Theoretical Studies on Two-Dimensional Nonlinear Optical Chromophores with Pyrazinyl Cores and Organic or Ruthenium(II) Ammine Electron Donors

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ABSTRACT: Density functional theory calculations have been carried out on twelve cationic, 2D nonlinear optical chromophores with pyrazinyl-bis(pyridinium) electron acceptors. These species contain either 4-(methoxy/dimethylamino)phenyl or pyridyl-coordinated $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}/\text{trans-}\{\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{py})\}^{2+}$ (py = pyridine) electron donor groups. The results are compared with data obtained by using experimental techniques including hyper-Rayleigh scattering and Stark (electroabsorption) spectroscopy previously (Coe, B. J. et al. *Inorg. Chem.* **2010**, 49, 10718 and *J. Org. Chem.* **2010**, 75, 8550). The B3LYP/6-311G(d) level of theory models the visible absorption spectra in MeCN for the $-\text{NMe}_2$ derivatives relatively well, while CAM-B3LYP/6-311G(d) gives better results for the $-\text{OMe}$ -substituted species. These spectra are dominated by intramolecular charge-transfer (ICT) bands. Static first hyperpolarizabilities β_0 are computed also at the B3LYP/6-311G(d) level. The overall extent of prediction of trends in the ICT bands and β_0 responses is partial, with the main discrepancies relating to the progression from one to two electron donor groups. The experimental data show that this structural change red-shifts the ICT bands and increases β_0 significantly, but only the second trend is reproduced to some extent by the calculations. The UV-vis absorption spectra of the Ru complexes in MeCN are modeled relatively well with B3LYP and the LANL2DZ/6-311G(d) mixed basis set, including 100 excited states. However, again some degree of disagreement between theory and experiment is evident, even when using a larger basis set like def2-TZVP for Ru. In particular, substantial red-shifts are predicted on adding a third metal center, while the measured spectra show corresponding small blue-shifts. The experimental trend of the total β_0 value increasing on moving from one to two Ru centers is predicted in the gas-phase, but not in MeCN. For both classes of chromophore, the β_{xxx} tensor component dominates in the asymmetric species, while β_{xyy} is the largest component for their two-fold symmetric counterparts.

Keywords: pyrazine derivatives, ruthenium complexes, two-dimensional chromophores, nonlinear optics, density functional theory

1. Introduction

A broad range of photonic technologies is set to benefit from studies of organic nonlinear optical (NLO) chromophores and materials.¹⁻⁴ This area has been subjected to extensive research, with theoretical calculations forming an increasingly sophisticated and important companion to experimental investigations. The first molecular compound to become commercially viable is the salt (*E*)-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST), especially useful for terahertz (THz) wave generation due to nonlinear frequency mixing of two laser beams.⁵⁻¹² The uses of THz radiation include security scanning, biomedical analysis and space communications.¹³⁻¹⁵ An ability to form high-quality single crystals (or other materials) displaying polar ordering of the active constituent molecules is critical to this and other related NLO effects like second harmonic generation (SHG) and linear electrooptic behavior. Besides purely organic compounds like DAST, transition metal complexes have received significant attention because they allow NLO behavior to be combined easily with redox, magnetic and other properties.¹⁶⁻³³ Various studies involving the use of metal-based redox to switch reversibly NLO effects demonstrate well the added value of such compounds.³⁴⁻⁴⁴

Molecular NLO properties stem from hyperpolarizabilities, which relate to the response of electronic charges to the oscillating applied electric field of a laser beam. Quadratic (second-order) effects are due to the first hyperpolarizability β , large values of which require noncentrosymmetric, π -conjugated molecules with electron donor and acceptor substituents. The β response is a third-rank tensor with multiple components, but the most heavily studied chromophores such as the DAS⁺ cation show a largely 1D response dominated by the β_{zzz} component, where the *z* direction is the long molecular axis. In addition to simple 1D dipoles, multidimensional species like 2D dipoles⁴⁵⁻⁶⁵ and 2D or 3D octupoles⁶⁶⁻⁸⁹ are of major interest. Such chromophores can offer significant advantages over 1D species, including larger NLO responses without the typical but undesirable accompanying decreased visible transparency. In V-shaped molecules, having more than one significant β component can prevent reabsorption of SHG polarized perpendicular to the

direction of the $\pi \rightarrow \pi^*$ intramolecular charge-transfer (ICT) transition dipole-moment μ_{12} . Also, phase-matching between the fundamental and harmonic waves may be facilitated with such C_{2v} symmetric species.⁴⁵

We have studied previously *N*-arylpyridinium chromophores,^{90–95} which show substantially increased static (nonresonant) first hyperpolarizabilities β_0 when compared with more traditional *N*-alkylpyridinium cations like DAS⁺. Also, we have investigated various 1D and 2D Ru^{II} ammine complexes of pyridinium-substituted ligands that show very large and redox-switchable β_0 responses.^{24,32} Some of our most recent work has involved 2D chromophores featuring 2,6-pyrazinyl cores connected to either two organic or two Ru^{II} ammine electron donors.^{96,97} In the present article, we describe theoretical studies on these unusual molecules, with the aim of rationalizing their electronic structures and optical properties.

2. Experimental Section

The molecular structures of the pyrazinyl chromophores **1–12** are shown in Figure 1. Structure optimizations^{98–100} and time-dependent density functional theory (TD-DFT) calculations were conducted by using the Gaussian 09 suite of programs.¹⁰¹ All structures were optimized in the gas phase by using the B3LYP exchange-correlation functional, noting that recent studies on Ru^{II} ammine complexes show that optimizing in a solvent medium prior to carrying out TD-DFT calculations affects the resulting excitation properties only slightly.¹⁰² The optimizations used the 6-311G(d) basis set for the purely organic chromophores **1–6**. A mixed basis set was adopted for the complexes **7–12**, with 6-311G(d) applied to all atoms except Ru, for which LANL2DZ was used. Regarding the molecular orientation, Gaussian 09 assigns the axes automatically. For the symmetric molecules **2, 3, 5, 6, 8, 9, 11** and **12**, the dipolar (pseudo- C_2 , passing through the two N atoms of the pyrazinyl ring, vector N–N_{pyz}) axis is taken as y , with the molecules lying in the xy plane (Figure 1). For the asymmetric species **1, 4, 7** and **10**, the coordinate system is similar, but the y axis is slightly tilted with respect to N–N_{pyz}.

For the purely organic species **1–6**, the first 50 electronic excited states were calculated by using B3LYP with the 6-311G(d) basis set. The other functionals M06, ω B97X and CAM-B3LYP were also used for selected chromophores, with the aim of optimizing correlations between experiment and theory. Switching the basis set between 6-311G(d) and 6-311G affects the results only slightly, while the choice of functional is critical. For the Ru complexes **7–12**, the first 100 excited states were calculated by using B3LYP and 6-311G(d)/LANL2DZ. In studies aimed at establishing the most useful method, the CAM-B3LYP functional was tried, as well as other basis sets, such as def2-TZVP on the Ru and def2-SV(P) on all other atoms in complex **7**. However, the resulting simulated UV–vis absorption spectra are very similar to that obtained by using LANL2DZ, so in the interest of economy the latter was chosen for most of the calculations. A conductor-like polarizable continuum model (CPCM)^{103,104} was used to account for the solvent acetonitrile (MeCN) in the TD-DFT calculations for all chromophores. Wavelength ranges of ca. 200–800 nm are

covered, and the UV–vis spectra simulated by using the GaussSum program.¹⁰⁵ To give the best matches with the experimental profiles, curves having a FWHM value of 3000 cm^{-1} were used for **1–6**, but a larger value of 5000 cm^{-1} was used for **7–12**. It should be noted that the adiabatic approximation used in TD-DFT cannot take into account double (or higher) excitations, which may be significant in highly conjugated, ICT chromophores.¹⁰⁶

First hyperpolarizabilities were calculated by using the B3LYP functional, as the analytical second derivatives of the dipole moment with respect to an external electric field. The polar calculation outputs the data in atomic units (au); these are converted into electrostatic units (esu) by multiplying by 8.6393×10^{-33} . Most calculations involved the static (zero-frequency or nonresonant) hyperpolarizabilities β_0 , but some dynamic (frequency-dependent) values were calculated also, to provide further comparisons with experimental data. For the purely organic species **1–6**, the 6-311G(d) basis set was used and β values were calculated in MeCN and in the gas phase. For the Ru complexes **7–12**, the calculations used the 6-311G(d)/LANL2DZ mixed basis set, also with and without solvent. Most of these calculations for the complexes were run also by using def2-TZVP on all atoms.

