Dipolar and Non-Dipolar Pyridine and Bipyridine Metal Complexes for Nonlinear Optics

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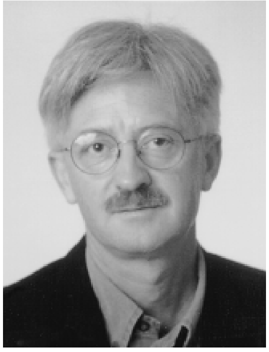
Keywords: Pyridine derivatives / Bipyridine derivatives / Metal complexes / Chromophores / Nonlinear optics

Metal complexes of pyridine and bipyridine-type ligands represent an important class of nonlinear optical (NLO) materials: (i) They can incorporate a variety of functionalised ligands with a wide range of metals which can give rise to tuneable NLO properties; (ii) they are generally associated with intense low-lying charge-transfer excitations such as metal to ligand charge-transfer (MLCT) or intraligand charge-transfer (ILCT); (iii) bipyridyl ligands are also good building blocks that allow the construction of octupolar complexes with a defined geometry and symmetry. This review describes the recent developments in the design of such dipolar and octupolar chromophores for second-order nonlinear optics.

Contents

1. Introduction

The search for new molecular materials with large second-order nonlinear optical properties (NLO) is currently the subject of considerable investigations due to their potential applications in photonic devices such as frequency doublers and electrooptic modulators.[1] Organic and met-



Hubert Le Bozec was born in Brittany, France. He entered the CNRS in 1978 and received his "Doctorat d'Etat" in 1981 from the University of Rennes 1, working under the supervision of Prof. Pierre Dixneuf. After a postdoctoral period in 1982 at the University of North Carolina (Chapel Hill, USA) with Prof. Thomas Meyer, he returned to Rennes and was promoted "Directeur de Recherche" in 1994. His research interests concern the coordination chemistry of bipyridyl metal complexes and their application in nonlinear optics as well as the chemistry of group-6 and group-8 carbene metal complexes.

Thierry Renouard was born in 1971 in Saint Brieuc, France. He studied Chemistry at the University of Rennes 1 and obtained his Ph. D. in 1998, under the supervision of Dr. Hubert Le Bozec. In the same year, he joined the group of Prof. Michael Grätzel at the Swiss Federal Institute of Technology in Lausanne as a Post-Doctoral fellow. His current research interest concerns the synthesis of novel sensitizers for photovoltaic cells.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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allo-organic materials are of particular interest because of their large NLO susceptibilities and fast response times; they also provide good architectural flexibility to tailor their molecular structures and maximize the optical nonlinearity.[2−4] Thus, extensive efforts are now directed towards the design and synthesis of efficient chromophores which can be incorporated into macroscopic assemblies such as polymers, to form materials exhibiting large NLO responses.[5−7]

Traditionally, chromophores possessing large molecular hyperpolarisability β responses contain donor and acceptor substituents linked through a π-backbone. A great deal of work has been carried out over the past 20 years toward the synthesis of noncentrosymmetric dipolar (or "push-pull") molecules such as functionalised benzene, stilbene, polyene or azobenzene derivatives.[8−12] Moreover, a comprehensive understanding of the design of dipolar organic molecules with optimised molecular hyperpolarisability β has been established − recent computational and experimental studies have introduced several concepts such as bond-length alternation (BLA),[13−16] reduced aromaticity in the ground state,[17] as well as the criterion of electron deficiency or excessivity[18] to establish structure-property relationships for nonlinear optical molecules.

Beyond this classical dipolar approach, a new concept of octupolar nonlinearities has been recently proposed on the basis of group theoretical and quantum mechanical studies.[19][20] The molecular hyperpolaribility β can be reduced into two irreducible components $\beta_{J=1}$ (dipolar part) and $\beta_{J=3}$ (octupolar part). For molecules belonging to purely octupolar space groups such as D_3, D_{3h}, T_d, and D_2, the vector part of β is canceled out and only the octupolar contribution of β remains. The advantages of using nondipolar chromophores include easier noncentrosymmetric arrangements and an improved nonlinearity/transparency trade-off. An increasing number of two- and three-dimensional (2D and 3D) octupolar molecules has appeared in the literature[21] with the development of the Hyper Raleigh Scattering technique (see Background). For example, research on octupolar structures has recently focused on organic molecules with threefold symmetry such as triamino-trinitrobenzenes derivatives,[22] crystal violet cation,[23] trisubstituted amines[24] and cyanine salts.[25]

In the late 1980s, the field of molecular materials for nonlinear optics was extended to organometallic and coordination compounds.[11][26] One reason is that they offer a wide range of metals with different oxidation states and ligands which can give rise to tuneable electronic properties. In addition many complexes are known to possess low-lying charge-transfer states which can be associated with large nonlinearities. Non-centrosymmetric structures can also be achieved by coordination of different ligands to a metal centre. For example, there has been considerable interest in using metallocenes, especially ferrocene derivatives, as donor groups since the pioneering work of Green and co-workers in 1987 who reported a second-harmonic generation (SHG) efficiency 62 times that of the urea standard for the compound (*Z*)-1-ferrocenyl-2-(4-nitrophenyl)ethene.[27][28] Metal complexes of nitrogen-heterocyclic ligands, such as pyridines and oligopyridines, represent another important class of NLO chromophores which have received increasing attention over the last ten years. These ligands, which can be easily functionalized, are among the most widely studied in coordination chemistry resulting in a wide choice of stable complexes.[29] They are generally associated with intense low-energy metal to ligand charge-transfer (MLCT) or intraligand charge-transfer (ILCT) [also known as ligand-centred (LC)] excitations. In addition, bipyridyl ligands are excellent building blocks for the construction of octupolar metal complexes like $[M(bpy)_3]^{n+}$ of D_3 symmetry and $[M(bpy)_2]^{n+}$ of D_{2d} symmetry. This microreview highlights the recent developments in the design of pyridyl- and bipyridyl-metal complexes for nonlinear optics. The first part is concerned with dipolar chromophores whereas the second part will deal with the more recent and promising field of octupolar metal complexes. In each section we have gathered the chromophores into two categories: (i) complexes in which the NLO response is dictated by a MLCT transition, and (ii) complexes with ligands bearing π-donor substituents in which the main charge-transfer governing the NLO response is an ILCT transition.

2. Background

The second-order nonlinear effect is correlated with quadratic (or first molecular) hyperpolarisability β. The dipole moment μ induced in a molecule by an intense external electric field E can be expressed by the relationship of Equation 1, where α is the linear polarisability, and β and γ the first and second molecular hyperpolarisability, respectively.

$$\mu = \alpha \cdot E + \beta \cdot E^2 + \gamma \cdot E^3 + \cdots \tag{1}$$

The coefficient β governs the magnitude of the second-order response, and vanishes in a centrosymmetric medium.

The experimental determination of β can be carried out by using the Electric-Field-Induced Second Harmonic generation (EFISH) method.[30−32] A high-voltage electric pulse breaks the centrosymmetry of the liquid by a dipolar orientation of the molecules. This technique allows determination of $\gamma + \mu \cdot \beta/5kT$, where γ is the cubic hyperpolarisability of the molecule, μ its dipole moment, and β the vectorial projection of the first hyperpolarisability tensor along the dipole direction. By neglecting the third order contribution, β can be evaluated. The ground state dipole moment can be measured independently by a classical method based on the Guggenheim law.[33] Modelling the dispersion of β for a two-level system according to Equation 2 enables us to extract a frequency-independent nonresonant $\beta(0)$ value.[31][34]

$$\beta = \frac{3e^2\hbar^2}{2mW^3} F(W,\omega) f \Delta\mu \tag{2}$$

With respect to Equation 2, W is the energy of the CT transition, ω the fundamental frequency, f the oscillator strength of the charge-transfer band, $\Delta\mu = \mu_{exc} - \mu_g$ the difference between excited- and ground-state moments, and F the dispersion factor, which is defined by Equation 3; β is related to the static hyperpolarisability coefficient $\beta(0)$ by $\beta = \beta(0)\cdot F(W,\omega)$.

$$F(W,\omega) = \frac{W^4}{\left[W^2 - (\hbar\omega)^2\right]\left[W^2 - (2\hbar\omega)^2\right]} \qquad (3)$$

The experimental determination of β can also be carried out with the Hyper-Raleigh Scattering (HRS), also termed Harmonic Light Scattering (HLS), method.[35][36] This is a unique technique for β measurement of nondipolar and/or ionic molecules. For such molecules the EFISH experiment is not possible as it requires uncharged species and a nonzero ground state dipole moment. The HRS method is based on an incoherent scattering of the second harmonic originating from the fluctuation of optically induced microscopic dipoles. The HRS harmonic response can be expressed as in Equation 4, where $I^{2\omega}$ is the scattered SHG intensity, I^{ω} is the intensity of the fundamental wave, G is a geometrical factor, N_1 (N_2) is the molecular density of the solute (solvent) and $<\beta_1{}^2>$ ($<\beta_2{}^2>$) is the orientational average of the square of the first hyperpolarisability of the solute (solvent).

$$I^{2\omega} = G(N_1<\beta_1{}^2> + N_2<\beta_2{}^2>)\,(I^{\omega})^2 \qquad (4)$$

The HLS technique also allows us to determine the individual components of the β tensor.[37] In the case of nondipolar molecules, the static hyperpolarisability $\beta(0)$ at zero-frequency may be calculated using a three-level model.[38] The dispersion factor is similar to that of a two-level system (Equation 3).

3. Dipolar Complexes

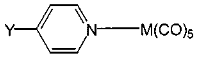
3.1 Dipolar Complexes with Metal-to-Ligand Charge-Transfer Transitions

In 1986, Frazier and co-workers[39] investigated for the first time the second-harmonic powder efficiencies of the 4-substituted group-6 metal carbonyl pyridyl complexes **1** (Figure 1). However, only very weak SHG efficiencies, from 0 to 1 relative to ammonium dihydrogen phosphate (ADP), were obtained. