Switchable Nonlinear Optical Metallochromophores with Pyridinium Electron Acceptor Groups

BENJAMIN J. COE

School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, U.K.

Received December 13, 2005

ABSTRACT
Organotransition metal complexes have much to offer as nonlinear optical (NLO) chromophores since they allow large hyperpolarizabilities to be combined with various other physical properties in an unparalleled diversity of molecular structures. This Account summarizes our synthetic chemistry driven investigations in the NLO research field, which have focused primarily on complexes of ruthenium, and to some extent iron. A number of fascinating discoveries are described, including the first demonstration of redox-induced switching of NLO behavior and chromophores which disobey the otherwise universal rule that elongation of polyene systems leads to continual increases in quadratic NLO responses.

I. Introduction

The inbuilt limitations of current semiconductor-based electronics in terms of speed, scale, and mode of operation have inspired much research in the areas of molecular electronics and photonics.[1] Because they can combine the already attractive properties and synthetic tailorability of purely organic molecules with extra functionalities, transition metal complexes have much to offer within this broad and exciting scientific field.[2] As an example of the use of bulk-level molecular electronic/photonic properties, nonlinear optical (NLO) materials are especially interesting.[3] NLO effects allow the manipulation of laser beams and can therefore be used in electro-optical data processing, and also revolutionary all-optical technologies. Second harmonic generation (SHG) or frequency doubling is the most readily understood and widely used NLO phenomenon, which allows for example the production of high-intensity green laser pointers. The dazzling light at a wavelength of 532 nm corresponds with the peak sensitivity of the human eye and arises from the SHG of a 1064 nm Nd^{3+}-based laser which is pumped by a 808 nm diode laser. Although the materials currently used in this and related devices are inorganic crystals such as potassium titanyl phosphate ($KTiOPO_4$) or lithium niobate ($LiNbO_3$), molecular compounds are also promising for NLO ap-

plications.[3] The attractive features of organic NLO materials include very large and ultrafast responses, high optical damage thresholds, and facile processability, and recently attention has focused increasingly on organotransition metal complexes.[4]

The creation of new molecular NLO materials begins with synthetic chemistry, and this area provides an excellent example of "molecular engineering" which can be guided by clear design principles. For purely organic chromophores, these rules are now well-established;[3] large molecular first hyperpolarizabilities β, which govern second-order (quadratic) NLO effects, are generally displayed by molecules having a strongly electron-donating group (D) connected to an electron-accepting unit (A) via a π-conjugated bridge. Such a polarizable dipolar compound also exhibits D→A intramolecular charge-transfer (ICT) excitations, and molecules with especially large β responses appear strongly colored because their ICT absorptions lie in the visible region of the electromagnetic spectrum. For purposes of comparison it is necessary to derive static first hyperpolarizabilities β_0 which are the intrinsic β responses in the absence of any resonance (note that actual absorption must be avoided in applications). Values of β_0 can be determined by using a two-state model for dipolar chromophores.[5] The salt *trans*-4′-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (**1**) is an appropriate reference, and we have used hyper-Rayleigh scattering (HRS) measurements to determine a β_0 value of 110×10^{-30} esu for the PF_6^- counterpart of this compound.[6] As an indication of the upper attainable limits, the polyene compound **2** is among the most active NLO chromophores known, with a β_0 of 1470×10^{-30} esu derived from electric-field-induced SHG measurements.[7]
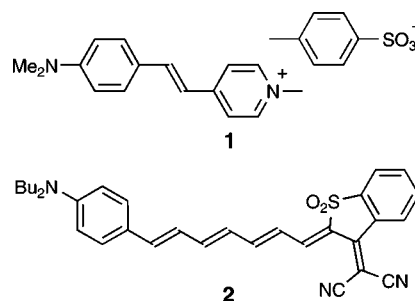

Moving beyond simple 1D dipolar species, the introduction of multiple D and/or A groups can generate a range of interesting chromophores, including octupolar species, but noncentrosymmetry is a universal requirement for a nonzero value of β. In a similar manner, bulk quadratic NLO effects can only be observed from materials which have a noncentrosymmetric structure. The quantity responsible for third-order (cubic) NLO effects, exemplified by third harmonic generation or frequency tripling, is the molecular second hyperpolarizability γ. The key requirement for large values of this parameter is an extensive π-conjugated system, with no symmetry restrictions at either the molecular or macroscopic levels.

Ben Coe was born in 1966 in Kingston-upon-Thames, U.K. He obtained his Ph.D. from Birmingham University, U.K., in 1991 under the supervision of Prof. J. A. McCleverty and Dr. C. J. Jones. A one year Temporary Lectureship at Birmingham preceded NATO-funded postdoctoral studies with Dr. T. J. Meyer at the University of North Carolina at Chapel Hill. He was appointed as a Lecturer in Chemistry at Manchester University in 1994 and is presently a Senior Lecturer. His current research interests concern the molecular electronic and photonic properties of organotransition metal complexes and related organic materials.

The first investigations into the NLO properties of transition metal complexes were reported in the 1980s, and since then this field has burgeoned.[4] Because coordinated metal centers often engage in π-bonding with organic ligating groups and with each other, they can be involved in several types of strongly allowed ICT processes, i.e., metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), or metal-to-metal/intervalence charge transfer (MM/IVCT). Complexed metals can also participate in less directional $\pi \rightarrow \pi^*$ electronic excitations. As in purely organic chromophores, such transitions are often associated with large values of β and/or γ. Furthermore, an unparalleled structural and electronic diversity makes metal complexes especially attractive for the creation of novel NLO materials. This Account summarizes our curiosity-driven investigations in the NLO research field, which have focused primarily on the quadratic NLO properties of ruthenium complexes. The intention is to highlight the key developments and discoveries which make this area especially fascinating and rewarding from a synthetic chemist's perspective.

II. Tuning the Optical Properties of Simple Dipolar Chromophores

Our initial studies focused on 1D dipolar complexes, using data obtained from HRS experiments with a 1064 nm laser in acetonitrile to derive structure–activity relationships for β. The HRS technique[8] has recently become widely applied and is particularly useful because it directly probes the quadratic NLO properties of various compounds, including charged species. Early experiments with complexes *trans*-[Ru^{II}(NH$_3$)$_4$(L^D)(L^A)]$^{n+}$ (L^D = an electron-rich ligand; n = 2 or 3) involved species where L^A is one of the electron-accepting ligands 4-acetylpyridine, ethylisonicotinate, or *N*-methyl-4,4′-bipyridinium (MeQ$^+$).[9] These complexes display intense, solvatochromic visible Ru$^{II} \rightarrow$ L^A MLCT absorptions which dominate the β responses.[9] Relatively large β_0 values are observed, in the range $10-130 \times 10^{-30}$ esu, with the largest for *trans*-[Ru^{II}(NH$_3$)$_4$(MeQ$^+$)-(dmap)][PF$_6$]$_3$ [dmap = 4-(dimethylamino)pyridine].[9] Extended π-conjugation causes the MeQ$^+$ complexes to have larger β_0 values than their analogues with monopyridyl L^A ligands.[9] Compound **3** crystallizes noncentrosymmetrically in the hexagonal space group $P6_3$, with the complex cations producing a strong projected component along the polar z axis, but twinning produces a net dipole cancellation at the macroscopic level.[9]
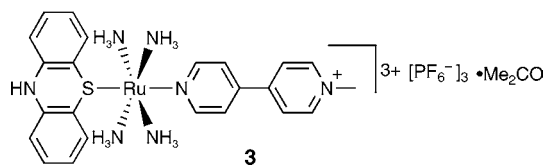
We have subsequently tuned and enhanced the molecular NLO responses of complex salts *trans*-[Ru^{II}(NH$_3$)$_4$-(L^D)(L^A)][PF$_6$]$_3$.[10-12] Consistent with the two-state model,[5] a reasonable linear relationship is observed between β_0 and $1/(E_{max})^2$ (E_{max} is the MLCT energy; Figure 1).[11] A key
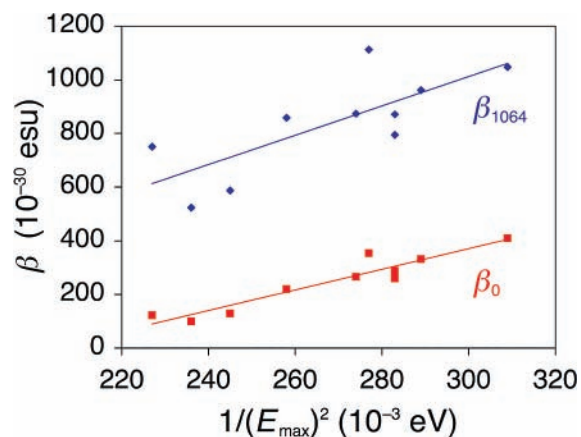

FIGURE 1. Plot of β against the inverse square of the MLCT energy for a series of salts *trans*-[Ru^{II}(NH$_3$)$_4$(L^D)(L^A)][PF$_6$]$_3$. Adapted from ref 11.

discovery emerging from these studies is that N-arylation of pyridinium A groups decreases E_{max} and increases β_0. The same effect is observed in purely organic chromophores, affording several new salts with large SHG activities.[6,13] The most active Ru^{II}-based chromophore revealed by these experiments is **4** ($\beta_0 = 410 \times 10^{-30}$ esu).[11]
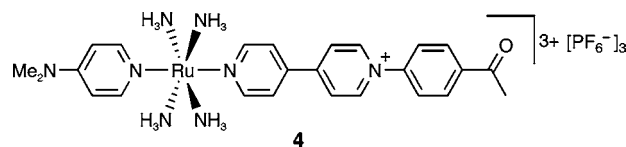
More recently, we have also used electronic Stark effect (electroabsorption) spectroscopy in butyronitrile glasses at 77 K to complement and rationalize the HRS results.[14] Applying the two-state equation $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{max})^2$ ($\Delta\mu_{12}$ is the dipole moment change accompanying the MLCT transition, and μ_{12} is the transition dipole moment) with the Stark-derived $\Delta\mu_{12}$ values gives estimated NLO responses which are free from any complications due to resonance effects implicit in HRS studies. INDO/SOS calculations on the pentaammine complexes predict the dipole properties reasonably well, but do not reliably reproduce E_{max} or β_0.[14] However, Lin et al. have found that time-dependent density functional theory (TD-DFT) affords good agreement with the HRS-derived β_0 values for some of our complexes.[15] Further UV–visible and cyclic voltammetric experiments show that replacing a neutral L^D ligand like dmap with a (probably N-coordinated) thiocyanate anion enhances the electron-donating ability of the Ru^{II} center (Figure 2).[16] As expected, larger β_0 values result (e.g., for **5** β_0[HRS] = 513 × 10^{-30} esu; β_0[Stark] = 553 × 10^{-30} esu), which can be twice those of the analogous *N*-methylimidazole (mim) complexes.[16]
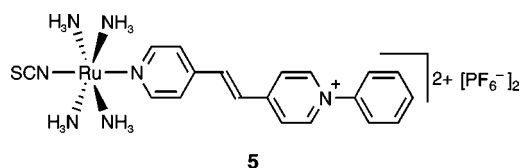
A desire to obtain more readily crystalline materials, often elusive with ammine species, led us to study Ru^{II}
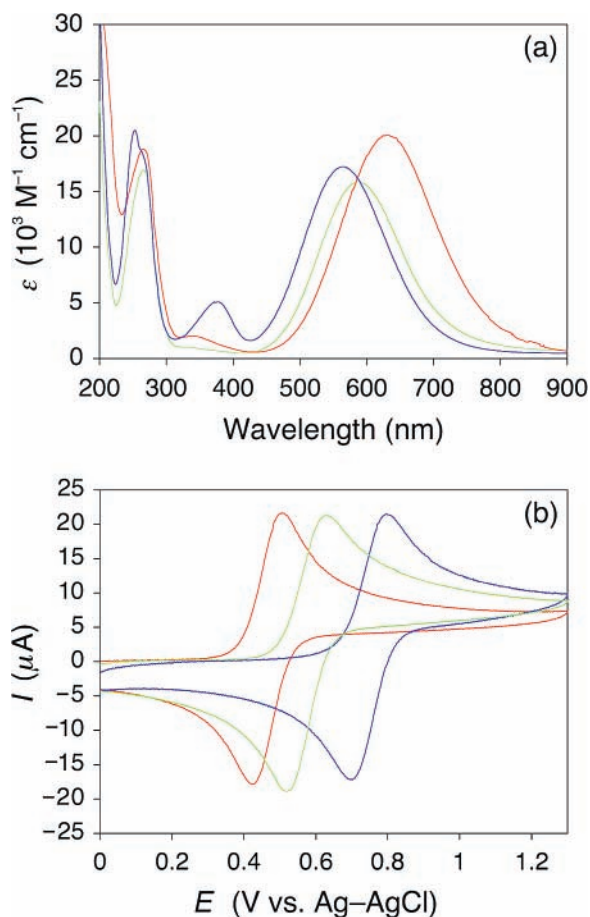
FIGURE 2. Tuning of (a) the MLCT wavelength and (b) Ru$^{III/II}$ reduction potential in the salts *trans*-[Ru^{II}(NH$_3$)$_4$(L^D)(MeQ$^+$)][PF$_6$]$_3$ at 295 K in acetonitrile. L^D = pyridine (py) (blue); NH$_3$ (green); NCS$^-$ (red). Adapted from ref 16.
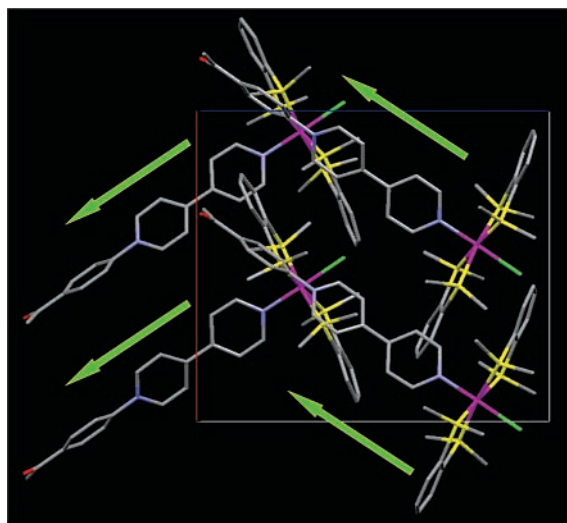

FIGURE 3. Crystal packing diagram of **6**, showing the noncentrosymmetric arrangement of the complexes (acetone solvent and anions omitted). The arrows approximate to the directions of the molecular dipolar axes. Adapted from ref 17.

complexes of the ligand 1,2-phenylenebis(dimethylarsine) (pdma).[17,18] These appear to be the only arsine species to have been investigated for NLO purposes. As expected, the decreased electron-richness of a *trans*-{Ru^{II}Cl(p-dma)$_2$}$^+$ center when compared with a {Ru^{II}(NH$_3$)$_5$}$^{2+}$ group produces higher Ru$^{III/II}$ potentials and MLCT energies, but varying the structure of the pyridinium-substituted ligand affords the same trends in both types of complex.[17] According to Stark results, the β_0 values of the pdma complexes are only slightly smaller than those of their {Ru^{II}(NH$_3$)$_5$}$^{2+}$ counterparts, partly due to unexpected changes in the relative magnitudes of μ_{12} upon freezing.[18] Data obtained from extensive crystallographic studies with the arsine species provide no evidence for ground-state charge transfer.[17] However, **6** crystallizes noncentrosymmetrically in the orthorhombic space group *Pna2$_1$* (Figure 3),[17] and with a β_0[Stark] of 170 × 10^{-30} esu may show substantial bulk NLO behavior.[18]
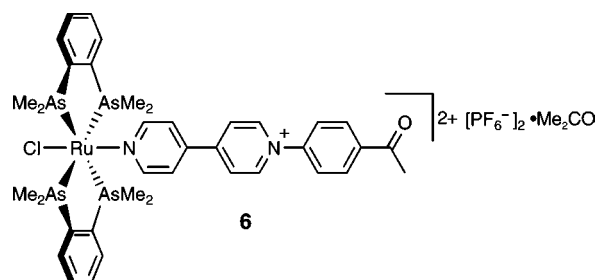
III. The First Demonstration of Redox Switching of NLO Responses

As already discussed, there are various good reasons for incorporating metal centers into NLO chromophores. The development of strategies for the molecular-level modulation of NLO behavior has attracted considerable interest recently,[19] and transition metals provide an ideal means to achieve this via their redox properties.

Having demonstrated that we can create dipolar Ru^{II}-based chromophores with very large NLO responses, we carried out a series of HRS experiments with pentaammine complexes to show that Ru^{II} → Ru^{III} oxidation causes β to decrease very substantially.[20] Attenuations of the NLO responses exceeding an order of magnitude are accompanied by complete bleaching of the MLCT absorptions (Figure 4), and both processes are fully reversible, in keeping with cyclic voltammetric studies.[20] While a {Ru^{II}(NH$_3$)$_5$}$^{2+}$ center is a powerful π-electron donor, the corresponding Ru^{III} moiety can act only as a σ-electron acceptor. The low reduction potentials of the {Ru^{II}(NH$_3$)$_5$}$^{2+}$ complexes (ca. 0.5 V vs Ag−AgCl in acetonitrile) mean that this switching occurs at only a small energetic cost.

