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Nonlinear Optical and Two-Photon Absorption Properties of Octupolar Tris(bipyridyl)metal Complexes

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The linear (absorption and emission) and nonlinear optical (NLO) properties of a series of D_3 [(Fe(II), Ru(II), Ni(II), Cu(II), Zn(II)] octupolar metal complexes featuring the 4,4′-bis[(dibutylamino)styryl]-2,2′-bipyridine ligand are reported. Zinc(II), nickel(II), and copper(II) complexes exhibit similar absorption spectra in the visible region ($\lambda_{\mathrm{ILCT}} = 474-476$ nm) which are assigned to intraligand charge-transfer (ILCT) bands. The quadratic and cubic NLO properties are strongly influenced by the nature of the metallic center. Harmonic light scattering studies at $\lambda = 1.91$ μm reveal that these chromophores display large first hyperpolarizabilities $\beta_{1.91}$ in the range of $(211-340) \times 10^{-30}$ esu; replacing the Zn(II) metal ion by Ni(II) or Cu(II) results in a decrease of the static β_0 coefficient by a factor of 1.5−1.6. *Z*-scan measurements at 765 and 965 nm reveal relatively large two-photon absorption cross-sections [$650 < \sigma_2 < 2200$ GM], showing that both β and σ_2 values can be tuned by simple modification of the metal ion.

Introduction

Since the early 1990s and the pioneering work of Zyss and co-workers,[1] the recognition of the increased potential of octupolar molecules in second-order nonlinear optics has sparked intense research. These molecules are also attractive for third-order nonlinear applications, including two-photon absorption (TPA), and recent experimental and theoretical studies on organic octupolar molecules with extended conjugation have revealed moderate to exceptionally large TPA cross-sections σ_2.[2] The TPA process has attracted significant recent attention, because compounds with strong TPA properties are required for applications in the field of materials science for optical storage,[3] optical limiting,[4] and microfabrication,[5] as well as in biology for imaging,[6] drug delivery,[7] or photodynamic therapy.[8]

The third-order optical nonlinearities of a large number of coordination and organometallic complexes have been reported over the past decade.[9] By contrast, a relatively small number of octupolar metal complexes have been investigated for their third-order and two-photon absorption properties. Recent studies have highlighted the potential of organometallic alkynylmetal complexes in this field,[10] and exceptionally high σ_2 values have been reported for pseudotetrahedral (D_{2d}) Schiff base zinc(II) and copper(I) complexes.[11] Very recently, TPA properties of iron(II) and ruthenium(II) trischelate complexes of quaterpyridinium ligands have also been investigated theoretically and experimentally by *Z*-scan, showing weak to moderate two-photon absorption behavior.[12]

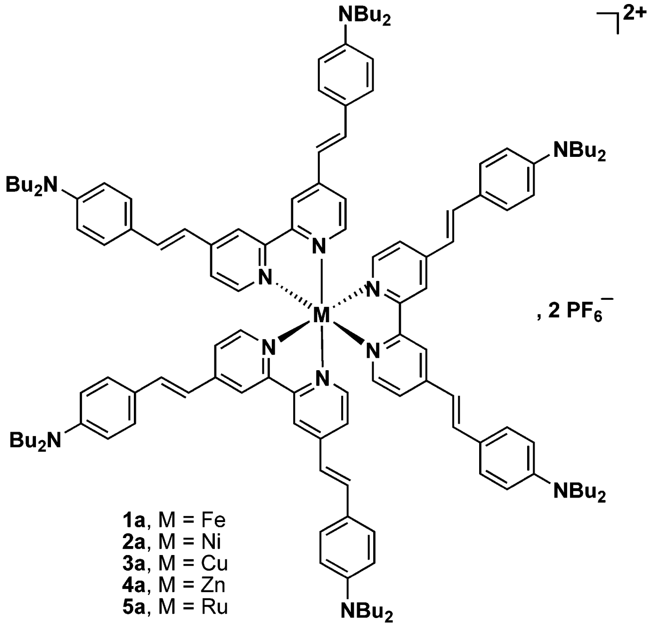

Figure 1. Chemical structure of **1a**−**5a**.