3. Results and Discussion

Figure 1. Chemical structures of the twelve pyrazinyl chromophores studied, showing the axis convention used in the calculations (approximate for **1**, **4**, **7** and **10**).

3.1. Structural Optimizations. Comparisons with geometric parameters obtained via X-ray crystallography on the purely organic compounds (see Figure 2 for selected bond distances) show reasonable agreement between theory and experiment. These representative examples show a maximum difference for the distances of ca. 0.04 Å (for the C–C bond between the phenylene and adjacent pyridyl rings in **1** and for the ethenylene C–C bond in **6**), but most of the differences are considerably smaller, and often ca. 0.01 Å or less.

The chromophores in the salts **[1]**[NO₃]₂•2.5H₂O and **[6]**[PF₆]₂•MeCN adopt twisted conformations, although the stilbazole units in the latter are almost planar.⁹⁷ The dihedral and torsion angles show a fair extent of agreement between theory and the structures observed crystallographically (Table 1), despite the calculations involving the isolated dications only.

TABLE 1: Twist Angles (deg) Determined via X-ray crystallography for the Salts [1][NO₃]₂•2.5H₂O and [6][PF₆]₂•MeCN, together with B3LYP/6-311G(d)-Calculated Data for the Optimized Chromophores 1 and 6

chromophore	pyr/pyz ^a	pyr/Ph ^a	pyr/pyr ^a	ethenylene/pyr ^b	ethenylene/Ph ^b	intra-pyz ^c
1 (X-ray)	28.6, ^d 34.2	11.3	18.3	–	–	3.0
1 (DFT)	24.2, ^d 42.9	5.1	30.7	–	–	1.5
6 (X-ray)	32.4	5.7	–	3.5	1.8	0.4
6 (DFT)	30.3	2.16	–	1.8	0.4	1.2

^a Dihedral angle between the planes of the adjacent aryl rings (pyr = pyridyl; pyz = pyrazinyl). ^b Torsion angle between the ethenylene unit and the attached pyr or Ph ring. ^c Dihedral angle between the two C–N–C subunits of the pyz ring. ^d For the 4-(dimethylamino)phenyl-substituted pyr ring.

3.2. Electronic Absorption Spectra. Initial studies with chromophore **1** showed that including a MeCN solvent CPCM improves the correlation between the simulated and experimental absorption spectra. Notably, gas-phase calculations yield a spectrum that differs quite markedly from that observed, with two separate low energy band maxima (see the Supporting Information, Figure S1). Therefore, a CPCM was employed in all further TD-DFT calculations. It is worth noting here that none of the chromophores **1–6** shows two low energy absorption maxima, even when studied in butyronitrile (PrCN) at 77 K for Stark spectroscopy. However, these frozen-solution spectra for **2**, **3**, **5** and **6** do show clear shoulders to high energy, and therefore were fitted by using three Gaussian components.⁹⁷

Purely Organic Species. Various different functionals, including B3LYP, B3P86, M06, ω B97X and PBE1PBE, were tried for selected dications, in order to determine the most appropriate method for calculating electronic excitations. B3LYP and B3P86 give similar results, and the simulated absorption spectra derived from using either of these two functionals correlate reasonably well with those measured experimentally for both the –NMe₂ and –OMe series of chromophores. The data obtained with B3LYP are collected in Table 2, and representative spectra for **1** and **6** are shown in Figure 3. Additional data are included in the Supporting Information; the predicted spectra for the other four chromophores (Figure S2), and the separate directional components of the transition dipole moments and dipole-

moment changes (Tables S1 and S2). For all of the dications **1–6**, using the M06/6-311G level of theory (Supporting Information, Figure S3) leads to blue-shifts of the E_{max} values by ca. 0.03–0.08 eV when compared to the results obtained with B3LYP/6-311G(d), while using ω B97X/6-311G (Supporting Information, Figure S4) gives much larger relative blue-shifts of ca. 0.4–0.6 eV. The CAM-B3LYP functional was also tried and gives improved results for the –OMe species (Supporting Information, Table S3 and Figure S5), but not for the –NMe₂ derivatives.

In each case, the calculations result in spectra with one main band in the visible region. At the B3LYP/6-311G(d) level, the calculated λ_{max} values are slightly blue-shifted when compared with experiments for the –NMe₂ derivatives, whereas red-shifts are predicted for the –OMe chromophores (Figures 3 and S2). Overall, the extent of agreement in λ_{max} values between theory and experiment is best for the –NMe₂ species.

TABLE 2: Results of B3LYP/6-311G(d) Calculations^a on the Chromophores 1–6, together with Data Obtained from UV–Vis Spectroscopic Measurements on the Salts [1–6][PF₆]₂

dication	$\lambda_{\text{exp}}, \text{nm}^b$ ($\epsilon, 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{max}^c (nm)	λ_{calc} (nm)	E_{calc} (eV)	f_{os}	μ_{12} (D)	$\Delta\mu_{12}$ (D)	main transitions (weight) ^d
1	493 (53.7)	484	484	2.56	1.34	11.77	9.80	H $\rightarrow$ L+1 (99%)
			391	3.17	0.16	3.64		H $\rightarrow$ L+2 (98%)
			316	3.92	0.50	5.80		H–4 $\rightarrow$ L (75%); H $\rightarrow$ L+5 (11%)
			312	3.97	0.11	2.67		H–4 $\rightarrow$ L (12%); H $\rightarrow$ L+4 (42%); H $\rightarrow$ L+5 (26%)
			292	4.25	0.14	2.95		H–6 $\rightarrow$ L (28%); H–6 $\rightarrow$ L+1 (11%); H–5 $\rightarrow$ L (51%)
2	515 (82.1)	484	515	2.40	0.59	8.01	2.86	H $\rightarrow$ L (94%)
			483	2.56	1.41	12.05	1.99	H–1 $\rightarrow$ L+1 (94%)
			455	2.72	0.56	7.37	3.66	H–1 $\rightarrow$ L (41%); H $\rightarrow$ L+1 (59%)
			373	3.32	0.19	3.84		H $\rightarrow$ L+2 (98%)
			224	5.53	0.16	2.78		H–3 $\rightarrow$ L+3 (45%); H–2 $\rightarrow$ L+4 (38%)
3	592 (82.9)	555	589	2.10	0.78	9.91	0.80	H $\rightarrow$ L (92%)
			554	2.24	2.32	16.55	2.08	H–1 $\rightarrow$ L+1 (92%)
			511	2.42	0.58	7.93	2.15	H–1 $\rightarrow$ L (47%); H $\rightarrow$ L+1 (55%)
			405	3.06	0.18	3.97		H $\rightarrow$ L+2 (98%)
			350	3.54	0.11	2.87		H–2 $\rightarrow$ L (44%); H–1 $\rightarrow$ L+3 (47%)
4	378 (36.2)	421	421	2.95	1.14	10.06	14.44	H $\rightarrow$ L+1 (99%)
			312	3.97	0.59	6.25		H–5 $\rightarrow$ L (13%); H–4 $\rightarrow$ L (77%)
			307	4.03	0.18	3.40		H–5 $\rightarrow$ L (59%); H–4 $\rightarrow$ L (19%)
5	393 (57.1)	424	438	2.83	1.07	9.99	–1.28	H $\rightarrow$ L (98%)
			414	2.99	0.68	7.75	–1.92	H–1 $\rightarrow$ L+1 (99%)
			404	3.07	0.42	6.04	–1.89	H–1 $\rightarrow$ L (39%); H $\rightarrow$ L+1 (61%)
			324	3.82	0.12	2.82		H $\rightarrow$ L+2 (98%)
			281	4.40	0.18	3.25		H–4 $\rightarrow$ L (88%)

