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Terpyridine Zn(II), Ru(III) and Ir(III) complexes as new asymmetric chromophores for nonlinear optics: first evidence for a shift from positive to negative value of the quadratic hyperpolarizability of a ligand carrying an electron donor substituent upon coordination to different metal centres

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The synthesis of 4′-(C_6H_4-*p*-NBu_2)-2,2′:6′,2″-terpyridine and the strongly enhanced second-order NLO response of its Zn(II), Ru(III) and Ir(III) complexes are reported, evidencing for the first time a shift from positive to negative value of the ligand quadratic hyperpolarizability by varying the nature of the metal centre.

Metal complexes of various pyridines,[1a–e] bipyridines[2] and phenanthrolines[1b,f] have been studied as molecules with enhanced second-order nonlinear optical (NLO) responses. These ligands, when bearing an electron donor substituent, upon coordination, show increased quadratic hyperpolarizability β_{vec} as measured by the Electric Field Induced Second Harmonic generation (EFISH) method.[3] This is due to a red shift of the intraligand charge transfer (ILCT) transition[1d,e,4a] which can be enhanced by increasing the acceptor properties of the metal centre.[1e] Besides chelation, imposing a rather planar arrangement of the π-delocalized system of flexible bipyridines, can lead to a stronger effect.[1f,2b] Therefore we investigated complexes with metal ions in relatively high oxidation state of other polychelated nitrogen donor π-delocalized ligands such as terpyridines carrying an electron donor substituent. Metal complexes of terpyridines have been studied for their photochemical and photophysical properties,[5] but to our knowledge, their NLO properties have never been investigated. Here, we report preliminary findings on an unexpected effect on β_{vec} of 4′-(C_6H_4-*p*-NBu_2)-2,2′:6′,2″-terpyridine (L) by coordination to Ru(III) and Ir(III).

This ligand was prepared (60% yield) by condensation of 4-(dibutylamino)benzaldehyde with 2-acetylpyridine (molar ratio 1 : 2) in the presence of ${}^tBuOK$ and NH_4OAc.[6] Further reaction with a stoichiometric amount of ZnY_2 (Y = Cl, CF_3CO_2) or MCl_3 (M = Ir, Ru) afforded [ZnY_2L] and [MCl_3L].[7] Because the ruthenium complex was not soluble enough in $CHCl_3$ for an accurate determination of either the dipole moment[8] or β_{vec}, the more soluble trifluoroacetyl derivative was prepared by exchange of the chloride ligand with silver trifluoroacetate.[7]

The dipole moment enhancement (μ EF) upon coordination of L to Zn(II) with different ancillary ligands Y (Table 1; μ EF = 3.8 and 4.7 for Y = Cl and CF_3CO_2, respectively, in accord with the increased electron withdrawing strength of Y) is higher than that occurring for other chelating nitrogen donor π-delocalized ligands (μ EF = 1.5–2.7).[1f,2b] This could be attributed to the trigonal bipyramidal geometry of terpyridine Zn(II) complexes[9] instead of the typical tetrahedral geometry of other chelated Zn(II) complexes. UV–visible spectra in $CHCl_3$ of all complexes (Table 1) show one strong absorption band around 416–465 nm attributed to the intraligand charge transfer (ILCT) transition, which emanates from the NBu_2 donor,[1d,e,4a] red-shifted ($\Delta\lambda_{max}$ = 56–105 nm) with respect to the free ligand ILCT band (λ_{max} = 360 nm) related to the increased acceptor properties of its π* orbitals upon coordination.[1d] The charge transfer character of these absorptions is confirmed by their relevant solvatochromism. Coordination to $ZnCl_2$ causes a red-shift of the ILCT band ($\Delta\lambda_{max}$ = 65 nm) similar to that for

Table 1 Electronic spectra, dipole moments, EFISH $\beta_{1.34}$ and $\beta_{CT,\,1.34}$ of 4′-(C_6H_4-*p*-NBu_2)-2,2′:6′,2″-terpyridine (L) and its complexes with Zn(II), Ru(III) or Ir(III)

Molecule	$\lambda_{max}{}^a$/nm	$\lambda_{max\ em}{}^{af}$ /nm	μ^{ag}/D	μ EF^h	$\mu\beta_{1.34}{}^{ai}/10^{-30}$ D cm^5 esu^{-1}	$\beta_{1.34}$ $(\beta_0)^j/10^{-30}$ cm^5 esu^{-1}	$\beta_{1.34}$ (EF)^k	f^{al}	$\Delta\mu_{eg}{}^m$/D	$\beta_{CT,\,1\ .34}{}^n$/ 10^{-30} cm^5 esu^{-1}
L	360^b	449	2.1	—	46	22 (15)	—	0.40	8.0	43
$ZnCl_2L$	425^b	503	8.0	3.8	538	67 (36)	3.0	0.33	10.8	98
$Zn(CF_3CO_2)_2L$	427^b	512	10	4.7	877	88 (47)	4.0	0.34	8.2	79
$IrCl_3L$	465^{bc}	624	7.9	3.8	−861	−109	5.0	0.81	−0.1	−4
	533^d							0.31	−2.9	−79
										−83
$Ru(CF_3CO_2)_3L$	416^b	590	9.2	4.3	−642	−70	3.2	0.15	12.7	48
	508^e							0.20	5.4	75
	911^e							0.04	15.8	−208
										−85

