field (FF) method that involves a double numerical differentiation of the dipole moment with respect to the applied electric field. The results of these calculations are presented in Table 3, together with β_0 values derived by applying eq 6 to the TD-DFT results. The extent of agreement between the calculated and experimentally measured parameters (Table 2) is relatively good for the cations in salts **1–4**, showing the expected decrease of ICT energy and the increase of β_0 that was also predicted²⁷ for related dimethylamino stilbazolium homologues using the sum over states (SOS) approach. However, the calculated values of μ_{12} and $\Delta\mu_{12}$ are systematically high and low, respectively. In contrast, the overall agreement between theory and experiment is somewhat variable for the Ru^{II} complex chromophores.⁶ⁱ The calculated values of E_{\max} , μ_{12} , and $\Delta\mu_{12}$ are all systematically high, with the exception of $\Delta\mu_{12}$ for the $n = 3$ complexes, and μ_{12} increases with n (even for $n = 3$). Nevertheless, the unprecedented empirical trend of β_0 maximizing at $n = 2$ for the Ru^{II} complexes is predicted by the FF approach,⁶ⁱ but unsurprisingly not by applying eq 6 to the TD-DFT data. The FF-derived β_0 values do confirm the superiority of the Ru^{II} D units when compared with the $-C_6H_4-4-NMe_2$ group for $n = 0$. No clear trend emerges from the FF results for the $n = 1$ or 2 systems, but the increases in β_0 for the cation in **4** vs both of the corresponding $n = 3$ complexes are much larger than those observed in the Stark-derived data.

Concerning the electronic absorption spectra, the lowest energy bands in the organic salts **1–4** correspond with $\pi \rightarrow \pi^*$ ICT transitions from the HOMOs to the LUMOs. The spectra of the complexes in **8–11** and **14–17** show low energy bands due to $d \rightarrow \pi^*$ MLCTs from the HOMOs (mainly derived from the Ru^{II} *d* orbitals) to the LUMOs and high energy ILCT bands

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for Salt 4

C1–N1	1.481(13)	C21–N3	1.491(14)
C2–N1	1.305(13)	C22–N3	1.316(14)
C2–C3	1.339(15)	C22–C23	1.360(16)
C3–C4	1.383(14)	C23–C24	1.390(14)
C4–C5	1.394(15)	C24–C25	1.408(14)
C4–C7	1.428(14)	C24–C27	1.416(15)
C5–C6	1.341(16)	C25–C26	1.310(15)
C6–N1	1.351(14)	C26–N3	1.344(13)
C7–C8	1.342(14)	C27–C28	1.332(14)
C8–C9	1.409(15)	C28–C29	1.403(15)
C9–C10	1.367(15)	C29–C30	1.349(15)
C10–C11	1.408(15)	C30–C31	1.398(15)
C11–C12	1.357(14)	C31–C32	1.329(15)
C12–C13	1.462(14)	C32–C33	1.464(16)
C13–C18	1.360(13)	C33–C34	1.405(14)
C13–C14	1.382(14)	C33–C38	1.412(14)
C14–C15	1.364(15)	C34–C35	1.397(15)
C15–C16	1.396(14)	C35–C36	1.385(15)
C16–N2	1.364(14)	C36–C37	1.361(14)
C16–C17	1.388(14)	C36–N4	1.393(14)
C17–C18	1.449(14)	C37–C38	1.346(14)
C19–N2	1.378(14)	C39–N4	1.511(14)
C20–N2	1.449(14)	C40–N4	1.415(14)
N1–C2–C3	121.0(10)	N3–C22–C23	121.6(11)
C2–C3–C4	123.4(11)	C22–C23–C24	122.0(11)
C3–C4–C5	113.1(10)	C23–C24–C25	112.9(10)
C3–C4–C7	122.8(11)	C23–C24–C27	122.4(10)
C5–C4–C7	124.0(11)	C25–C24–C27	124.7(10)
C6–C5–C4	122.4(11)	C26–C25–C24	123.1(10)
C5–C6–N1	120.5(10)	C25–C26–N3	121.8(10)
C8–C7–C4	127.9(11)	C28–C27–C24	127.9(10)
C7–C8–C9	126.1(11)	C27–C28–C29	126.9(11)
C10–C9–C8	124.7(12)	C30–C29–C28	124.1(11)
C9–C10–C11	124.7(12)	C29–C30–C31	129.1(11)
C12–C11–C10	122.7(11)	C32–C31–C30	123.7(12)
C11–C12–C13	128.2(10)	C31–C32–C33	128.6(11)
C18–C13–C14	117.2(9)	C34–C33–C38	115.6(10)
C18–C13–C12	117.7(10)	C34–C33–C32	125.8(10)
C14–C13–C12	125.0(9)	C38–C33–C32	118.6(10)
C15–C14–C13	122.3(10)	C35–C34–C33	121.0(10)
C14–C15–C16	122.6(11)	C36–C35–C34	120.8(11)
N2–C16–C17	120.4(10)	C37–C36–C35	118.0(10)
N2–C16–C15	123.3(11)	C37–C36–N4	122.6(10)
C17–C16–C15	116.3(10)	C35–C36–N4	119.4(10)
C16–C17–C18	120.0(10)	C38–C37–C36	122.5(10)
C13–C18–C17	121.5(10)	C37–C38–C33	122.1(10)
C2–N1–C6	119.4(9)	C22–N3–C26	118.5(10)
C2–N1–C1	122.5(10)	C22–N3–C21	120.7(10)
C6–N1–C1	118.0(10)	C26–N3–C21	120.8(11)
C16–N2–C19	120.8(10)	C36–N4–C40	120.3(10)
C16–N2–C20	118.9(10)	C36–N4–C39	120.7(10)
C19–N2–C20	120.1(10)	C40–N4–C39	117.8(10)

due to transitions from the highest occupied π orbitals to the LUMOs. The topologies of the orbitals involved in these transitions for **1–4** and **8–11** are shown in Figure 5. The excitation energies of the $\pi \rightarrow \pi^*$ transitions (ICT in **1–4** and ILCT in **8–11** and **14–17**) are predicted rather accurately by the TD-DFT calculations and show the expected bathochromic shifts on extending the conjugation path lengths. In contrast, the prediction of the MLCT excitations is not accurate, and the calculated energies are 0.15–0.52 eV above the experimental values determined in acetonitrile solution at 298 K (Table 1) or 0.31–0.78 eV above the experimental results in butyronitrile glasses at 77 K (Table 2). Because of D–A interactions between the solvent and the hydrogens of the NH₃ ligands, which can affect the charge on the Ru^{II} centers, the MLCT bands are more sensitive to the medium than are the $\pi \rightarrow \pi^*$ absorptions (see above). Thus, the differences between the calculated and

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experimental MLCT excitation energies can be primarily attributed to large positive solvatochromic shifts.

The changes in excitation energies on lengthening the polyenic spacers can be rationalized on the basis of interorbital gaps: the HOMO–LUMO gap decreases by 0.92 eV on passing from **1** to **4**, and the (HOMO–3)–LUMO gap decreases by 1.88 eV on moving from **8** to **11**, thus supporting the expected bathochromic shifts observed for these transitions. In contrast, the variation in the HOMO–LUMO gap in **8**–**11** is only 0.08 eV, and the increased correlation (i.e., configuration interaction) on lengthening the spacer overcomes this small decrease and gives rise to an overall slight hypsochromic shift in the MLCT bands.⁶¹ It is also noteworthy that the HOMOs of **8** and **14** are essentially ruthenium d orbitals, but the HOMOs of the higher homologues have a degree of π -character that increases with n . Also, while the LUMOs for the metal complexes have significant electron density on most of the atoms of the acceptor ligand, as n increases, the electron density on the carbons bridging the two aromatic rings begins to dominate. This phenomenon, along with the increased excitation energies, is responsible for the lower $\Delta\mu_{12}$ and β_0 values of **11** and **17** when compared with those of **10** and **16**, respectively. The high $\Delta\mu_{12}$ and μ_{12} values calculated for $n < 3$ suggest that the actual HOMOs and/or LUMOs are less delocalized than those calculated.

Crystallographic Study. We have previously reported that salt **6** and its $n = 2$ counterpart crystallize in the noncentrosymmetric space group Cc and show large powder SHG efficiencies that are similar to that of DAST.^{9a,c} The new salt **4** has now also been crystallographically characterized; a representation of the molecular structure is shown in Figure 6, and selected interatomic distances and angles are presented in Table 5. The two independent cations in the unit cell show somewhat different degrees of planarity, with torsion angles between the pyridyl and phenyl rings of 22.94(4) and 5.38(6)°. Unfortunately, this compound crystallizes centrosymmetrically in the triclinic space group $P\bar{1}$ and thus is not expected to show any bulk quadratic NLO effects. However, given the especially large β_0 values of the cation in **4**, determined via both Stark spectroscopy and FF calculations (694 and 609×10^{-30} esu, respectively), this chromophore is a promising candidate for pronounced bulk NLO effects if incorporated into suitable noncentrosymmetric structures. Indeed, the corresponding tosylate salt has already been found to display a moderate SHG efficiency of 6 times a urea reference when using a 1907-nm laser, although crystallographic data for that compound are unavailable.^{2b,c} Related salts of

several other benzenesulfonate anions have also been reported to show SHG activity, but actual magnitudes were not given.¹⁴

Conclusion

Stark spectroscopic studies on purely organic salts containing chromophores with $-C_6H_4-4-NMe_2$ D and pyridinium A groups reveal that extension of polyene chain bridges leads to red-shifting of the ICT absorption bands and increasing $\Delta\mu_{12}$ and β_0 . In contrast, related species containing pyridyl-coordinated $\{Ru^{II}(NH_3)_5\}^{2+}$ or *trans*- $\{Ru^{II}(NH_3)_4L\}^{2+}$ (L = mim or pyridine) centers as π -electron donors display highly unusual optical behavior in that their MLCT absorptions blue-shift as the number of *trans*-ethylene units n increases, with β_0 effectively maximizing at $n = 2$. TD-DFT and FF calculations corroborate the experimentally observed trends for both types of compound, although the calculated parameters for the Ru^{II} complexes differ from those obtained experimentally. The contrasting dependencies of the optical properties on polyene chain length for the two classes of compound studied can be attributed to the degree of D–A electronic coupling. Electrochemical, 1H NMR and Stark spectroscopic data all show that π -orbital overlap is more effective in the purely organic compounds than in their Ru^{II} counterparts. Hence, communication between the two ends of the molecules is sufficiently strong in the organics that β_0 and μ_{12} continually increase at least up to $n = 3$. Furthermore, H_{ab} remains constant on moving from $n = 2$ to 3. However, the less effective D–A communication in the Ru^{II} complexes becomes increasingly evident over long polyene bridges, so that β_0 , μ_{12} , and H_{ab} decrease above $n = 2$. It is clear that the Ru^{II} pyridyl ammine centers are generally more effective than a $-C_6H_4-4-NMe_2$ group as π -electron donors, in terms of enhancing β_0 . However, in the cases where $n = 3$, even the NLO effects associated with combined MLCT and ILCT transitions cannot compete with the very large β_0 response associated with the single ICT process in the purely organic chromophore.

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