6	450 (63.1)	497	515	2.41	1.45	12.63	0.51	H → L (99%)
			487	2.55	1.43	12.15	−0.48	H−1 → L+1 (100%)
			462	2.68	0.47	6.78	−0.59	H−1 → L (47%); H → L+1 (53%)
			360	3.43	0.13	3.20		H → L+2 (98%)
			318	3.89	0.11	2.69		H−4 → L (57%); H−1 → L+3 (25%)

^a Only transitions with $f_{\text{os}} > 0.10$ are included. ^b λ_{max} value for band in visible region measured with [1–6][PF₆]₂ in MeCN.⁹⁷ ^c λ_{max} value derived from the simulated absorption spectrum. ^d H = HOMO, L = LUMO.

Figure 3. B3LYP/6-311G(d)-calculated (blue) and experimental (green) UV-vis spectra of (a) **1** and (b) **6**. The ϵ -axes refer to the experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorptions. The oscillator strength axes refer to the individual calculated transitions (red).

Figure 4. B3LYP/6-311G(d)-derived contour surface diagrams of the MOs involved in the dominant low energy electronic transitions for cations (a) **2** and (b) **5** (isosurface value 0.03 au).

The orbitals involved in the main visible transitions for cations **2** and **5** are shown in Figure 4, while all other orbitals involved in the transitions listed in Table 2 are shown in the Supporting Information (Figure S6). As expected, the low energy electronic excitations have substantial ICT character. The HOMOs are located primarily on the 4-

(dimethylamino/methoxy)phenyl units, while the LUMOs are based more on the pyrazinyl core and attached pyridinium groups.

Experimentally, adding a second electron donor group (i.e. **1** $\rightarrow$ **2** or **4** $\rightarrow$ **5**) decreases $E_{\max}$ by ca. 0.1 eV and increases molar extinction coefficients ϵ by over 50%.⁹⁷ The latter change is clearly attributable to enhanced π -orbital overlap when two donors are present. These increases in absorption intensities are reproduced theoretically for both series of chromophores, but a (slight) decrease in $E_{\max}$ is predicted for the –OMe series only. In contrast, the observed large decreases in $E_{\max}$ (ca. 0.3–0.4 eV) on extending the conjugation are modeled accurately for both series, while theory predicts also substantial accompanying intensity increases that are not actually observed (Table 2).

For the symmetric chromophores **2**, **3**, **5** and **6**, the two lowest energy transitions have the largest μ_{12} values, with dominant components μ^x_{12} (Table S1), signifying polarization along the x axis. The next lowest energy transition, which also contributes to the main ILCT band, is dominated by μ^y_{12} , and therefore polarized along the y axis. The dipole moments μ of the ground and excited states of these V-shaped molecules are directed along the y axis. For the asymmetric species **1** and **4**, the situation is different; the single lowest energy transition within the main ILCT band still has a dominant μ^x_{12} , but also a substantial μ^y_{12} component, and the dipole moments are directed primarily along the x axis.

The predicted total dipole-moment changes $\Delta\mu_{12}$ for the low-energy transitions do not agree well with those measured via Stark spectroscopy in PrCN at 77 K.⁹⁷ The latter show relatively small variations within a range of ca. 11–18 D, while theory indicates that the asymmetric species **1** and **4** have values significantly larger than the other chromophores. These discrepancies between theory and experiment are probably attributable at least in part to the different environments of the chromophores; the calculations treat only the cations in the gas phase (ground states) or MeCN (excited states), while the measurements involve a PrCN frozen glass medium that includes the PF_6^- counter-anions. As expected based on the molecular structures, the calculated dipole-moment changes are dominated by their y components for the symmetric species, but the x components dominate for their asymmetric

counterparts (Table S2). The larger $\Delta\mu_{12}$ values predicted for **1** and **4** are attributable primarily to especially large values of μ_x for the excited states.

The TD-DFT calculations confirm the experimental observations that the ICT bands of the $-\text{NMe}_2$ derivatives are red-shifted and more intense when compared to those of their $-\text{OMe}$ analogues. However, the calculated decreases in E_{max} (ca. 0.2–0.4 eV) on replacing $-\text{OMe}$ with $-\text{NMe}_2$ are somewhat smaller than those measured (ca. 0.7–0.8 eV). These two trends are due to the stronger electron-donor ability and enhanced π -orbital overlap of the $-\text{NMe}_2$ group. Therefore, the amine derivatives have smaller HOMO–LUMO energy gaps (HLGs, Table 3). Also consistent with experimental data, the HLG decreases on extending the π -conjugation (i.e. **2** $\rightarrow$ **3** or **5** $\rightarrow$ **6**).

Cyclic voltammetric measurements on the salts $[\mathbf{1-6}][\text{PF}_6]_2$ in MeCN show irreversible behavior,⁹⁷ but the potentials observed for the net reductive processes are largely consistent with the LUMO energies predicted by TD-DFT (Table 3). Thus, within each series, the LUMO is destabilized when a 4,4'-bipyridyl (4,4'-bpy) unit is replaced by an electron-donor-substituted fragment, but then a small relative stabilization occurs on extending the π -conjugation. Small relative stabilizations of the LUMOs on replacing $-\text{NMe}_2$ with $-\text{OMe}$ are also predicted, matching the experimental observations for the symmetric species, although the 4,4'-bpy derivatives show identical first reduction potentials.

TABLE 3: B3LYP/6-311G(d)-Calculated Frontier Orbital Energies, HOMO–LUMO Energy Gaps and Energy Maxima from the Simulated UV–Vis Spectra for the Chromophores 1–6, together with Data obtained from Cyclic Voltammetric Measurements on the Salts $[\mathbf{1-6}][\text{PF}_6]_2$

dication	1	2	3	4	5	6
HOMO energy (eV)	–6.09	–6.01	–5.74	–6.77	–6.72	–6.28
LUMO energy (eV)	–3.70	–3.31	–3.40	–3.78	–3.53	–3.61
HLG (eV)	2.39	2.70	2.34	2.99	3.19	2.67
E_{max} (eV)	2.56	2.56	2.23	2.95	2.92	2.49
E_{pc}^a (V)	–0.32	–0.60	–0.52	–0.32	–0.51	–0.43

^a Reduction potential vs. Ag–AgCl reference electrode for the first cathodic wave measured in MeCN solutions ca. 10^{-3} M in $[\mathbf{1-6}][\text{PF}_6]_2$ and 0.1 M in $[\text{N}(\text{C}_4\text{H}_9\text{-}n)_4]\text{PF}_6$ at a 2 mm disk glassy carbon working electrode with a scan rate of 200 mV s^{–1} (ferrocene internal reference $E_{1/2} = 0.44$ V).⁹⁷

Ruthenium Complexes. As for **1–6**, including a CPCM gives better correlation with the experimental absorption spectra; for **10**, the maximal energy of the visible band is significantly overestimated in the gas phase at the B3LYP/LANL2DZ/6-311G(d) level of theory (see the Supporting Information, Figure S7). Interestingly, using the CAM-B3LYP long-range corrected functional greatly overestimates the energy for the lowest energy band of complex **7**. Other recent studies with Ru^{II} ammine complexes have shown similarly poor performance by this functional.¹⁰⁷ Using B3LYP with the def2-TZVP basis set on the Ru and def2-SV(P) on all other atoms gives a spectrum closely resembling that obtained with LANL2DZ for **7** (see the Supporting Information, Figure S8).

Initially, the TD-DFT computations were run with 50 excited states, as for **1–6**. For the monometallic complexes **7** and **10**, the simulated spectra thus derived match well with those measured. However, for the bimetallic systems **8** and **11**, these calculations failed to model any transitions in the UV region. Therefore, for the bi- and trimetallic complexes it was necessary to use an increased number of excited states (100) in order to include high-energy transitions. This approach is computationally expensive, but worthwhile because all of the complexes show bands just below 300 nm that are even more intense than their visible absorptions. The data obtained including the first 100 excited states for all the complexes are collected in Table 4, and representative spectra for **9** and **10** are shown in Figure 5. The spectra for the other four complexes are shown in Figure S9 (Supporting Information), and the components of the transition dipole moments and dipole-moment changes are in Tables S4 and S5.

TABLE 4: Results of B3LYP/LANL2DZ/6-311G(d) Calculations^a on the Chromophores 7–12, together with Data Obtained from UV–Vis Spectroscopic Measurements on the Salts [7–12][PF₆]_n (n = 4, 6 or 8)

complex	λ_{exp} , nm ^b (ϵ , 10 ³ M ⁻¹ cm ⁻¹)	λ_{max} ^c (nm)	λ_{calc} (nm)	E_{calc} (eV)	f_{os}	μ_{12} (D)	$\Delta\mu_{12}$ (D)	main transitions (weight) ^d
7	707 (17.7)	677	692	1.79	0.12	4.12	40.40	H → L (93%)
	288 (32.6)	320	667	1.86	0.18	4.99	59.76	H → L+1 (92%)
			324	3.82	0.91	7.93		H-5 → L (69%); H → L+6 (18%)
			282	4.39	0.27	4.04		H-8 → L (47%); H-8 → L+1 (13%); H-7 → L (26%)
			276	4.49	0.22	3.58		H-8 → L (11%); H-8 → L+1 (49%); H-7 → L+1 (24%)
8	713 (30.3)	683	693	1.79	0.43	7.93	20.55	H → L (92%)
	285 (32.6)	291	658	1.88	0.14	4.35	53.40	H-1 → L+1 (89%)
			298	4.15	0.24	3.92		H-9 → L+1 (74%)
			292	4.23	0.14	2.97		H-8 → L (12%); H-6 → L (14%); H-6 → L+1 (71%)
			292	4.24	0.60	6.13		H-8 → L (59%); H-1 → L+8 (13%)
			280	4.42	0.16	3.07		H-8 → L+1 (81%)
			267	4.63	0.20	3.41		H-10 → L (15%); H-10 → L+1 (49%); H-9 → L+1 (10%)
9	711 (30.0)	720	751	1.65	0.25	6.30		H → L (98%)
	459 (10.3)	476	714	1.74	0.38	7.58		H-1 → L+1 (89%)
	287 (33.5)	309	705	1.76	0.20	5.52		H → L+1 (83%); H-1 → L (11%)
			476	2.60	0.17	4.18		H-7 → L+2 (97%)
			322	3.85	0.43	5.46		H-11 → L (16%); H-2 → L+14 (10%); H-1 → L+7 (15%); H → L+12 (11%)
			310	3.99	0.59	6.26		H-11 → L (75%); H → L+6 (15%)
			297	4.17	0.20	3.53		H-11 → L+1 (54%); H-1 → L+6 (23%); H → L+7 (19%)
10			286	4.33	0.29	4.18		H-12 → L+1 (92%)
	675 (17.6)	631	634	1.96	0.29	6.27	32.06	H-2 → L (41%); H-2 → L+1 (23%); H-1 → L (22%); H-1 → L+12 (11%)
	379 (7.3)	322	354	3.49	0.11	2.89		H-2 → L+3 (12%); H-2 → L+6 (11%); H-1 → L+3 (36%); H → L+12 (11%)
	288 (38.0)		324	3.82	0.90	7.86		H-6 → L (72%); H → L+12 (11%)

11	674 (31.1) 384 (12.4) 285 (33.6)	645 301	312	3.97	0.11	2.76	6.70	H-9 → L (15%); H-8 → L (35%); H-6 → L+1 (20%)
			282	4.39	0.35	4.56		H-9 → L (53%); H-9 → L+1 (11%); H-8 → L (24%)
			275	4.49	0.17	3.15		H-9 → L+1 (56%); H-8 → L+1 (23%)
			648	1.91	0.60	9.06		H-3 → L+1 (24%); H-2 → L (72%)
			362	3.42	0.14	3.30		H-3 → L+3 (73%)
			343	3.61	0.18	3.66		H-5 → L+6 (19%); H-4 → L+7 (21%); H-3 → L+3 (13%)
			325	3.81	0.11	2.75		H-1 → L+14 (19%); H → L+15 (22%)
			315	3.93	0.15	3.22		H-3 → L+9 (23%); H-2 → L+8 (44%)
			301	4.11	0.19	3.52		H-11 → L+1 (81%)
			296	4.19	0.86	7.36		H-10 → L (88%)
12	665 (32.2) 465 (17.2) 382 (16.4) 282 (42.4)	695 486 323	283	4.37	0.16	3.12		H-10 → L+1 (91%)
			715	1.73	0.39	7.75		H-7 → L (21%); H → L (66%)
			711	1.74	0.13	4.48		H-7 → L (61%); H → L (23%)
			702	1.76	0.15	4.70		H-1 → L (89%)
			675	1.84	0.17	4.94		H-3 → L+1 (14%); H-1 → L+1 (64%)
			673	1.84	0.12	4.19		H → L+1 (84%)
			469	2.64	0.19	4.39		H-8 → L+2 (88%)
			341	3.63	0.22	3.98		H-5 → L+7 (13%); H-4 → L+7 (14%); H-4 → L+8 (26%); H-2 -
			323	3.83	0.29	4.43		H-3 → L+18 (24%); H-2 → L+19 (28%)
			323	3.84	0.11	2.78		H-7 → L+6 (12%); H-3 → L+18 (25%); H-2 → L+19 (21%)
			317	3.91	0.43	5.40		H-14 → L (38%); H-8 → L+5 (36%)
			317	3.91	0.27	4.29		H-14 → L (38%); H-8 → L+5 (60%)

^a Only transitions with $f_{\text{os}} > 0.10$ are included. ^b λ_{max} value for bands measured with [7-12][PF₆]_n (n = 4, 6 or 8) in MeCN. ⁹⁶ ^c λ_{max} value derived from the simulated absorption spectrum. ^d H = HOMO, L = LUMO.

Figure 5. B3LYP/LANL2DZ/6-311G(d)-calculated (blue) and experimental (green) UV-vis spectra of (a) **9** and (b) **10**. The ϵ -axes refer to the experimental data only and the vertical axes of the calculated data are scaled to match the main experimental absorptions. The oscillator strength axes refer to the individual calculated transitions (red).

Figure 6. B3LYP/LANL2DZ/6-311G(d)-derived contour surface diagrams of the MOs involved in the dominant low energy electronic transitions for complexes (a) **7** and (b) **8** (isosurface value 0.03 au).

The orbitals involved in the main visible transitions for the $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complexes **7** and **8** are shown in Figure 6, while all other orbitals involved in the transitions listed in Table 4 are shown Figures 7 and 8 or in the Supporting Information (Figure S10). As expected, the low energy electronic excitations are of MLCT character. The donor orbitals

are located largely on the Ru atoms, while the acceptor orbitals are spread across the conjugated ligand framework, especially on the pyz and pyridinium rings. The more intense, higher energy transitions involve purely ligand-based orbitals, confirming their $\pi \rightarrow \pi^*$ character assigned previously.⁹⁶

Experimentally, relatively weak absorptions attributed to $\text{Ru}^{\text{II}} \rightarrow \text{py}$ (in **10–12**) and/or $\text{Ru}^{\text{II}} \rightarrow \text{pyz}$ MLCT excitations (in **9** and **12**) are observed between the two main bands.⁹⁶ Theoretically, $\text{Ru}^{\text{II}} \rightarrow \text{py}$ character is predicted to contribute to the transitions at 354 nm in **10**, 343 nm in **11**, and 341 and 323 nm (the latter involving the central Ru atom) in **12**. Depictions of the relevant orbitals involved for **10** and **11** are shown in Figure 7, while those for **12** are in the Supporting Information (Figure S10). The relatively low energy transitions at 476 nm in **9**, and 469 nm in **12** are predicted to have $\text{Ru}^{\text{II}} \rightarrow \text{pyz}$ character, with the donor orbital being mostly the $4d_{zy}$ on the central Ru atom, and the acceptor orbital located primarily on the pyz ring (Figure 8).

The main trend evident from the experimental spectra is that the E_{max} value of the dominant MLCT band increases by ca. 0.1 eV when axial NH_3 ligands are replaced with py.⁹⁶ This effect is observed also with 1D Ru^{II} ammine chromophores,^{108,109} and attributed mainly to relative stabilization of the HOMO by the π -accepting py, confirmed by measurements of $\text{Ru}^{\text{III/II}}$ reduction potentials via cyclic voltammetry (Table 5).^{96,108,109} The calculated HOMO and LUMO energies of the complexes **7–12** are also shown in Table 5. As expected, the HOMO energies are lower for the *trans*- $\{\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{py})\}^{2+}$ complexes than for their $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogues, while the LUMO energies are constant or vary only slightly as py replaces NH_3 . Therefore, the HLG increases by 0.13–0.19 eV, and E_{max} increases by ca. 0.1 eV, as observed experimentally.

Figure 7. B3LYP/LANL2DZ/6-311G(d)-derived contour surface diagrams of the MOs involved in the $\text{Ru}^{\text{II}} \rightarrow \text{py}$ MLCT transitions for complexes (a) **10** (354 nm) and (b) **11** (343 nm) (isosurface value 0.03 au).

Figure 8. B3LYP/LANL2DZ/6-311G(d)-derived contour surface diagrams of the MOs involved in the $\text{Ru}^{\text{II}} \rightarrow \text{pyz}$ MLCT transitions for complexes (a) **9** (476 nm) and (b) **12** (469 nm) (isosurface value 0.03 au).

On moving from one to two Ru centers (i.e. **7** $\rightarrow$ **8** or **10** $\rightarrow$ **11**), the sum of the f_{os}/μ_{12} values for the low energy MLCT band approximately doubles, paralleling the observed changes in ϵ (Table 4). Small accompanying increases in λ_{max} are predicted, agreeing with the experiments only for the $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complexes **7** and **8**. For the mono- and bimetallic complexes **7**, **8**, **10** and **11**, the one or two transitions that dominate the low energy MLCT bands are largely x -polarized (Table S4). In the trimetallic species, the two main lowest energy transitions are also x -polarized, while the next lowest energy transition is y -polarized.

As for the purely organic chromophores **1–6**, the predicted $\Delta\mu_{12}$ values for the low energy transitions are very different from those measured via Stark spectroscopy in frozen butyronitrile.⁹⁶ The latter are essentially identical for the PF_6^- salts of the pairs **7/8** (ca. 16 D)

and **10/11** (ca. 19 D). The calculated dipole-moment changes are dominated by their x components for the monometallic complexes **7** and **10** (Table S5), but the y component dominates for the bimetallic **11**. However, the situation is different for **8**, which although structurally similar to **11** shows dominant x components. These results can be rationalized by inspection of the MOs involved in the low energy transitions. For **11**, the transition at 1.91 eV involves HOMO-3 $\rightarrow$ LUMO+1 and HOMO-2 $\rightarrow$ LUMO (Table 4), and all of these MOs are distributed symmetrically across the complex (Figures 7b and S10). In contrast, for **8**, the transition at 1.79 eV has HOMO $\rightarrow$ LUMO character, while that at 1.88 eV is HOMO-1 $\rightarrow$ LUMO+1. The latter MOs are all distributed asymmetrically (Figure 6b), corresponding with transitions within the two sides of the molecule. Therefore, the x components dominate the accompanying dipole-moment changes, while the y components are nevertheless significant.

TABLE 5: B3LYP/LANL2DZ/6-311G(d)-Calculated Frontier Orbital Energies, HOMO-LUMO Energy Gaps and Energy Maxima from the Simulated UV-Vis spectra for the Chromophores 7–12, together with Data obtained from Cyclic Voltammetric Measurements on the Salts [7–12][PF₆]_n (n = 4, 6 or 8)

complex	7	8	9	10	11	12
HOMO energy (eV)	−6.01	−6.04	−6.20	−6.20	−6.26	−6.39
LUMO energy (eV)	−4.00	−4.03	−4.35	−4.00	−4.08	−4.41
HLG (eV)	2.01	2.01	1.85	2.2	2.18	1.98
E_{max} (eV)	1.83	1.82	1.72	1.97	1.92	1.78
$E_{1/2}[\text{Ru}^{\text{III/II}}]^a$ (V)	0.52	0.52	0.53	0.69	0.69	0.71
			1.00			1.11
$E_{1/2}[\text{ligand}]^a$ (V)	−0.26	−0.29	−0.32	−0.23	−0.24	−0.25

^a Reduction potential vs. Ag–AgCl reference electrode measured in MeCN solutions ca. 10^{-3} M in [7–12][PF₆]_n (n = 4, 6 or 8) and 0.1 M in [N(C₄H₉-n)₄]PF₆ at a 2 mm disk glassy carbon working electrode with a scan rate of 200 mV s^{−1} (ferrocene internal reference $E_{1/2} = 0.44$ V). The ligand-based processes are generally not properly reversible ($i_{\text{pc}} > i_{\text{pa}}$).⁹⁶

Adding a third Ru donor (i.e. **8** → **9** or **11** → **12**) leads to no significant change in the ϵ values, with small blue-shifts in the dominant MLCT band. In contrast, the calculations predict significant red-shifts accompanied by increases of ca. 50% or more in the sum of the f_{os}/μ_{12} values. Both the HOMOs and LUMOs are stabilized, the latter to a relatively larger extent, and the MLCT energy gaps decrease (see the Supporting Information, Figure S11). In addition to the spectroscopic studies, the predicted significant LUMO stabilizations are inconsistent with the electrochemical measurements, which show only slight changes in the potential for the first ligand-based reduction process (Table 5). Given their relatively complex structures, it is unsurprising that the modeling of the trimetallic species is of limited quantitative accuracy.

3.3. Quadratic Nonlinear Optical Properties. The B3LYP/6-311G(d) level of theory provides reasonable results from the TD-DFT calculations for the metal-free chromophores **1–6**, while B3LYP/LANL2DZ/6-311G(d) is best for the complexes **7–12** (see above). Therefore, these approaches were applied in first hyperpolarizability calculations also.