We have previously described quadratic nonlinear optical (NLO) studies on octupolar tris[4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridine]metal(II) complexes **1a** (Fe), **4a** (Zn), and **5a** (Ru), which possess very large molecular first hyperpolarizability coefficients β.[13] Interestingly, a recent theoretical calcula-

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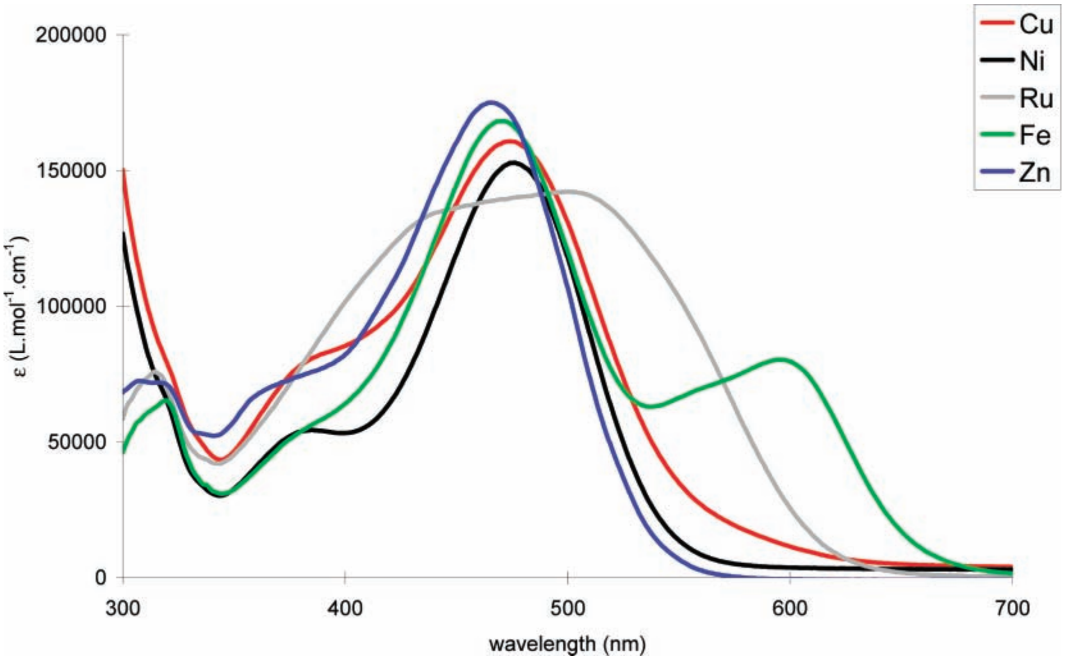

Figure 2. UV−vis spectra of **1a**−**5a** in dichloromethane.

TABLE 1: Absorption, Emission, and Quadratic Nonlinear Optical Data[a]

compd	$\lambda_{max}{}^{b}$ ($\epsilon_{max}{}^{c}$)	$\lambda_{em}{}^{b}$	$\beta_{1.91}{}^{d}$	$\beta_0{}^{d}$
1a (M = Fe)	470 (168), 573 (75)	645	235 ± 35^{f}	
2a (M = Ni)	476 (153)	627	211 ± 32	149 ± 22
3a (M = Cu)	474 (161)	630	229 ± 34	161 ± 24
4a (M = Zn)	474 (175)	644	340 ± 51^{f}	240 ± 36
5a (M = Ru)	446 (142), 513 (150)	721^{e}	340 ± 51^{f}	

[a] Measurements were carried out in dichloromethane. [b] Units of nanometers. [c] Units of 10^3 M^{-1} cm^{-1}. [d] Units of 10^{-30} esu. [e] ^{3}MLCT emission. [f] Reference 13c.

tion by Liu et al. predicted a very large TPA response (σ_2(calcd) = 19151 GM at λ_{max} = 827 nm) for the zinc complex **4a**.[14] The experimental measurement of such tris(bipyridine)metal complexes therefore seemed to be very appealing. Herein we report the third-order NLO and TPA data for the series of metallooctupoles **1a**−**5a** (Figure 1), including the new tris(bipyridyl)metal complexes **2a** (M = Ni) and **3a** (M = Cu). The linear and second-order nonlinear properties of **2a** and **3a** are also described, and the important role of the central metal ion in both β and σ_2 values is underlined.

Experimental Section

General Physical Measurements. UV−vis spectra were recorded on a Kontron Uvikon 941 spectrophotometer in diluted dichloromethane solution (ca. 10^{-5} M). Fluorescence experiments were performed in dilute dichloromethane solution (ca. 10^{-5} M) using a PTI spectrometer. Elemental analyses were performed at the Centre Regional de Mesures Physiques de l'Ouest (Rennes, France).

Materials. The ligand 4,4′-bis[(dibutylamino)styryl]-2,2′-bipyridine (DBAS-bpy, **a**)[15] and the complexes [Fe(DBAS-bpy)$_3$](PF$_6$)$_2$ (**1a**),[13c] [Zn(DBAS-bpy)$_3$](PF$_6$)$_2$ (**4a**),[13c] and [Ru(DBAS-bpy)$_3$](PF$_6$)$_2$ (**5a**)[13c] were prepared as described earlier. All other reagents were obtained commercially and used without purification.

HLS Measurements. The 1.91 μm fundamental beam was emitted by a high-pressure (30 bar), 50 cm long Raman cell pumped by a Nd^{3+}:YAG laser operating at 1.06 μm and providing pulses of 15 ns duration at a 10 Hz repetition rate. The back-scattered 1.91 μm Raman emission was collected at a 45° incidence angle by use of a dichroic mirror to eliminate most of the residual 1.06 μm pump photons. Our reference sample was a concentrated (10^{-2} M) solution of ethyl violet, its octupolar $\beta = \beta_{J=3}$ value being calibrated at 1.91 μm with respect to that of the *N*-(4-nitrophenyl)prolinol (NPP) reference dipolar molecule, leading to $\beta = 170 \times 10^{-30}$ esu for ethyl violet at 1.91 μm.[16a] It must be noted that most classical organic solvents are not transparent at 1.91 μm. Chlorinated solvents are an exception, so dichloromethane was used for the HLS measurements. The HLS photons at 955 nm were focused onto a Hamamatsu R632-01 photomultiplier tube using two collecting lenses. The signal detected was then sampled and averaged using a boxcar and processed by a computer. The reference beam was collected at a 45° incidence angle by a glass plate and focused onto a highly nonlinear NPP powder, which was used as the frequency doubler.[16b] The variation of the scattered second harmonic intensity from the solution was recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, both signals scaling as the square of the incoming fundamental intensity. Values for β were then inferred from the slopes of the resulting lines.[16c]

***Z*-Scan Measurements.** The measurements of the real and imaginary parts of the third-order polarizability γ were performed at 765 and 965 nm using a laser system consisting of a Clark-MXR CPA-2001 regenerative amplifier and a Light Conversion TOPAS optical parametric amplifier (OPA) with a frequency-doubling attachment and using doubling of the signal or doubling of the idler for the two wavelengths, respectively. The system provided approximately 150 fs pulses at a repetition rate that was chosen to be 250 or 98 Hz in some measurements

TABLE 2: Cubic Nonlinear Optical Data at 765 and 965 nm[a]

compd	765 nm				965 nm			
	λ_{real}[b]	γ_{imag}[b]	$\lvert\gamma\rvert$[b]	σ_2[c]	γ_{real}[b]	γ_{imag}[b]	$\lvert\gamma\rvert$[b]	σ_2[c]
1a (M = Fe)	−8600 ± 2200	7100 ± 1000	11000 ± 2500	1900 ± 300				
2a (M = Ni)	−4700 ± 1000	2400 ± 250	5300 ± 1200	650 ± 100	−2500 ± 600	6600 ± 500	7000 ± 600	1100 ± 100
3a (M = Cu)	−6300 ± 3700	3900 ± 900	7400 ± 4000	1050 ± 300	−8600 ± 1000	4900 ± 800	10000 ± 1000	830 ± 130
4a (M = Zn)	−5300 ± 3600	6400 ± 1600	8300 ± 4000	1700 ± 500	−5800 ± 500	5100 ± 200	7700 ± 500	860 ± 20
5a (M = Ru)	−4300 ± 1600	8200 ± 800	9200 ± 2000	2200 ± 300				

[a] Measurements were carried out in dichloromethane. [b] Units of 10^{-36} esu. [c] Units of 10^{-50} cm^4 s.

(the repetition rate was reduced from the usual operating rate of 1 kHz to reduce the possibility of thermal contributions to the nonlinear effects). Closed- and open-aperture *Z*-scans[17] were recorded for dichloromethane solutions of the compounds, which were placed in 1 mm path length glass cells. The focal spot had a radius w_0 in the range 40−70 μm. This resulted in the Rayleigh length, $Z_R = (\pi w_0^2)/\lambda$, being greater than 3 mm; measurements of solutions in 1 mm thick glass cells with ca. 1 mm thick glass walls could therefore be treated in the thin sample approximation.[18]

Due to deviations from a Gaussian character of the beam from the OPA, the truncated Airy pattern approach discussed by Rhee et al.[19] was occasionally used. The measurements were calibrated against *Z*-scans taken on the pure solvent and on silica and glass plates of thicknesses in the range 1−3 mm. The nonlinearity of silica was taken as $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1}.[20] The light intensities were determined from *Z*-scan measurements on the silica plates and adjusted to obtain nonlinear phase shifts for the measured samples in the range 0.5−1.0 rad, corresponding to peak intensities on the order of 100 GW cm^{-2}. The real and imaginary parts of the hyperpolarizability of the solute were obtained from concentration dependences of the real and imaginary parts of the nonlinear phase shift[18] obtained by numerical fitting of the open and closed aperture scans according to eqs 27 and 30 of ref 17. Typically, the accuracy of the *Z*-scan curve fit allowed for the determination of the phase shift with an accuracy of a few percent. The two-photon absorption cross sections (which are proportional to the imaginary parts of the hyperpolarizabilities) were also calculated from the concentration dependences of the imaginary part of the phase shift.

Syntheses. *[Ni(DBAS-bpy)$_3$](PF$_6$)$_2$ (**2a**).* $NiCl_2 \cdot 6H_2O$ (77.3 mg, 0.33 mmol) and 3 equiv of DBAS-bpy (**a**) (600 mg, 1.0 mmol) were dissolved in ethanol (30 mL). The mixture was heated under reflux for 15 h. The solution was then cooled to room temperature, and an excess of $NaPF_6$ (554 mg, 3.3 mmol) in water (250 mL) was added. The orange-red precipitate was filtered off and washed with pentane. The product was then dissolved in dichloromethane and dried with $MgSO_4$. After filtration and evaporation of the solvent, the solid was further washed with pentane and dried under vacuum to afford an orange powder: yield 580 mg (80%); UV−vis (CH_2Cl_2) λ_{max} = 476 nm (210000). Anal. Calcd for $C_{126}H_{162}F_{12}N_{12}NiP_2$: C, 68.00; H, 7.44; N, 7.66. Found: C, 67.66; H, 7.36; N, 7.50.

*[Cu(DBAS-bpy)$_3$](PF$_6$)$_2$ (**3a**).* $CuCl_2 \cdot 2H_2O$ (32.2 mg, 0.19 mmol) and 3 equiv of DBAS-bpy (**a**) (350 mg, 0.57 mmol) were dissolved in ethanol (15 mL). The mixture was heated under reflux for 15 h. The solution was then cooled to room temperature, and an excess of $NaPF_6$ (319 mg, 1.90 mmol) in water (250 mL) was added. The orange-red precipitate was filtered off and washed with pentane. The product was then dissolved in dichloromethane and dried with $MgSO_4$. After filtration and evaporation of the solvent, the solid was further washed with pentane and dried under vacuum to afford an orange powder: yield 300 mg (80%); UV−vis (CH_2Cl_2) λ_{max} = 474 nm (155000). Anal. Calcd for $C_{126}H_{162}CuF_{12}N_{12}P_2$: C, 68.85; H, 7.43; N, 7.65. Found: C, 68.64; H, 7.61; N, 7.60.