Although Sakaguchi et al. had previously attributed a 30% photoswitching of SHG from Langmuir−Blodgett films of a [Ru^{II}(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridyl) derivative to the change in β on MLCT excitation,[21] our report was the first convincing demonstration of redox switching of NLO effects. Similar effects for both quadratic and cubic optical nonlinearities have subsequently been reported by other workers using several types of metal complexes,[22] including Ru^{II} σ-acetylides. Of course, it is also important
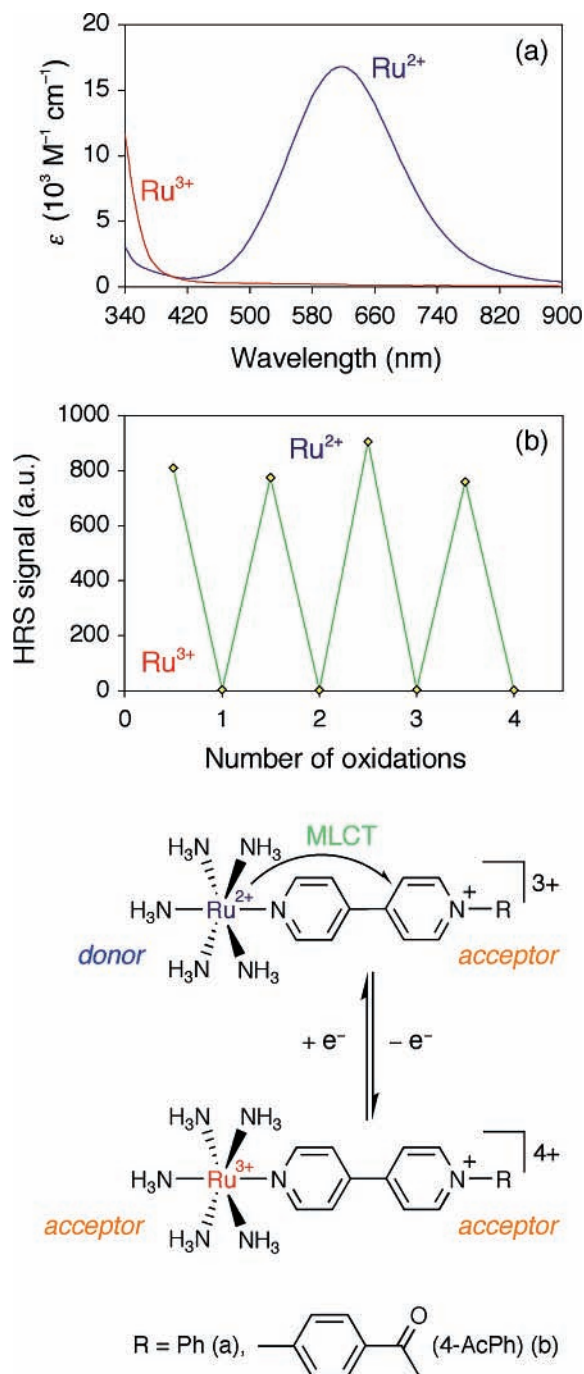
FIGURE 4. Redox switching of (a) MLCT absorption and (b) molecular quadratic NLO response in ruthenium pentaammine complexes. Adapted from ref 20.

to remember that our proof-of-principle results are applicable to various related systems, including multidimensional Ru^{II} complexes (see later).

In very recent HRS and Stark studies with complexes containing {Fe^{II}(CN)$_5$}$^{3-}$ D centers, we have discovered that acidification causes large blue-shifts in the MLCT bands, accompanied by substantial decreases in β_0. Such complexes are therefore novel examples of chromophores which are amenable to protic switching as well as metal-based redox switching (according to cyclic voltammetry).
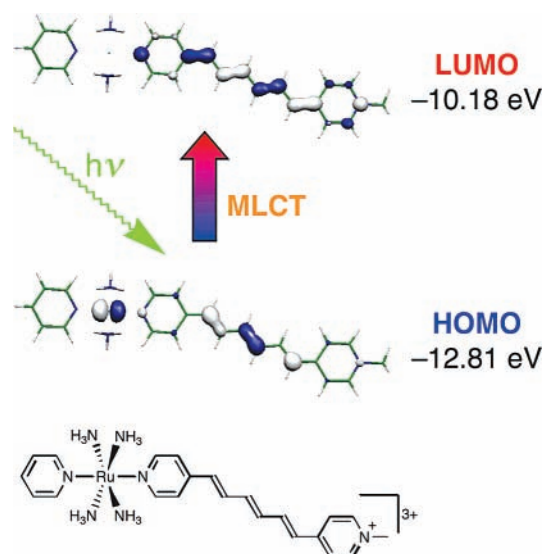
FIGURE 5. TD-DFT-derived 0.05 contour surfaces of the MOs involved in the lowest energy (nominally MLCT) transition for the complex in **10**. Adapted from ref 24.

IV. Unusual Effects of π-Conjugation Extension in Polyenes and Polyynes

Because extending conjugated systems normally causes red-shifting of ICT bands and increases $\Delta\mu_{12}$,[3] causing D–A polyenes such as **2** to possess large β_0 values,[7] we prepared some extended dipolar Ru^{II} complexes.[18,23–25] Initial studies with ammine species revealed very unusual optical behavior.[23,24] Within three series (e.g., **7–14**), the

L^D = py; n = 0 (**7**), 1 (**8**), 2 (**9**), 3 (**10**)
L^D = NH$_3$; n = 0 (**11**), 1 (**12**), 2 (**13**), 3 (**14**)
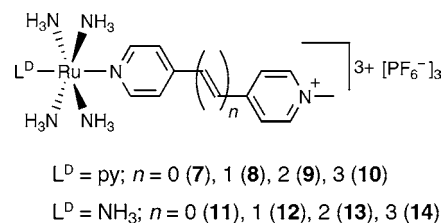
MLCT band unexpectedly blue-shifts as n increases from 1 to 3.[23,24] The β_0 values derived from HRS and Stark measurements are very large and maximize at n = 2, in complete contrast to all other known D–A polyenes in which β_0 increases steadily with n.[23,24] TD-DFT and finite field (FF) calculations generally predict the observed trends in both the linear and NLO properties.[24] The TD-DFT results show that the degree of π character of the HOMO increases with n and hence the lowest energy transition gains in intraligand charge-transfer (ILCT) character (Figure 5).[24] The E_{max} and $\Delta\mu_{12}$ values for this transition are therefore respectively larger and smaller than would be the case for a pure MLCT excitation, causing β_0 to decrease.[24] Selected data for **7–14** are shown in Table 1.

Stark spectroscopic studies on the *trans*-{Ru^{II}Cl(p-dma)$_2$}$^+$ analogues of **7–14** show that these also display unusual MLCT blue-shifting as n increases beyond 1.[18] A severalfold increase in β_0 is observed on moving from n = 1 to 2, and a further increase appears to occur for the

Table 1. Selected Experimental and Calculated Data for Salts 7–14 and 17–20[24,29]

salt	n	λ_{max}^a (nm)	λ_{max}^b (nm)	E_{max}^b (eV)	μ_{12}^b (D)	$\Delta\mu_{12}$ (D)	H_{ab} (cm^{-1})	β_0^c (10^{-30} esu)	β_0^d (10^{-30} esu)	β_0^e (10^{-30} esu)
7	0	566	611	2.03	6.1	16.2	4900	171		192
11	0	590	645	1.92	5.2	13.8	4700	120		112
17	0	420	423	2.93	7.7	13.2	9000	108		74
8	1	563	638	1.94	6.0	19.3	4100	218		259
12	1	595	681	1.82	5.5	16.2	4100	175		112
18	1	470	480	2.58	9.1	16.3	7700	236		150
9	2	552	631	1.97	8.2	25.1	4300	514	565	271
		356	370	3.35	6.5	11.7	10000	51		
13	2	584	675	1.84	7.9	22.4	4300	482	546	156
		354	377	3.29	6.8	12.7	9700	64		
19	2	487	503	2.47	9.1	20.4	6600	328		269
10	3	542	625	1.98	7.0	28.6	3500	412	546	212
		392	404	3.07	9.3	12.5	10300	134		
14	3	568	669	1.85	7.2	27.1	3500	475	576	134
		392	408	3.04	7.4	14.5	8700	101		
20	3	500	523	2.37	11.8	24.0	6700	694		609

^{a} In acetonitrile at 295 K. ^{b} In butyronitrile at 77 K. ^{c} Calculated from $3\Delta\mu_{12}(\mu_{12})^2/(E_{max})^2$ ($\pm20\%$ error). ^{d} Sum of the β_0 values for the MLCT and ILCT bands (where present). ^{e} From FF calculations.
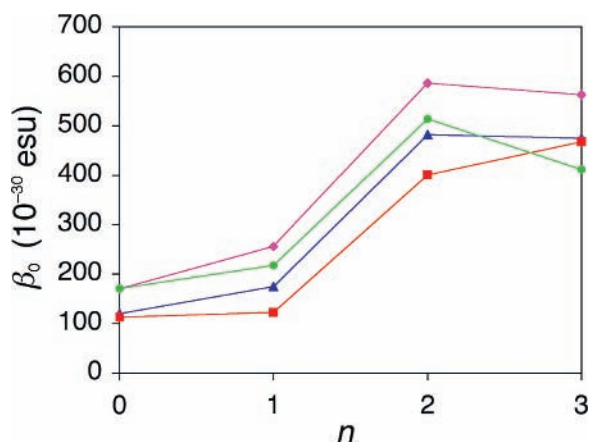

FIGURE 6. Stark-derived β_0 values as a function of n for complexes of pyridyl polyene ligands (only dominant MLCT transitions considered); green = py series (**7**–**10**); pink = analogous series with trans mim ligands; blue = pentaammine series (**11**–**14**); red = trans-{Ru^{II}Cl(pdma)$_2$}$^+$ series.

$n = 3$ complex, but this is only small and within the experimental errors (Figure 6).[18] Very recently, we have turned our attention to related ethynyl-containing complex salts (e.g., **15** and **16**).[25] In acetonitrile solutions at

$n = 1$ (**15**), 2 (**16**)
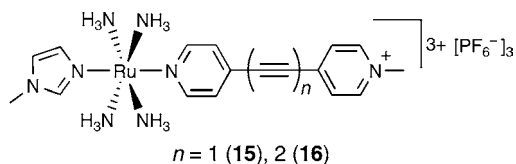
295 K, the MLCT bands of these complexes blue-shift with conjugation extension, as for their ethenyl analogues.[25] However, at 77 K in butyronitrile, the MLCT bands of the ethynyl chromophores display more normal red-shifts as n increases.[25] The latter observation provides a marked contrast with the polyene complexes which show consistently unusual optical behavior.[23,24] While the β_0[Stark] values for the ethynyl systems generally increase on
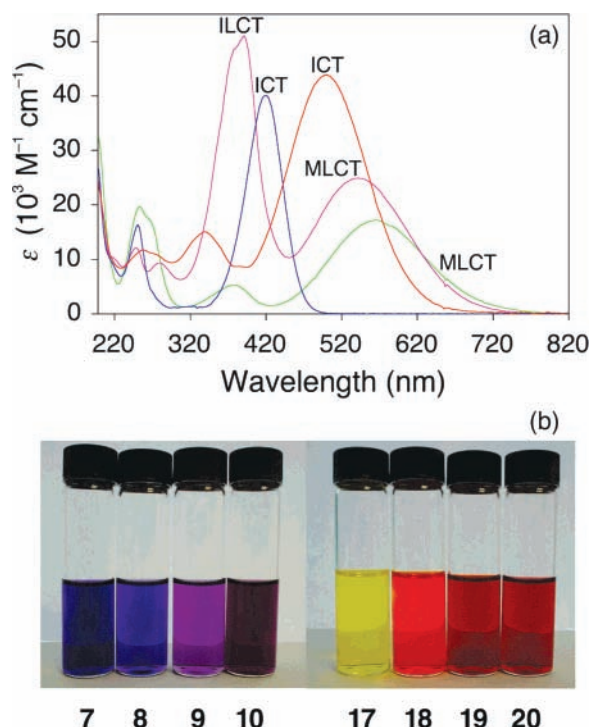

FIGURE 7. (a) UV–visible absorption spectra of salts **7** (green), **10** (pink), **17** (blue) and **20** (red) at 295 K in acetonitrile. (b) Photographs of the solutions for the two series **7**–**10** and **17**–**20**.

moving from $n = 0$ to 2, β_0[HRS] maximizes at $n = 1$ for two of the ammine series, but increases on moving from $n = 1$ to 2 for the pdma complexes.[25] In keeping with studies on purely organic chromophores,[26] both HRS and Stark data show that these ethynyl-containing complexes generally show smaller β_0 values than their ethenyl counterparts. The inferiority of the ethynyl systems in terms of NLO response is most evident when $n = 2$, principally due to larger increases in μ_{12} (and hence D–A π-electronic coupling) on extension in the ethenyl chromophores.[25]

V. Comparisons with Purely Organic Chromophores

A key objective of our research is to draw detailed, quantitative, and systematic comparisons between the optical properties of transition metal complexes and closely related purely organic chromophores. Rather surprisingly, very few other such studies have been reported by other workers,[27] and these are of limited scope in terms of the variety of data considered.

Experiments with molecules having 4-(dimethylamino)-phenyl or pyridyl-coordinated {Ru^{II}(NH$_3$)$_5$}$^{2+}$ D units linked directly to pyridinium A groups show that the Ru^{II} center is the more effective π-electron donor, yielding enhanced β_0 responses.[28] Although π-orbital overlap is stronger in the purely organic chromophores, this is more than offset by the much higher energy of the Ru^{II}-based HOMO.[28] Subsequent studies including TD-DFT and FF calculations show that extending polyene bridges in purely
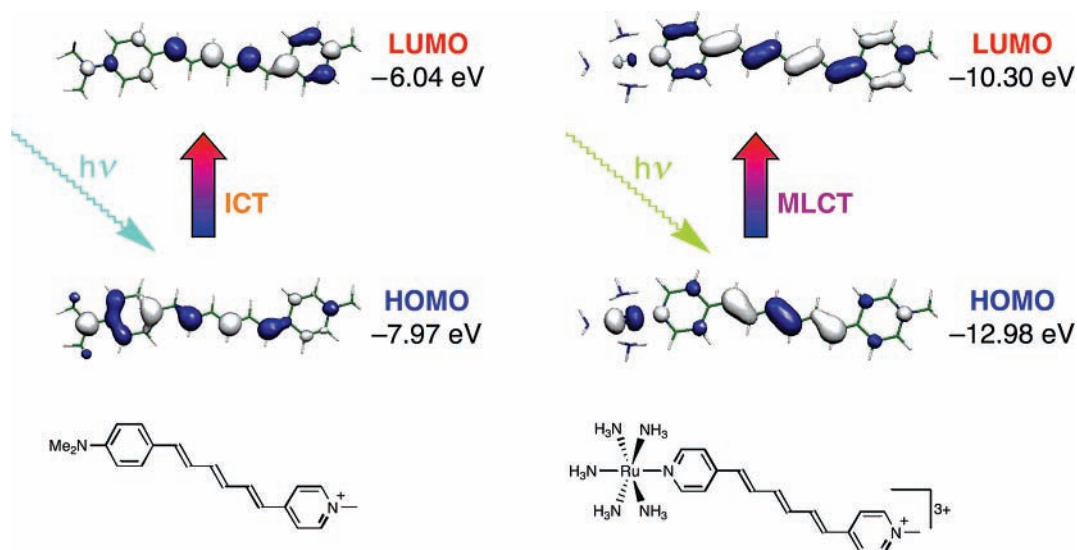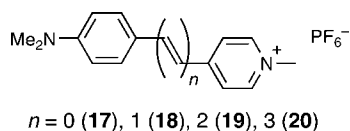
FIGURE 8. TD-DFT-derived 0.05 contour surfaces of the MOs involved in the lowest energy transitions for the cations in **20** and **14**. Adapted from ref 29.

organic chromophores (e.g., **17**–**20**) affords normal optical

n = 0 (**17**), 1 (**18**), 2 (**19**), 3 (**20**)

behavior, i.e., decreasing ICT energies and increasing $\Delta\mu_{12}$ and β_0.[29] The marked contrast with our Ru^{II} pyridyl polyenyl complexes (e.g., **7**–**10**; see Figure 7 for representative UV–visible spectra) arises from variations in the degree of D–A electronic coupling, which is shown by electrochemical, ^{1}H NMR, and Stark measurements to be more effective in the organic compounds.[28,29] Furthermore, the D–A communication in the complexes falls off with distance, so that β_0, μ_{12}, and H_{ab} (the electronic coupling matrix element) all decrease above n = 2.[29] The benefits in terms of NLO response of replacing a 4-(dimethylamino)phenyl group with a more electron-rich Ru^{II} pyridyl ammine center are therefore lost when n = 3.[29] The HOMO and LUMO for the cation in **20** and for the related complex in **14** are shown in Figure 8, and selected data for **17**–**20** are shown in Table 1.

VI. Two-Dimensional V-Shaped Complexes

As well as 1D dipoles, various multidimensional chromophores can possess NLO properties, including C_{2v} symmetric 2D dipolar species.[30] In a 1D molecule, the dipolar axis is normally taken as z and the β_{zzz} tensor component is then dominant. In contrast, C_{2v} dipoles display electronic transitions having μ_{12} perpendicular to the C_2 axis, leading to significant off-diagonal β components β_{zyy}. Such unusual compounds are attractive for avoiding the well-documented NLO efficiency–transparency tradeoff (because the second/third harmonic photons generated via β_{zyy} are polarized perpendicular to the transition dipole and cannot be reabsorbed), and also offer new possibilities for achieving phase-matched SHG.

We have investigated complexes with *cis*-{$Ru^{II}(NH_3)_4$}$^{2+}$ centers coordinated to monodentate 4,4′-bipyridinium ligands (**21**–**24**)[31] and related chelating derivatives of 2,2′:4,4″:4′,4‴-quaterpyridyl,[31,32] which are the first reported charged 2D NLO metallochromophores. These

R = Me (**21**), Ph (**22**), 4-AcPh (**23**), (**24**)
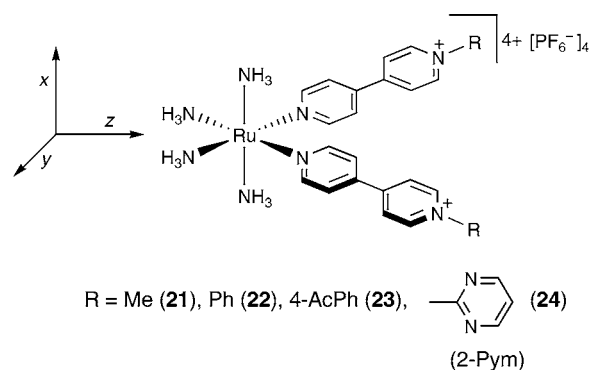
(2-Pym)

complexes show multiple MLCT bands, with energies decreasing in the order R = Me > Ph > 4-AcPh > 2-Pym (Figure 9), as the pyridinium groups become more electron-
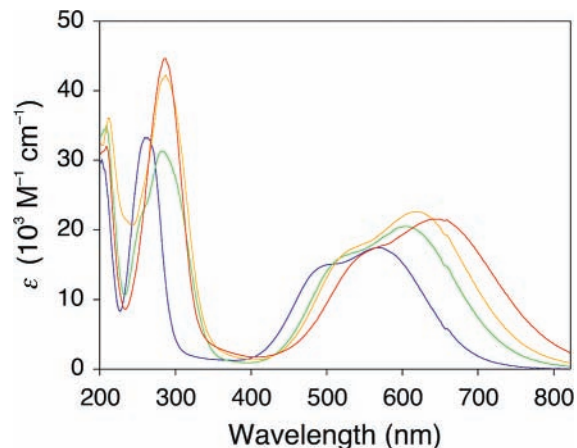

FIGURE 9. UV-visible absorption spectra of salts **21** (blue), **22** (green), **23** (gold), and **24** (red) at 295 K in acetonitrile.
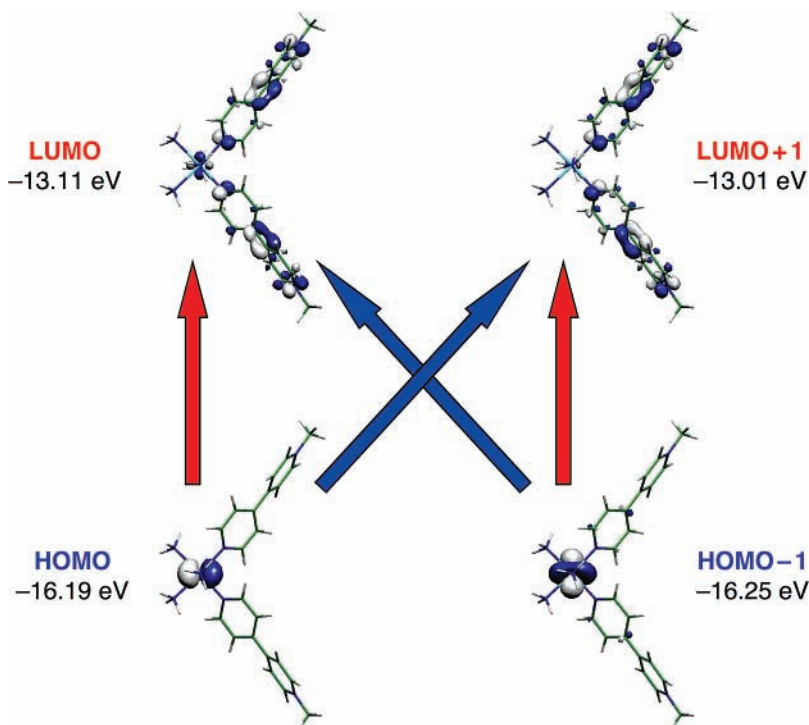
FIGURE 10. TD-DFT-derived 0.06 contour surfaces of the MOs involved in the two lowest energy (MLCT) transitions for the complex in **21**. The red arrows represent the *y*-polarized transitions corresponding with β_{zyy}, while the blue arrows represent the *z*-polarized transitions corresponding with β_{zzz}.

deficient.[31,32] This trend mirrors that observed in related 1D dipoles.[12] We have subjected our 2D complexes to HRS with an 800 nm laser and Stark studies, using Gaussian fitting to deconvolute the MLCT transitions.[31,32] These chromophores display two substantial β components, β_{zzz} and β_{zyy}, the difference between which is most pronounced for the nonchelated systems.[32] TD-DFT shows that the lowest energy MLCT transition is associated with β_{zyy} and the higher energy transition with β_{zzz} (Figure 10), with the former component being the larger.[32] Selected data for **21–24** are shown in Table 2. It is noteworthy that the electrochemistry of these compounds indicates that they possess potential for redox-induced switching of optical properties over multiple states.

Further studies with these 2D complexes have revealed that **21**·H_2O and the BPh_4^- analogue of **23** crystallize noncentrosymmetrically in the respective space groups $P2_1$ and $Fmm2$. However, it appears that the dipoles largely cancel each other out (Figure 11), so these materials may exhibit only limited bulk NLO effects.

VII. Three-Dimensional Octupolar Complexes

Various studies with octupolar NLO metallochromophores have been reported, in particular derivatives of $[Ru^{II}(bpy)_3]^{2+}$ and closely related species.[33] However, all such chromophores bear electron-donating substituents, so their dominant electronic transitions correspond with ILCT excitations which are directionally opposed to the MLCT transitions. We have prepared the complex salts

Table 2. Selected Experimental and Calculated Data for Salts 21–24 and 25–31[32,34]

salt	$\lambda_{max}{}^a$ (nm)	$\lambda_{max}{}^b$ (nm)	$E_{max}{}^b$ (eV)	$\mu_{12}{}^b$ (D)	$\Delta\mu_{12}$ (D)	$\beta_0{}^c$ (10^{-30} esu)	$\beta_{800}{}^d$ (10^{-30} esu)	$\beta_0{}^e$ (10^{-30} esu)
21	570	628	1.98	6.7	10.1	137	139	$\beta_{zyy} = 70$
	502	518	2.39	5.2	11.3	62		$\beta_{zzz} = 18$
22	606	632	1.96	7.4	13.8	231	127	
	528	512	2.42	4.6	9.9	42		
23	620	684	1.81	7.6	12.1	248	142	
	536	558	2.22	5.6	13.0	95		
24	644	731	1.97	7.9	11.7	298	143	
	558	589	2.10	5.9	12.3	110		
25	486	496	2.50	4.2	7.9	26	170	$\beta_{yyy} = -\beta_{yxx}$
	394	396	3.13	5.8	10.3	41		$= 25.3$
26	496	502	2.47	4.2	10.0	34	270	
	410	407	3.04	6.7	13.5	76		
27	498	506	2.45	3.7	11.5	31	281	
	416	416	2.98	5.1	12.8	44		
28	498	507	2.45	4.0	11.1	35	290	
	416	414	2.99	5.5	14.1	56		
29	574	581	2.14	4.4	6.1	30	78	$\beta_{yyy} = -\beta_{yxx}$
	440	444	2.79	5.8	11.2	56		$= 11.4$
30	584	590	2.10	4.5	7.4	39	80	
	454	461	2.69	6.1	13.9	82		
31	586	596	2.08	4.3	7.9	39	110	
	460	469	2.64	6.4	16.4	112		

^{a} In acetonitrile at 295 K. ^{b} In butyronitrile at 77 K; data for the two fitted Gaussian components. ^{c} Calculated from $3\Delta\mu_{12}(\mu_{12})^2/(E_{max})^2$ ($\pm20\%$ error). ^{d} Measured with a 800 nm Ti^{3+}:sapphire laser, assuming a single major tensor component ($\pm15\%$ error). ^{e} From FF calculations.

25–31 which are fundamentally different from existing species because they feature electron-accepting pyridinium substituents. Their optical properties are therefore associated almost exclusively with MLCT processes, in-
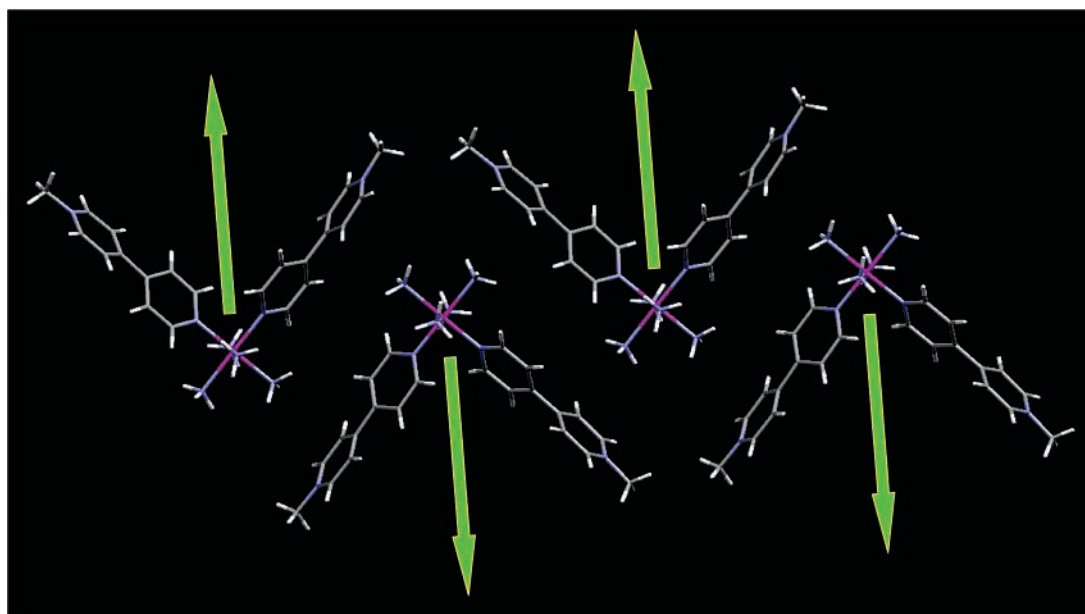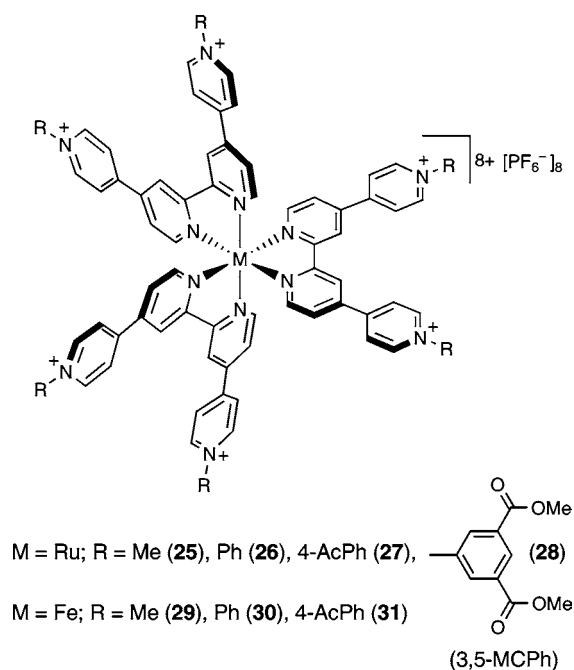
FIGURE 11. Crystal packing diagram of **21**·H$_2$O, showing the noncentrosymmetric arrangement of the complexes (water and anions omitted). The arrows approximate to the directions of the molecular dipolar axes.

troducing greater scope for rational maximization and metal-based redox switching of β.

M = Ru; R = Me (**25**), Ph (**26**), 4-AcPh (**27**),   (**28**)

M = Fe; R = Me (**29**), Ph (**30**), 4-AcPh (**31**)

(3,5-MCPh)

The salts **25**−**31** all display two resolved MLCT bands, the energies of which show rather less sensitivity to R than is the case in related 1D or 2D chromophores.[34] The MLCT bands of the Fe^{II} complexes are less intense and red-shifted when compared with those of their Ru^{II} counterparts (Figure 12), due to increased electron density at the Fe^{II} centers.[34] We have studied **25**−**31** using 800 nm HRS and Stark spectroscopy, the latter revealing that these ground-state octupolar D_3 chromophores exhibit two substantial β components which are associated with transitions to dipolar excited states.[34] The HRS β values are larger for the Ru^{II} complexes (but resonantly en-
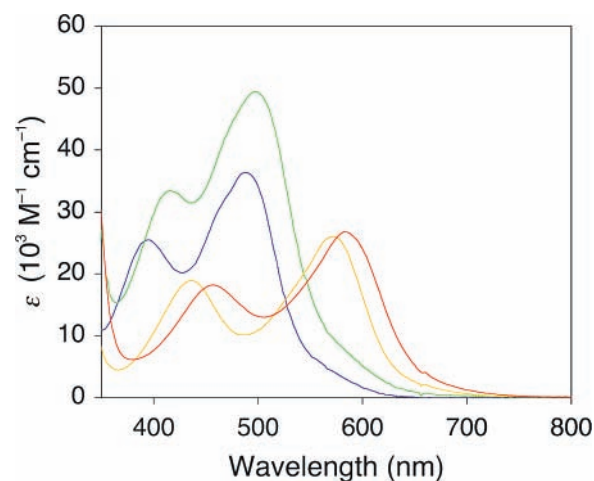

FIGURE 12. UV−visible absorption spectra of salts **25** (blue), **27** (green), **29** (gold), and **31** (red) at 295 K in acetonitrile.

hanced), while the Stark analyses afford larger β_0 values for the Fe^{II} complexes, in contrast to FF predictions.[34] TD-DFT calculations on the cations in **25** and **29** reveal pairs of orthogonally(x,y)-polarized degenerate transitions; the most intense low energy MLCT transitions involve LUMOs that are concentrated on the coordinated pyridyl rings, while the LUMOs involved in the next lowest energy MLCT transitions also have important contributions from the pyridinium rings (Figure 13).[34] These results agree with the empirical observation that the higher energy MLCT bands are more sensitive to changes in R (Figure 12).[34] Selected data for **25**−**31** are shown in Table 2.

VIII. Conclusions and Outlook

Our studies to date afford several key conclusions. Perhaps most importantly, the large β_0 responses of 1D dipolar Ru^{II} ammine complexes compare favorably with those of all but the very best known purely organic species, and Ru$^{III/II}$
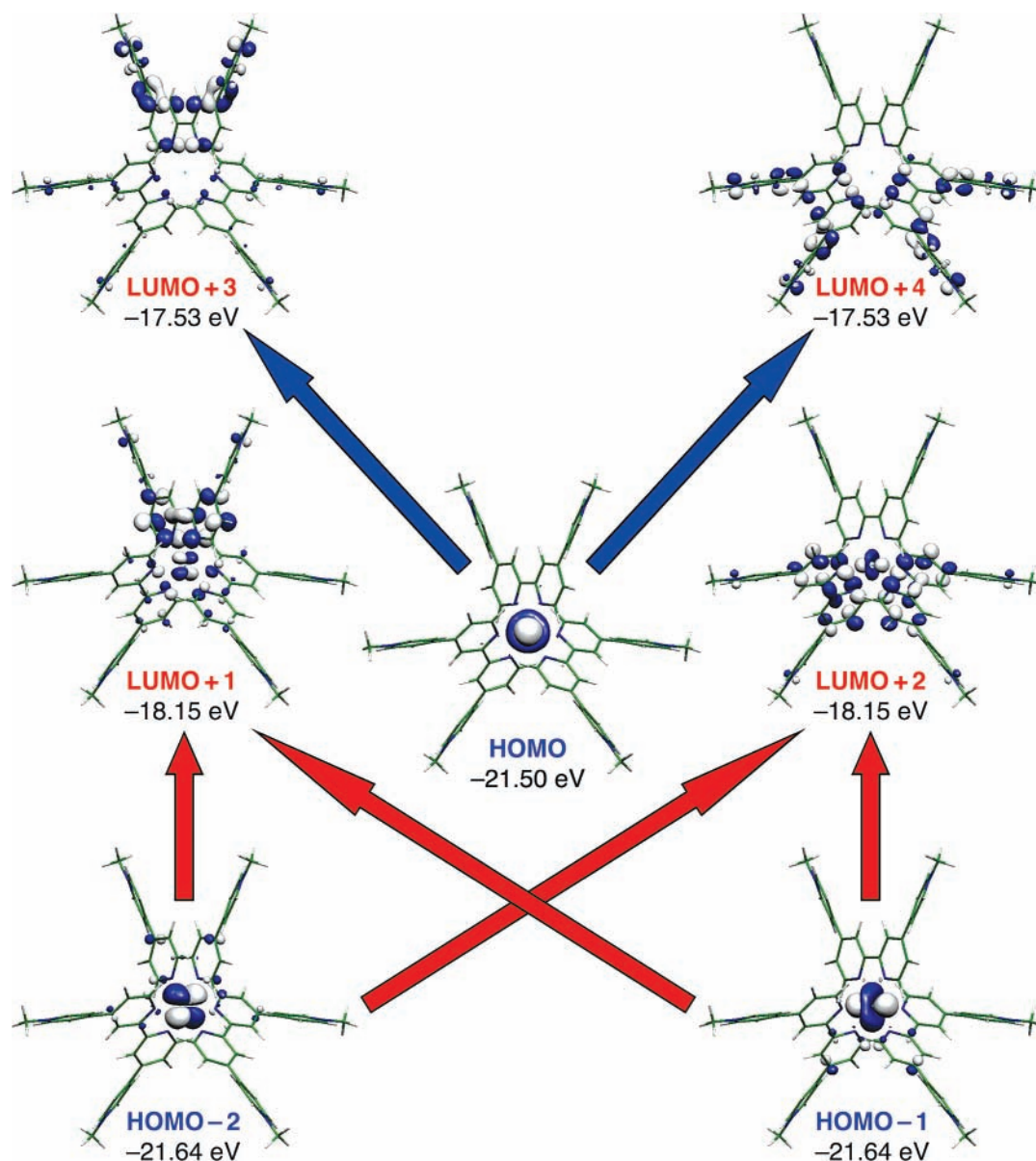
FIGURE 13. TD-DFT-derived 0.05 contour surface diagrams of the MOs involved in the MLCT excitations for the complex in **25**. The red arrows represent the dominant *x*- and *y*-polarized transitions corresponding with the low energy band, while the blue arrows represent the pairs of dominant *x*- and *y*-polarized transitions corresponding with the high energy band. The *z* axis is aligned with the C_3 axis, and the *y* axis is aligned with one of the C_2 axes. Adapted from ref 34.

redox allows facile reversible switching of β. However, extending polyenyl/ynyl systems is only partially reliable as an approach to increasing the NLO responses of Ru^{II} pyridyl complexes, in contrast with related purely organic pyridinium chromophores. Hence, while Ru^{II} ammine centers can act as better electron donors when compared with a classical 4-(dimethylamino)phenyl unit in relatively short molecules, the benefits of using a Ru^{II}-based donor are lost in extended systems. Moving to multidimensional species, we have found that connecting *cis*-{Ru^{II}(NH$_3$)$_4$}$^{2+}$ centers to pyridinium groups produces unusual charged 2D dipoles in which the off-diagonal β_{zyy} component dominates over β_{zzz}. Finally, ground-state octupolar D_3 chromophores comprising [M^{II}(bpy)$_3$]$^{2+}$ (M = Ru or Fe) cores with six peripheral pyridinium groups exhibit two substantial β components of equal magnitude but op-

posite sign ($\beta_{yyy} = -\beta_{yxx}$) which are associated with transitions to dipolar excited states.

So, what comes next? Currently there is still scope for further molecular-level studies, with the overall aim of optimizing the NLO properties of metallochromophores. An accompanying major objective will be to investigate further the possibilities for switching optical behavior in such compounds, especially multidimensional systems, via redox or protic changes. Of course, any real applications will require materials; these could be pure crystalline solids, but more likely ordered thin films or doped matrices, etc. Furthermore, other issues such as thermal/photochemical stability and transparency at technologically important wavelengths will have to be addressed. Whether such practical challenges can be met remains to be seen, but further intriguing fundamental scientific

discoveries undoubtedly await. It is also worth noting that NLO-based studies with metal complexes may have unforeseen spinoff relevance to other areas of molecular electronics/photonics, e.g., photovoltaic devices. Certainly, our work has helped to establish ruthenium complexes as versatile and fascinating NLO compounds with a promising future.

References

(1) (a) Kelley, T. W.; Baude, P. F.; Gerlach, C.; Ender, D. E.; Muyres, D.; Haase, M. A.; Vogel, D. E.; Theiss, S. D. Recent Progress in Organic Electronics: Materials, Devices, and Processes. *Chem. Mater.* **2004**, *16*, 4413–4422. (b) Maruccio, G.; Cingolania, R.; Rinaldi, R. Projecting the Nanoworld: Concepts, Results and Perspectives of Molecular Electronics. *J. Mater. Chem.* **2004**, *14*, 542–554.
(2) (a) Coe, B. J.; Curati, N. R. M. Metal Complexes for Molecular Electronics and Photonics. *Comments Inorg. Chem.* **2004**, *25*, 147–184. (b) Low, P. J. Metal Complexes in Molecular Electronics: Progress and Possibilities. *Dalton Trans.* **2005**, 2821–2824.
(3) (a) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997. (b) *Nonlinear Optical Properties of Matter: From Molecules to Condensed Phases*; Papadopoulos, M. G., Leszczynski, J., Sadlej, A. J., Eds.; Kluwer: Dordrecht, 2006.
(4) (a) Lacroix, P. G. Second-Order Optical Nonlinearities in Coordination Chemistry: The Case of Bis(salicylaldiminato)metal Schiff Base Complexes. *Eur. J. Inorg. Chem.* **2001**, 339–348. (b) Di Bella, S. Second-Order Nonlinear Optical Properties of Transition Metal Complexes. *Chem. Soc. Rev.* **2001**, *30*, 355–366. (c) Coe, B. J. Non-Linear Optical Properties of Metal Complexes. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Oxford, U.K., 2004; Vol. 9, pp 621–687.
(5) (a) Oudar, J. L. Optical Nonlinearities of Conjugated Molecules. Stilbene Derivatives and Highly Polar Aromatic Compounds. *J. Chem. Phys.* **1977**, *67*, 446–457. (b) Di Bella, S. On the Determination of the Molecular Static First Hyperpolarisability: How Reliable are Literature Data? *New J. Chem.* **2002**, *26*, 495–497.
(6) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Wostyn, K.; Clays, K.; Persoons, A.; Brunschwig, B. S.; Coles, S. J.; Gelbrich, T.; Light, M. E.; Hursthouse, M. B.; Nakatani, K. Quadratic Optical Nonlinearities of N-Methyl and N-Aryl Pyridinium Salts. *Adv. Funct. Mater.* **2003**, *13*, 347–357.
(7) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. Large Quadratic Hyperpolarizabilities with Donor–Acceptor Polyenes Exhibiting Optimum Bond Length Alternation: Correlation Between Structure and Hyperpolarizability. *Chem.—Eur. J.* **1997**, *3*, 1091–1104.
(8) Hendrickx, E.; Clays, K.; Persoons, A. Hyper-Rayleigh Scattering in Isotropic Solution. *Acc. Chem. Res.* **1998**, *31*, 675–683.
(9) Coe, B. J.; Chamberlain, M. C.; Essex-Lopresti, J. P.; Gaines, S.; Jeffery, J. C.; Houbrechts, S.; Persoons, A. Large Molecular Quadratic Hyperpolarizabilites in Donor/Acceptor-Substituted trans-Tetraammineruthenium(II) Complexes. *Inorg. Chem.* **1997**, *36*, 3284–3292.
(10) Coe, B. J.; Essex-Lopresti, J. P.; Harris, J. A.; Houbrechts, S.; Persoons, A. Ruthenium(II) Ammine Centres as Efficient Electron Donor Groups for Quadratic Non-Linear Optics. *Chem. Commun.* **1997**, 1645–1646.
(11) Coe, B. J.; Harris, J. A.; Harrington, L. J.; Jeffery, J. C.; Rees, L. H.; Houbrechts, S.; Persoons, A. Enhancement of Molecular Quadratic Hyperpolarizabilities in Ruthenium(II) 4,4'-Bipyridinium Complexes by N-Phenylation. *Inorg. Chem.* **1998**, *37*, 3391–3399.
(12) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Persoons, A.; Jeffery, J. C.; Rees, L. H.; Gelbrich, T.; Hursthouse, M. B. Tuning of Charge-Transfer Absorption and Molecular Quadratic Nonlinear Optical Properties in Ruthenium(II) Ammine Complexes. *J. Chem. Soc., Dalton Trans.* **1999**, 3617–3625.
(13) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Clays, K.; Olbrechts, G.; Persoons, A.; Hupp, J. T.; Johnson, R. C.; Coles, S. J.; Hursthouse, M. B.; Nakatani, K. Quadratic Nonlinear Optical Properties of N-Aryl Stilbazolium Dyes. *Adv. Funct. Mater.* **2002**, *12*, 110–116.
(14) Coe, B. J.; Harris, J. A.; Brunschwig, B. S. Electroabsorption Spectroscopic Studies of Dipolar Ruthenium(II) Complexes Possessing Large Quadratic Nonlinear Optical Responses. *J. Phys. Chem. A* **2002**, *106*, 897–905.
(15) Lin, C.-S.; Wu, K.-C.; Snijders, J. G.; Sa, R.-J.; Chen, X.-H. TDDFT and ab initio Study on the Quadratic Hyperpolarizabilities of trans-Tetraammineruthenium(II) Complexes. *Acta Chim. Sin.* **2002**, *60*, 664–668.
(16) Coe, B. J.; Jones, L. A.; Harris, J. A.; Sanderson, E. E.; Brunschwig, B. S.; Asselberghs, I.; Clays, K.; Persoons, A. Molecular Quadratic Non-Linear Optical Properties of Dipolar trans-Tetraammineruthenium(II) Complexes with Pyridinium and Thiocyanate ligands. *Dalton Trans.* **2003**, 2335–2341.
(17) Coe, B. J.; Beyer, T.; Jeffery, J. C.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E. A Spectroscopic, Electrochemical and Structural Study of Polarizable, Dipolar Ruthenium(II) Arsine Complexes as Models for Chromophores with Large Quadratic Non-Linear Optical Responses. *J. Chem. Soc., Dalton Trans.* **2000**, 797–803.
(18) Coe, B. J.; Harries, J. L.; Harris, J. A.; Brunschwig, B. S.; Coles, S. J.; Light, M. E.; Hursthouse, M. B. Syntheses, Spectroscopic and Molecular Quadratic Nonlinear Optical Properties of Dipolar Ruthenium(II) Complexes of the Ligand 1,2-Phenylenebis(dimethylarsine). *Dalton Trans.* **2004**, 2935–2942.
(19) (a) Coe, B. J. Molecular Materials Possessing Switchable Quadratic Nonlinear Optical Properties. *Chem.—Eur. J.* **1999**, *5*, 2464–2471. (b) Asselberghs, I.; Clays, K.; Persoons, A.; Ward, M. D.; McCleverty, J. Switching of Molecular Second-Order Polarisability in Solution. *J. Mater. Chem.* **2004**, *14*, 2831–2839.
(20) Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. Efficient, Reversible Redox-Switching of Molecular First Hyperpolarizabilities in Ruthenium(II) Complexes Possessing Large Quadratic Optical Nonlinearities. *Angew. Chem., Int. Ed.* **1999**, *38*, 366–369.
(21) Sakaguchi, H.; Gomez-Jahn, L. A.; Prichard, M.; Penner, T. L.; Whitten, D. G.; Nagamura, T. Subpicosecond Photoinduced Switching of Second-Harmonic Generation from a Ruthenium Complex in Supported Langmuir—Blodgett Films. *J. Phys. Chem.* **1993**, *97*, 1474–1476.
(22) Selected examples: (a) Weyland, T.; Ledoux, I.; Brasselet, S.; Zyss, J.; Lapinte, C. Nonlinear Optical Properties of Redox-Active Mono-, Bi-, and Trimetallic σ-Acetylide Complexes Connected through a Phenyl Ring in the Cp*(dppe)Fe Series. An Example of Electro-Switchable NLO Response. *Organometallics* **2000**, *19*, 5235–5237. (b) Malaun, M.; Reeves, Z. R.; Paul, R. L.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.; Asselberghs, I.; Clays, K.; Persoons, A. Reversible Switching of the First Hyperpolarisability of an NLO-Active Donor-Acceptor Molecule Based on Redox Interconversion of the Octamethylferrocene Donor Unit. *Chem. Commun.* **2001**, 49–50. (c) Cifuentes, M. P.; Powell, C. E.; Humphrey, M. G.; Heath, G. A.; Samoc, M.; Luther-Davies, B. Organometallic Complexes for Nonlinear Optics. 24. Reversible Electrochemical Switching of Nonlinear Absorption. *J. Phys. Chem. A* **2001**, *105*, 9625–9627. (d) Sporer, C.; Ratera, I.; Ruiz-Molina, D.; Zhao, Y.-X.; Vidal-Gancedo, J.; Wurst, K.; Jaitner, P.; Clays, K.; Persoons, A.; Rovira, C.; Veciana, J. A Molecular Multiproperty Switching Array Based on the Redox Behavior of a Ferrocenyl Polychlorotriphenylmethyl Radical. *Angew. Chem., Int. Ed.* **2004**, *43*, 5266–5268.
(23) Coe, B. J.; Jones, L. A.; Harris, J. A.; Brunschwig, B. S.; Asselberghs, I.; Clays, K.; Persoons, A. Highly Unusual Effects of π-Conjugation Extension on the Molecular Linear and Quadratic Nonlinear Optical Properties of Ruthenium(II) Ammine Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 862–863.

(24) Coe, B. J.; Jones, L. A.; Harris, J. A.; Brunschwig, B. S.; Assel-berghs, I.; Clays, K.; Persoons, A.; Garín, J.; Orduna, J. Syntheses and Spectroscopic and Quadratic Nonlinear Optical Properties of Extended Dipolar Complexes with Ruthenium(II) Ammine Electron Donor and *N*-Methylpyridinium Acceptor Groups. *J. Am. Chem. Soc.* **2004**, *126*, 3880–3891.

(25) Coe, B. J.; Harries, J. L.; Helliwell, M.; Brunschwig, B. S.; Harris, J. A.; Asselberghs, I.; Hung, S.-T.; Clays, K.; Horton, P. N.; Hursthouse, M. B. Syntheses and Quadratic Optical Nonlinearities of Ruthenium(II) Complexes with Ethynyl-Connected *N*-Methylpy-ridinium Electron Acceptors. *Inorg. Chem.* **2006**, *45*, 1215–1227.

(26) Selected examples: (a) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. Experimental Investigations of Organic Molecular Nonlinear Optical Polariz-abilities. 2. A Study of Conjugation Dependences. *J. Phys. Chem.* **1991**, *95*, 10643–10652. (b) Morley, J. O. Theoretical Study of the Electronic Structure and Hyperpolarizabilities of Donor–Acceptor Cumulenes and a Comparison with the Corresponding Polyenes and Polyynes. *J. Phys. Chem.* **1995**, *99*, 10166–10174.

(27) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. Calculation and Electronic Description of Quadratic Hyperpolarizabilities. Toward a Molecular Understanding of NLO Responses in Organotransi-tion Metal Chromophores. *J. Am. Chem. Soc.* **1992**, *114*, 10338–10357. (b) Kanis, D. R.; Lacroix, P. G.; Ratner, M. A.; Marks, T. J. Electronic Structure and Quadratic Hyperpolarizabilities in Orga-notransition-Metal Chromophores Having Weakly Coupled π-Net-works. Unusual Mechanisms for Second-Order Response. *J. Am. Chem. Soc.* **1994**, *116*, 10089–10102. (c) Reis, H.; Raptis, S. G.; Papadopoulos, M. G. Comparison of the Non-Linear Optical Properties of a Dimethylaminostilbene Derivative Containing a Molybdenum Mononitrosyl Redox Centre and of *p,p*′-Dimethyl-aminonitrostilbene, Calculated by *ab-initio* Methods. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3901–3905.

(28) Coe, B. J.; Harris, J. A.; Clays, K.; Persoons, A.; Wostyn, K.; Brunschwig, B. S. A Comparison of the Pentaammine(pyridyl)-ruthenium(II) and 4-(Dimethylamino)phenyl Groups as Electron Donors for Quadratic Non-Linear Optics. *Chem. Commun.* **2001**, 1548–1549.

(29) Coe, B. J.; Harris, J. A.; Brunschwig, B. S.; Garín, J.; Orduna, J.; Coles, S. J.; Hursthouse, M. B. Contrasting Linear and Quadratic Nonlinear Optical Behavior of Dipolar Pyridinium Chromophores with 4-(Dimethylamino)phenyl or Ruthenium(II) Ammine Electron Donor Groups. *J. Am. Chem. Soc.* **2004**, *126*, 10418–10427.

(30) Representative examples: (a) Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Leung, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. (Dicyanomethylene)pyran Derivatives with *C*₂ᵥ Sym-metry: An Unusual Class of Nonlinear Optical Chromophores. *J. Am. Chem. Soc.* **1996**, *118*, 12950–12955. (b) Di Bella, S.; Fragalà, I.; Ledoux, I.; Zyss, J. Dipolar Donor–Acceptor-Substi-tuted Schiff Base Complexes with Large Off-Diagonal Second-Order Nonlinear Optical Tensor Components. *Chem.—Eur. J.* **2001**, *7*, 3738–3743. (c) Yang, M.-L.; Champagne, B. Large Off-Diagonal Contribution to the Second-Order Optical Nonlinearities of Λ-Shaped Molecules. *J. Phys. Chem. A* **2003**, *107*, 3942–3951.

(31) Coe, B. J.; Harris, J. A.; Brunschwig, B. S. Determination of the Molecular Quadratic Non-Linear Optical Responses of V-Shaped Metallochromophores by using Stark Spectroscopy. *Dalton Trans.* **2003**, 2384–2386.

(32) Coe, B. J.; Harris, J. A.; Jones, L. A.; Brunschwig, B. S.; Song, K.; Clays, K.; Garín, J.; Orduna, J.; Coles, S. J.; Hursthouse, M. B. Syntheses and Properties of Two-Dimensional Charged Nonlinear Optical Chromophores Incorporating Redox-Switchable *cis*-Tet-raammineruthenium(II) Centers. *J. Am. Chem. Soc.* **2005**, *127*, 4845–4859.

(33) Maury, O.; Le Bozec, H. Molecular Engineering of Octupolar NLO Molecules and Materials Based on Bipyridyl Metal Complexes *Acc. Chem. Res.* **2005**, *38*, 691–704.

(34) Coe, B. J.; Harris, J. A.; Brunschwig, B. S.; Asselberghs, I.; Clays, K.; Garín, J.; Orduna, J. Three-Dimensional Nonlinear Optical Chromophores Based on Metal-to-Ligand Charge-Transfer from Ruthenium(II) or Iron(II) Centers. *J. Am. Chem. Soc.* **2005**, *127*, 13399–13410.

AR050225K