The calculated β_{tot} value is the overall magnitude of the first hyperpolarizability related to the individual tensor components according to¹¹⁰

$$\beta_{\text{tot}} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}} \quad (1)$$

and

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \quad (2)$$

Experimentally,^{96,97} the NLO activity of the PF_6^- salts of chromophores **1–12** was assessed by using the hyper-Rayleigh scattering (HRS) technique^{111–114} with MeCN solutions. HRS is a direct method for determining β responses, but is complicated by resonance effects which mean that a two-state approximation must be used to derive β_0 values. β_{HRS} values are calculated by using the following equations¹¹³

$$\langle \beta_{\text{HRS}}^2 \rangle = \langle \beta_{\text{ZZZ}}^2 \rangle + \langle \beta_{\text{YYY}}^2 \rangle \quad (3)$$

$$\begin{aligned} \langle \beta_{\text{ZZZ}}^2 \rangle = & \frac{1}{7} \beta_{xxx}^2 + \frac{1}{7} \beta_{yyy}^2 + \frac{1}{7} \beta_{zzz}^2 + \\ & \frac{6}{35} \beta_{xxx} \beta_{xyy} + \frac{6}{35} \beta_{xxx} \beta_{xzz} + \frac{6}{35} \beta_{yyy} \beta_{yzz} + \frac{6}{35} \beta_{yyy} \beta_{yxx} + \frac{6}{35} \beta_{zzz} \beta_{zxx} + \frac{6}{35} \beta_{zzz} \beta_{zyy} + \\ & \frac{9}{35} \beta_{xxy}^2 + \frac{9}{35} \beta_{xxz}^2 + \frac{9}{35} \beta_{yyx}^2 + \frac{9}{35} \beta_{yyz}^2 + \frac{9}{35} \beta_{zxx}^2 + \frac{9}{35} \beta_{zzy}^2 + \\ & \frac{6}{35} \beta_{xxy} \beta_{yzz} + \frac{6}{35} \beta_{yyz} \beta_{zxx} + \frac{6}{35} \beta_{zxx} \beta_{xyy} + \\ & \frac{12}{35} \beta_{xyz}^2 \end{aligned} \quad (4)$$

$$\begin{aligned}
\langle \beta_{YZZ}^2 \rangle = & \frac{1}{35} \beta_{xxx}^2 + \frac{1}{35} \beta_{yyy}^2 + \frac{1}{35} \beta_{zzz}^2 - \\
& \frac{2}{105} \beta_{xxx} \beta_{xyy} - \frac{2}{105} \beta_{xxx} \beta_{xzz} - \frac{2}{105} \beta_{yyy} \beta_{yzz} - \frac{2}{105} \beta_{yyy} \beta_{yxx} - \frac{2}{105} \beta_{zzz} \beta_{zxx} - \frac{2}{105} \beta_{zzz} \beta_{zyy} + \\
& \frac{11}{105} \beta_{xxy}^2 + \frac{11}{105} \beta_{xxz}^2 + \frac{11}{105} \beta_{yyx}^2 + \frac{11}{105} \beta_{yyz}^2 + \frac{11}{105} \beta_{zxx}^2 + \frac{11}{105} \beta_{zzy}^2 - \\
& \frac{2}{105} \beta_{xxy} \beta_{yzz} - \frac{2}{105} \beta_{yyz} \beta_{zxx} - \frac{2}{105} \beta_{zxx} \beta_{xyy} + \\
& \frac{8}{35} \beta_{xyz}^2
\end{aligned} \tag{5}$$

The upper case subscripts refer to macroscopic observables in laboratory coordinates, while the lower case refer to molecular coordinates. HRS depolarization ratios $\rho^{115-117}$ were calculated by using

$$\rho = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{YZZ}^2 \rangle} \tag{6}$$

Where necessary, appropriate substitutions were made for certain equivalent (or pseudo-equivalent) β tensor components in eqns. (4) and (5), e.g. $\beta_{xxy} = \beta_{yxx}$, $\beta_{xxz} = \beta_{zxx}$ and $\beta_{yyz} = \beta_{zyy}$, etc.

Stark spectroscopy¹¹⁸⁻¹²¹ has been applied also to all of the salts, except for those of the trimetallic complexes **9** and **12**. The latter method yields β_0 values indirectly by treating the ICT absorptions (deconvoluted into three Gaussian components for the symmetric, purely organic chromophores) within the framework of a two-state model.

Purely Organic Species. The static β values calculated for chromophores **1-6** in MeCN and in the gas phase are shown in Table 6, together with selected experimentally measured data.⁹⁷ The results of the two different types of measurement agree broadly, showing that (i) β_0 increases on moving along the series **1** $\rightarrow$ **2** $\rightarrow$ **3** and **4** $\rightarrow$ **5** $\rightarrow$ **6**, and (ii) the β_0 values of the $-NMe_2$ -substituted species are about two or more times larger than those of their $-OMe$ analogues. Both of these trends are consistent with intuition and analogies

with other known compounds. HRS ρ measurements confirm that the NLO responses of the symmetric chromophores are strongly two-dimensional, as expected because they have two electron donors connected to a central acceptor in a V-shape.⁹⁷ The observed substantial decrease in ρ on moving from the asymmetric chromophore **1** to the symmetric **2** and **3** is reproduced by the calculations.

Regardless of any quantitative agreement (see below), it is reasonable to expect that molecular structure-activity trends should be consistent between the experimental and predicted data. Inspection of the latter in Table 6 yields the following trends: (i) the β_{tot} and β_{HRS} values are always substantially larger in MeCN than in the gas phase; (ii) the $-\text{NMe}_2$ derivatives show consistently larger β_{tot} and β_{HRS} values than their $-\text{OMe}$ analogues; (iii) extending the π -conjugation increases β_{tot} and β_{HRS} . The latter two trends agree with the experimental data (see above), while the large solvent effect is unsurprising because the electronic transitions calculated via TD-DFT also show strong sensitivity to the medium. In contrast, the experimentally observed trend of the total β_0 value increasing significantly on adding a second electron donor group (i.e. **1** $\rightarrow$ **2** or **4** $\rightarrow$ **5**) is not well replicated by the theory. For β_{tot} , *decreases* are predicted for both pairs, in MeCN and in the gas phase. On the other hand, corresponding slight increases are predicted for the β_{HRS} values.

Given that y corresponds with the dipolar axis for the symmetric chromophores **2**, **3**, **5** and **6**, their two lowest energy, x -polarized transitions (see above and Table S1) are associated with the “off-diagonal” β_{xy} tensor component. The next lowest energy, lower intensity y -polarized transition is associated with β_{yy} . The predicted dominance of β_{xy} for these molecules (Table 6) is therefore consistent with the results of the TD-DFT calculations. Also, the electronic structures and TD-DFT results for the asymmetric species **1** and **4** agree with the expected dominance of β_{xx} .

Due to the use of different conventions to define β values, amongst other factors, direct, quantitative comparisons between calculated and measured values are often problematic.^{122–124} In our previous experimental studies,⁹⁷ we use the so-called perturbation series or B -convention,¹²² while Gaussian 09 uses the T -convention, giving values that should be twice those obtained when using the B -convention. The HRS β_0 values for **1–6** are in

every case markedly smaller than either the calculated β_{tot} or β_{HRS} in MeCN (Table 6), probably due in part at least to the relatively poor applicability of the two-state model to the low energy absorption bands of such V-shaped molecules. The measured HRS β_{800} values are corrected for resonance enhancement via eq. 7 (E_f is the energy of the laser fundamental),^{125,126} which is a fair approximation for dipolar chromophores in which β is associated mainly with a single ICT excitation.

$$\beta = \beta_0 \frac{E_{\text{max}}^2}{\left[1 - (2E_f)^2 (E_{\text{max}}^2)^{-1}\right] \left[(E_{\text{max}})^2 - E_f^2\right]} \quad (7)$$

in which

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{(E_{\text{max}})^2} \quad (8)$$

In addition to the question of the applicability of eq. 7, HRS β_0 values are more accurate when the laser fundamental and second harmonic wavelength are well removed from absorption bands. The challenges involved in deriving β_0 reliably, especially from HRS measurements, are considered in detail elsewhere.^{127–130} The dynamic β_{HRS} values calculated for chromophores **1–6** in MeCN are shown in the Supporting Information (Table S6). Notably, these contrast with the predicted static β_{HRS} values (Table 6) in showing a decrease on moving from **1** to **2**, but essentially no change on moving from **4** to **5**.

In contrast to HRS, the Stark-based approach employs the two-state model differently by applying eq. 8 with parameters measured for an ICT band. This method has the advantages of avoiding completely complications due to resonance, and chromophores with multiple ICT bands may be analysed, assuming that eq. 8 is valid for each individual transition. For **1–6**, the Stark-derived β_0 values are closer in magnitude to the predicted β_{tot} values in MeCN, being about half as large in four out of six cases, but remarkably similar for **3** (Table 6).

TABLE 6: Static First Hyperpolarizabilities (10^{-30} esu) Calculated at the B3LYP/6-311G(d) Level for the Chromophores 1–6, together with Data obtained from HRS and Stark Spectroscopic Measurements on the Salts [1–6][PF₆]₂

dication	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_x	β_y	β_z	β_{tot}	β_{HRS}^c	ρ^d	β_{HRS}^e	ρ^e	β_0^f	$\Sigma[\beta_0]^g$
1^a	455	203	66.5	25.7	−7.86	−6.69	−5.24	−1.31	−0.67	0.24	520	229	−12.9	568	240	4.8	126 ± 13	3.7 ± 0.6	40 ± 4	232
1^b	204	86.8	15.8	9.75	−4.34	−2.03	−1.73	−0.45	−0.17	0.08	219	96.4	−5.99	239	103	4.5				
2^a	−0.05	400	−0.03	83.8	0.00	−0.43	0.00	0.00	−3.75	0.00	−0.08	480	0.00	480	254	3.0	265 ± 15	2.4 ± 0.4	102 ± 6	296
2^b	−0.02	167	0.00	20.3	0.00	0.033	0.00	0.00	−1.16	0.00	−0.03	185	0.00	185	104	2.7				
3^a	0.00	762	0.00	113	0.00	−2.00	0.00	0.00	−4.07	0.00	0.00	871	0.00	871	475	2.8	340 ± 25	2.2 ± 0.3	183 ± 13	903
3^b	0.00	265	0.00	21.4	0.00	−0.26	0.00	0.00	−1.22	0.00	0.00	285	0.00	285	163	2.6				
4^a	214	114	32.8	16.7	−3.36	−3.69	−4.12	−0.86	0.02	0.52	246	130	−6.96	279	120	4.5	290 ± 30		24 ± 2	61
4^b	128	71.8	10.2	9.04	−3.26	−1.44	−1.76	−0.36	0.13	0.23	137	80.9	−4.78	159	71	4.1				
5^a	0.00	209	0.00	38.6	−5.67	0.00	−6.93	0.00	0.05	0.90	0.00	248	−11.7	248	132	2.9	550 ± 55		14 ± 1	104
5^b	0.00	119	0.00	14.1	−4.68	0.00	−2.54	0.00	0.15	0.42	0.00	133	−6.81	134	74	2.7				
6^a	0.00	462	0.00	64.1	−16.4	0.00	−12.3	0.00	−0.89	2.12	0.00	525	−26.6	526	288	2.8	570 ± 60		103 ± 11	268
6^b	0.00	208	0.00	17.5	−5.24	0.00	−3.65	0.00	−0.32	0.91	0.00	226	−7.98	226	128	2.6				

^a In MeCN (or measured with PF₆[−] salts in solution; in MeCN at 293 K for HRS data; in butyronitrile (PrCN) at 77 K for Stark spectroscopic data).⁹⁷ ^b In the gas phase. ^c Derived by using eqs. 3–5. ^d Depolarization ratio calculated by using eq. 6. ^e Dynamic values measured via HRS with an 800 nm Ti³⁺:sapphire laser (ρ values could not be determined reliably for [4–6][PF₆]₂). ^f Static first hyperpolarizability estimated from the measured β_{HRS} via the two-state model (eq. 7); the values for [4][PF₆]₂ and (especially) [5][PF₆]₂ are underestimated due to proximity of the ICT maximum to the second harmonic wavelength at 400 nm. ^g The total static first hyperpolarizability associated with the ICT bands, determined by applying eq. 8 to the data obtained at 77 K (estimated experimental error ±20%).

TABLE 7: Static First Hyperpolarizabilities (10^{-30} esu) Calculated at the B3LYP/6-311G(d)/LANL2DZ Level for the Chromophores 7–12, together with Data obtained from HRS and Stark Spectroscopic Measurements on the Salts [7–12][PF₆]_n (n = 4, 6 or 8)

complex	β_{xxx}	β_{xyx}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_x	β_y	β_z	β_{tot}	β_{HRS}^c	ρ^d	β_{HRS}^e	ρ^e	β_0^d	$\Sigma[\beta_0]^e$
7^a	611	192	37.2	21.2	−5.81	−2.50	−2.29	0.17	−0.07	0.09	648	213	−8.01	682	286	4.8	600 ± 40	3.5 ± 0.3	257 ± 17	252
7^b	54.2	87.2	−15.0	16.6	−2.31	1.02	−1.43	−0.42	0.05	0.03	38.8	104	−3.70	111	61	3.3				
8^a	48.2	418	10.5	42.4	−8.41	−0.97	−3.04	0.56	−0.02	0.41	59.2	460	−11.0	464	258	2.7	765 ± 165	2.3 ± 0.7	336 ± 72	662
8^b	25.4	209	4.45	16.4	−3.39	−0.44	−0.97	0.22	0.00	0.15	30.1	226	−4.21	228	129	2.6				
9^a	−0.97	863	0.98	102	−2.55	−0.51	1.30	−0.21	−2.25	−0.71	−0.20	962	−1.95	962	534	2.7	600 ± 100	2.3 ± 0.5	261 ± 43	
9^b	−18.5	1166	−4.13	132	7.49	−0.13	0.63	−0.10	−0.18	−0.32	−22.7	1298	7.81	1298	720	2.7				
10^a	532	145	18.6	16.7	−2.95	−1.32	−1.86	−0.71	−0.40	0.18	550	162	−4.64	573	241	4.8	550 ± 50	3.9 ± 0.4	200 ± 18	259
10^b	206	101	−13.0	18.2	−1.93	0.86	−1.40	−0.41	−0.03	0.06	193	119	−3.25	227	109	4.3				
11^a	0.41	373	0.05	38.3	2.44	0.00	−1.14	0.00	−0.58	0.28	0.46	411	1.58	411	230	2.7	900 ± 100	3.7 ± 0.3	326 ± 36	816
11^b	0.15	340	0.02	26.3	1.60	0.00	−0.42	0.00	−0.16	0.11	0.17	367	1.30	367	208	2.6				
12^a	−5.11	870	−0.87	82.0	−11.7	0.34	−1.75	0.01	−1.72	−0.10	−6.01	946	−13.6	946	535	2.7	900 ± 100	3.4 ± 0.3	309 ± 34	
12^b	2.05	1487	0.80	111	−3.71	−0.37	−2.84	0.00	−0.21	−0.11	2.85	1598	−6.66	1598	910	2.6				

^a In MeCN (or measured with PF₆[−] salts in solution; in MeCN at 293 K for HRS data; in PrCN at 77 K for Stark spectroscopic data).⁹⁶ ^b In the gas phase. ^c Derived by using eqs. 3–5. ^d Depolarization ratio calculated by using eq. 6. ^e Dynamic values measured via HRS with a 1064 nm Nd³⁺:YAG laser. ^f Static first hyperpolarizability estimated from the measured β_{HRS} via the two-state model (eq. 7). ^g The total static first hyperpolarizability associated with the MLCT bands, determined by applying eq. 8 to the data obtained at 77 K (estimated experimental error ±20%).

Ruthenium Complexes. The static β values calculated for complexes **7–12** in MeCN and the gas phase are shown in Table 7, together with selected experimentally measured data.⁹⁶ Both HRS and Stark measurements show that the bimetallic complexes have larger β_0 values than their monometallic counterparts.⁹⁶ This pattern is consistent with the experimental data obtained for the related purely organic species (see above). Notably, Stark measurements were not attempted for the trimetallic complexes due to complications introduced by the presence of directionally opposed MLCT transitions. As expected, both measured and predicted ρ values indicate significant two-dimensionality in the NLO responses of the bi- and trimetallic chromophores, although the experimental values for **[11][PF₆]₆** and **[12][PF₆]₈** are higher than expected.

The theoretically-derived static data for the mono- and bimetallic complexes (Table 7) show the same trend as noted for the metal-free chromophores **1–6** (Table 6), i.e. that the β_{tot} and β_{HRS} values are increased in MeCN. However, the opposite is found for the trimetallic complexes **9** and **12**. Interestingly, the experimentally observed trend of the total β_0 value increasing on moving from one to two Ru centers (i.e. **7** $\rightarrow$ **8** or **10** $\rightarrow$ **11**) is not predicted for either β_{tot} or β_{HRS} in MeCN, *but is reproduced for both parameters in the gas phase*. The calculations predict further increases in β_{tot} and β_{HRS} for the trimetallics, with or without MeCN. While the experimental data show no consistent effect on changing the trans ligand(s) from NH₃ to py, the calculations in MeCN afford relatively larger β_{tot} and β_{HRS} values for the mono- and bimetallic {Ru^{II}(NH₃)₅}²⁺ complexes **7** and **8**, but the opposite is predicted in the gas-phase. For the trimetallics in MeCN, β_{tot} is only slightly larger for **9** than **12**, while β_{HRS} is essentially the same for both complexes. Again, increases in both β_{tot} and β_{HRS} are predicted on moving from **9** to its py analogue **12** in the gas phase.

The dynamic β_{HRS} values calculated for complexes **7–12** in MeCN are shown in the Supporting Information (Table S7). These data show the same trend as the predicted static β_{HRS} values in MeCN (Table 7), with decreases on moving from **7** to **8**, or from **10** to **11**, then large increases on adding a third Ru center in **9** or **12**.

Given their molecular structures and x-polarization of the low energy transitions (see above and Table S4), the predicted dominance of the β_{xxx} tensor component for the

monometallic complexes **7** and **10**, but β_{xy} for the bimetallics **8** and **11** confirm expectations. In this respect, the trimetallic species **9** and **12** behave like their bimetallic counterparts. As for most of **1–6**, the Stark-derived β_0 values for **7** and **10** are about half as large as their β_{tot} values in MeCN, consistent with expectations, while the β_{tot} values are relatively smaller for **8** and **11**.

Other basis sets were tested to investigate if the experimental trends could be better reproduced. The larger, more computationally expensive def2-TZVP provides results similar to those from 6-311G(d)/LANL2DZ in TD-DFT (see above). Hyperpolarizabilities modeled at the B3LYP/def2-TZVP level in MeCN for **7** and **8** also follow the same pattern as those from the mixed basis set approach (see above and the Supporting Information, Table S8), but with slightly increased magnitudes. Using def2-TZVP again gives smaller β_{tot} and β_{HRS} values in the gas phase, when compared with MeCN.

4. Conclusion

A range of computations has been performed on two series of chromophores with pyrazinyl cores that were the subjects of recent experimental studies. TD-DFT confirms that the low energy electronic transitions have ICT character, involving the Ru^{II} center(s) as donors in the metal complexes. Multiple MLCT bands are evident for all except the mono- and bimetallic $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complexes.

For the purely organic $-\text{NMe}_2$ derivatives, the most accurate modeling of the visible absorption spectra in MeCN is achieved by using either the B3LYP or B3P86 functional with the 6-311G(d) basis set. In contrast, using instead CAM-B3LYP gives the best results for the $-\text{OMe}$ -substituted species. The experimentally observed trends in the ICT bands are predicted only partially, irrespective of the method applied. Moving from one to two electron donor groups decreases E_{max} by ca. 0.1 eV, but the calculations predict little or change. However, the accompanying observed increases in absorption intensity are reproduced theoretically for both series of chromophores. The large decreases in E_{max} (ca. 0.3–0.4 eV) on inserting ethenylene linkages are modeled accurately also, albeit with substantial intensity increases

that are not found in the experimental spectra. The red-shifts of the ICT bands on replacing –OMe with –NMe₂ are predicted, but to a lesser extent than observed. The calculated LUMO energies are largely consistent with data measured by cyclic voltammetry. The B3LYP/6-311G(d) β_{tot} and β_{HRS} values increase when a MeCN solvent model is included, –OMe groups are replaced with –NMe₂, or the π -conjugation extends. The latter two trends agree with the data derived from HRS or Stark spectroscopy experiments, while the observed trend of the total β_0 value increasing significantly on adding a second electron donor group is replicated only partially by the theory, with slight increases predicted for β_{HRS} but not for β_{tot} . As expected, for the symmetric chromophores, β_{xyy} is the most significant tensor component, while β_{xxx} dominates in the asymmetric species.

For the Ru complexes, the UV–vis absorption spectra in MeCN are modeled well by using B3LYP with the LANL2DZ/6-311G(d) mixed basis set. 100 excited states are included in the calculations in order to account for the high energy bands. Notably, using instead CAM-B3LYP gives relatively poor results for a representative complex, and using the def2-TZVP basis set for the Ru center(s) gives results very similar to those obtained by using LANL2DZ. Theory predicts the experimental trend that E_{max} of the dominant MLCT band increases by ca. 0.1 eV when axial NH₃ ligands are replaced with py, due to relative stabilization of the HOMO by py. However, predicted significant stabilizations of the LUMO on moving from two to three Ru centers are inconsistent with the almost constant electrochemical potential for the first ligand-based reduction. The experimental observation that E_{max} of the dominant MLCT band varies only slightly with the number of Ru centers is not well reproduced by the calculations. In particular, substantial red-shifts are predicted on moving from two to three metals, while the measured spectra show corresponding small blue-shifts. The observed increases in absorption intensity on moving from one to two Ru centers are reproduced accurately, but then further large increases are predicted, in contrast with the measured spectra which show negligible further changes. Comparing the trends in B3LYP/6-311G(d)/LANL2DZ β values with experimental data is possible for the mono- and bimetallic complexes only. The predictions for the latter show that β_{tot} and β_{HRS} increase in MeCN vs. the gas phase, but the opposite is found for the trimetallic complexes. The experimental trend

of the total β_0 value increasing on moving from one to two Ru centers is predicted in the gas phase, but not in MeCN. The calculations predict further increases in β_{tot} and β_{HRS} for the trimetallics, with or without MeCN. Changing the trans ligand(s) from NH_3 to py gives no consistent effect experimentally, while the mono- and bimetallic $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complexes have larger β_{tot} and β_{HRS} values in MeCN, but the opposite is predicted in the gas phase. For the trimetallics, relatively larger β values are also predicted for the py complex in the gas phase, but there are only small differences between the values for the two related complexes in MeCN. As expected, the β_{xxx} tensor component dominates for the monometallic complexes, while β_{xyy} is most significant for the bi- and trimetallic species. Using def2-TZVP gives β_{tot} and β_{HRS} results broadly similar to those obtained with LANL2DZ.

Finally, these studies demonstrate that current computational methods are very useful in helping to rationalize the electronic structures and optical properties of novel NLO chromophores. However, it is also clear (and not unexpected) that the quantitative accuracy of predictions diminishes as the systems depart further from a relatively simple 1D dipolar motif.

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Supporting Information Available: additional simulated UV–vis spectra, MO contour surface diagrams, calculated data and Cartesian coordinates of theoretically optimized geometries for **1–12** (PDF), complete references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Graphical Abstract

Pyrazine-based chromophores with either 4-(methoxy/dimethylamino)phenyl or pyridyl-coordinated $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}/\text{trans-}\{\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{py})\}^{2+}$ (py = pyridine) electron donor groups have been subjected to density functional theory calculations. The results are compared with experimental data obtained from techniques including hyper-Rayleigh scattering and Stark spectroscopy. Some aspects of the observed properties are reproduced accurately, while others are not.