Results and Discussion

The synthesis of bipyridyl chromophore **a** as well as the corresponding octupolar [(**a**)$_3$M](PF$_6$)$_2$ [M = Fe (**1a**), Zn (**4a**), Ru (**5a**)] complexes were described elsewhere.[13c,15] The paramagnetic tris(bipyridyl) dicationic Ni(II) and Cu(II) complexes **2a** and **3a** were classically obtained from the corresponding metal dichloride and 3 equiv of **a** in refluxing ethanol followed by an anion metathesis with sodium hexafluorophosphate (Figure 1).

The new complexes **2a** and **3a** were fully characterized by UV−vis and emission spectroscopy (Table 1) and gave satisfactory microanalyses (see the Experimental Section). As is the case with the zinc complex **4a**, complexes **2a** and **3a** exhibit only one strong absorption band in the visible region (λ_{ILCT} = 474−476 nm), which are assigned to intraligand charge-transfer (ILCT) bands. The complexation of ligand **a** induces a substantial bathochromic shift of the absorption band, the results indicating that this shift is rather insensitive to the nature of the central metal ion (Figure 2). Photoluminescence is also observed for **2a** and **3a** in diluted dichloromethane solution (Table 1). These complexes exhibit a broad structureless emission band assigned to ligand-centered emission, with large Stokes shifts ranging from 5059 cm^{-1} for **2a** to 5224 cm^{-1} for **3a** and the λ_{em} values decreasing slightly in the order $Zn^{2+} \approx Fe^{2+} > Cu^{2+} \approx Ni^{2+}$.[21]

The harmonic light scattering (HLS) technique was used for the molecular first hyperpolarizability (β) measurements. The measurements were performed at a fundamental wavelength of 1.91 μm to render any contribution to the HLS signal from two-photon fluorescence negligible. The values of $\beta_{1.91}$ and static hyperpolarizabilities β_0 for **2a** and **3a** are given in Table 1, together with previously reported data for **1a**, **4a**, and **5a**.[13c] It is appropriate to compare the β_0 values of **2a** and **3a** to that of the zinc complex **4a**, because all these species exhibit similar absorption spectra. The comparison is less accurate with the HLS data of **1a** (Fe) and **5a** (Ru), since β_0 cannot be derived for these complexes which display additional metal-to-ligand charge-transfer (MLCT) transitions in the visible region that are directionally opposed to the ILCT transitions.[13c] These data clearly show that replacing the Zn(II) metal ion by Ni(II) or Cu(II) results in a substantial decrease of β_0 by a factor of 1.5−1.6. This is somewhat surprising if we consider that **2a**−**4a** display an ILCT transition at approximately the same energy and the oscillator strengths are also quite similar. Other factors such as the geometry of the complexes can be taken into account, particularly for the d^9 Cu(II) **3a**, which should possess a strongly distorted octahedral configuration.[22] We note also that a similar enhancement (by a factor of 1.7−2.0) is seen on proceeding from Ni(II) and Cu(II) cyano Schiff base complexes

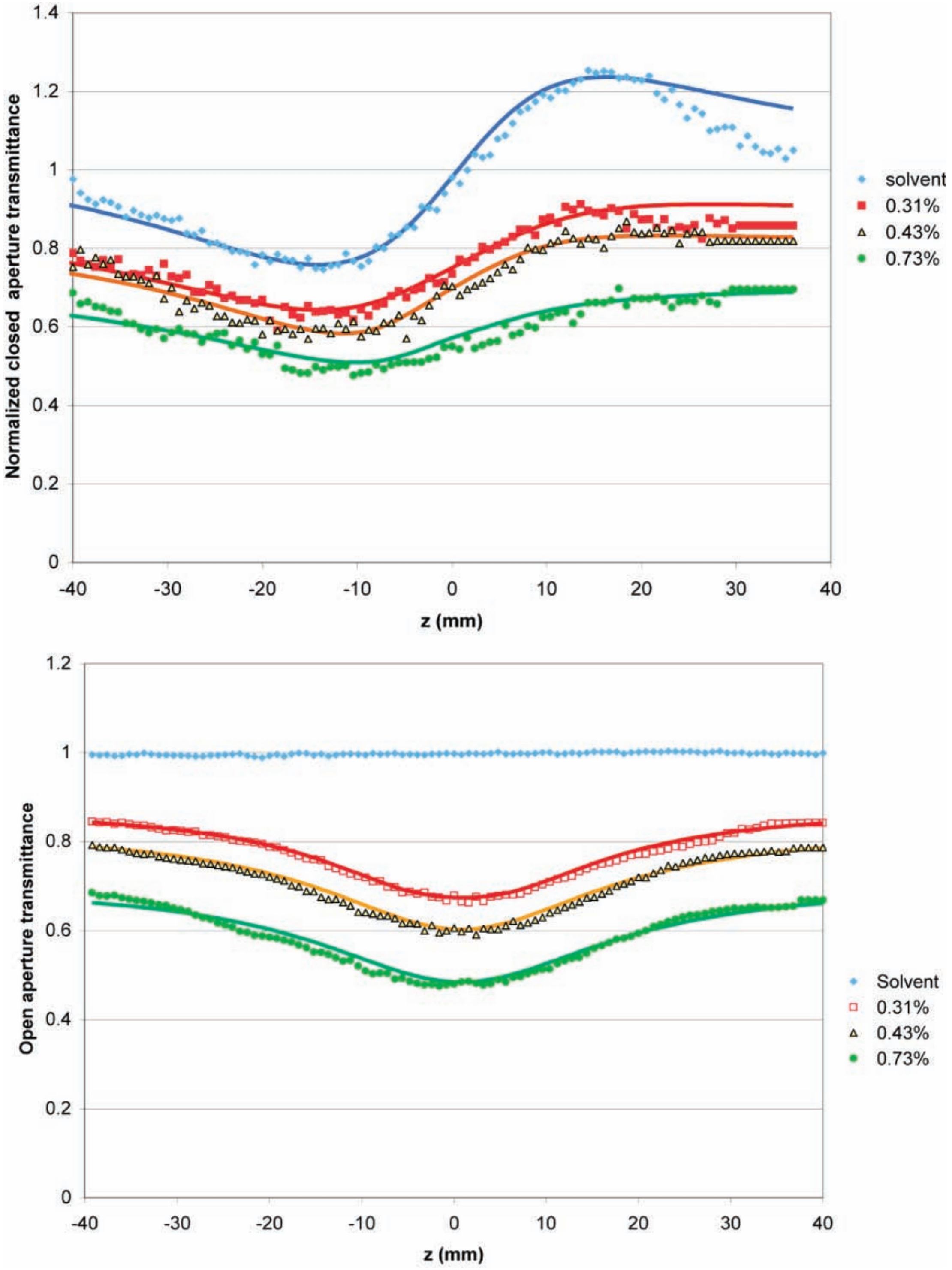

Figure 3. Closed-aperture (top) and open-aperture (bottom) *Z*-scan traces for dichloromethane solvent and three concentrations of **3a** at 965 nm. The transmittance values have been normalized to that of the solvent at low power, taken to be 1.0. Note that low-power transmittances of the three solutions amount to 0.842, 0.787, and 0.663, respectively, for the three concentrations marked in the figure.

to the corresponding Zn(II) complex;[23] similar to those in the present study, these complexes have almost coincident absorption maxima, and the β enhancement could not be satisfactorily explained. Although the trend observed in Table 1 is not well understood, this result evidences the strong influence of the central metal ion on the quadratic nonlinear optical responses of such complexes.

Molecular third-order nonlinearities were determined in dichloromethane by *Z*-scan at 765 and 965 nm for the Ni, Cu, and Zn compounds. The latter wavelength was chosen to correspond to twice the value of the main one-photon absorption wavelength peak for the compounds. The real and imaginary parts of the third-order polarizability γ as well as the TPA cross sections σ_2 (which are related to γ_{imag}) are collected in Table 2, and typical *Z*-scan traces are depicted in Figure 3. It should be noted that the copper compound showed relatively strong one-photon absorption at the measurement wavelength of 765 nm and a weaker absorption at 965 nm, which resulted in the need for an appropriate correction in the computation of the nonlinear properties of its solutions. In contrast, the remaining compounds showed insignificant absorption at 765 and 965 nm at the concentrations at which they were examined (approximately 0.3−1%, w/w).