[a] In $CHCl_3$. [b] Attributed to the ILCT of the ligand. [c] Due to the anomalous high intensity and the slightly negative $\Delta\mu_{eg}$, an expected MLCT transition[13] is under the ILCT transition. [d] Assigned to MLCT according to ref. 13. [e] Assigned to LMCT according to refs. 14 and 15. [f] λ_{max} of the emission. [g] Measured by the Guggenheim method according to ref. 8. [h] μ EF is the μ enhancement factor (μ complex/μ free terpyridine. [i] Measured by the EFISH technique. [j] In parentheses β_0 calculated using the equation $\beta_0 = \beta_\lambda(1-(2\lambda_{max}/\lambda)^2)(1-(\lambda_{max}/\lambda)^2)$ of ref. 1*e*. [k] $\beta_{1.34}$ EF is $\beta_{1.34}$ enhancement factor ($\beta_{1.34}$ complex/$\beta_{1.34}$ free terpyridine. [l] *f* is the oscillator strength obtained from the integrated absorption coefficient. [m] $\Delta\mu_{eg}$ is the difference between excited- and ground-state molecular dipole moments, obtained from solvatochromic data; see ref. 4. [n] Quadratic hyperpolarizability tensor along the charge transfer direction.

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other nitrogen donor chelating ligands with π-delocalized bridges connecting the chelating aromatic structure and the donor substituent such as 4-(*trans*-CH=CHC_6H_4-*p*-NBu_2)-4′-CH_3-2,2′-bipy[2b] ($\Delta\lambda_{max}$ = 72 nm), 4,4′-bis(*trans*-CH=CHC_6H_4-4′-NBu_2)-2,2′-bipy[2c] ($\Delta\lambda_{max}$ = 58 nm) or 5-(*trans*-CH=CHC_6H_4-4′-NMe_2)-1,10-phen[1f] ($\Delta\lambda_{max}$ = 55 nm). However it is much higher than that for a phenanthroline with a donor substituent directly bound to the aromatic system such as 5-NMe_2-1,10-phenanthroline ($\Delta\lambda_{max}$ = 13 nm).[1f] Therefore this large red-shift suggests a strong stabilizing effect on the terpyridine π* orbitals due to chelation.

The enhanced β_{vec} value of L, measured at a non-resonant wavelength of 1.34 μm ($\beta_{1.34}$),[10,11] upon coordination to 'ZnY_2' remains positive as in other Zn(II) complexes with related π delocalized ligands.[1f,2] The enhancement factor $\beta_{1.34}$ EF is higher for the more electron-withdrawing ancillary ligand CF_3CO_2 (Table 1). However, upon coordination of L to $IrCl_3$ or $Ru(CF_3CO_2)_3$, $\beta_{1.34}$ increases significantly its absolute value, in agreement with a relevant red shift of the ILCT transition, but the sign becomes negative. This is a new observation: for the first time different metal centres, which all behave as significant Lewis acids according to the $\Delta\lambda_{max}$ red shift of the ligand ILCT,[1e] can influence not only the absolute value but also the sign of the quadratic hyperpolarizability of a nitrogen donor π-delocalized ligand bearing a strong electron-donor group. A solvatochromic investigation, carried out by use of absorption and emission data[4a] and using a large series of solvents,[4b] confirms that also β_{CT} (the quadratic hyperpolarizability tensor along the charge-transfer direction) is positive for Zn(II) complexes and negative for Ir(III) and Ru(III) complexes. An analysis of the contributions of the various absorption bands to β_{CT} according to the two-level model,[12] shows that the enhancement of the quadratic hyperpolarizability of L upon coordination to Zn(II) is due, as in other Zn(II) complexes,[1f,2] to both a red-shift of the ILCT transition and a positive $\Delta\mu_{eg}$ (Table 1). However for the Ir(III) complex the second order NLO response is not dominated by the ligand ILCT transition only but there is a contribution of at least a weaker band at 533 nm and also of another band, probably a MLCT transition,[13] located under the ILCT absorption at 465 nm. This hypothesis is supported by the unexpected slightly negative $\Delta\mu_{eg}$ and the high intensity of the absorption band at 465 nm. The band at 533 nm can be tentatively assigned to a MLCT (metal to ligand charge transfer) transition according to literature[13] and to its negative $\Delta\mu_{eg}$. On the other hand, in the terpyridine Ru(III) complex, the negative sign of the quadratic hyperpolarizability originates from the high contribution to the second order NLO response of an absorption band at 911 nm, in opposition to the positive contribution of another band at 508 nm and to the expected positive contribution of the ILCT transition at 416 nm. The new transitions, both characterized by a positive value of $\Delta\mu_{eg}$, can be tentatively assigned to LMCT (ligand to metal charge transfer) transitions.[14–16] However the absorption at 911 nm is located at lower energy then the second harmonic (λ = 670 nm) and therefore produces a negative and dominating contribution to the quadratic hyperpolarizability when this latter is measured at an incident wavelength of 1.34 μm.

Of course the assignment of the new absorption bands to MLCT transitions in Ir(III) and to LMCT transitions in Ru(III) complexes must be confirmed by a Raman-shift investigation which is underway. In conclusion we have shown for the first time that while the second order NLO response of π-delocalized nitrogen donor ligands carrying a donor group in complexes with low oxidation state soft metal centres (*e.g.* Rh(I) $4d^8$, Ir(I) $5d^8$, Os(II) $5d^6$, W(0) $5d^6$)[1c–e] or even with relatively hard Zn(II) $3d^{10}$ centres[1f,2] is dictated only by their ILCT transition, in borderline metal centres like Ir(III) $5d^6$ or Ru(III) $4d^5$ this response is influenced also by LMCT or even MLCT transitions, in such a way that it can change its sign (see the Ir(III) complex). This change of sign was reported only in low oxidation state metal complexes when the substituent of this kind of ligands is an electron acceptor group.[1b,d,e]

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