The five compounds have broadly similar nonlinear properties at 765 nm, being strong two-photon absorbers and exhibiting strongly negative real parts of the third-order polarizability. Large error brackets do not allow for comment on the effect of metal variation on the magnitudes of the real parts of γ, all values being similar although that for Fe is greater than those for Ni and Ru. $|\gamma|$ values are less sensitive to the effects of wavelength dispersion and are arguably a better parameter for assessing cubic NLO merit; examination of these data reveals the trend Fe ≥ Ru ≥ Zn ≥ Cu ≥ Ni at 765 nm. In contrast to the γ_{real} data, there are meaningful differences between the values of the imaginary parts of γ and therefore between the σ_2 values. The following conclusions can be drawn from these data: (i) large TPA cross sections are observed for **1a**−**5a** (in the range 650−2200 GM), and (ii) the nickel and to a lesser extent copper chromophores have lower σ_2 values than those found for the three other complexes (Ru ≥ Fe ≥ Zn ≥ Cu > Ni).

Complexes **2a**−**4a** were also examined at 965 nm, all complexes exhibiting self-defocusing with a γ_{real} trend of Ni < Zn < Cu and $|\gamma|$ varying as Ni ≈ Zn < Cu. All complexes are two-photon absorbers at this wavelength, with σ_2 values following the order Cu ≈ Zn < Ni. Thus, while absolute values of the NLO coefficients vary at the two wavelengths, the signs remain invariant, and the data vary by at most a factor of 2−3.

A major difficulty is in ensuring that one estimates TPA maxima. While it is possible to resort to a point-by-point TPA spectral determination,[24] this is very time-consuming. Recent theoretical studies of **4a** carried out simultaneously with our current studies (but in which the butyl groups have been replaced with computationally easier methyl groups) predict one-photon absorption maxima at 461 and 468 nm[14] or 463 and 475 nm[25] and two-photon maxima at 827 and 943 nm[14] or 603, 822, and 949 nm.[25] Our approach in the present work was to evaluate the TPA merit at wavelengths corresponding to twice the experimental linear optical absorption maxima, and the longer wavelength studies at 965 nm can usefully be compared with the theoretical results at 943−949 nm. The experimental result (860 ± 20 GM) is significantly lower than the outcome from theory (9965 GM,[14] 4132 GM[25]), a marked difference despite the slight shift in wavelength; this possibly highlights a problem with current computational capabilities for these systems.

Conclusions

In this study we have described the linear properties and second- and third-order nonlinearities of a series of octupolar tris[4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridine]metal(II) complexes. These compounds are found to display relatively large first hyperpolarizabilities [211×10^{-30} esu < $\beta_{1.91}$ < 340×10^{-30} esu] and TPA cross section values [650 GM < σ_2(765 nm) < 2200 GM]. Tuning the β and σ_2 values is made possible by simple modification of the metal ion. These results point out the important role of the metallic core not only as a template, but also for its direct participation in the NLO activity, which, however, is still not well understood.[26] Furthermore, the σ_2 values are significantly larger than those recently reported by Coe et al.[12] for tris(bipyridine)iron(II) and -ruthenium(II) complexes substituted by electron-acceptor pyridinium groups [σ_2(750 nm) = 4−180 GM]. Thus, this work also indicates the importance of π-donor-conjugated substituents, and consequently of ILCT vs MLCT transitions, to enhance the two-photon absorption properties of such chromophores and suggests that the two-photon activity of D_3 metal tris(bipyridyl) complexes could be significantly enhanced upon increasing the π-conjugated backbone, i.e., by using ligands such as 4,4′-bis-[(dibutylamino)distyryl]-2,2′-bipyridine for which a record β_0 value of 655×10^{-30} esu was obtained with Zn(II).[13c] These results will be reported in due course.

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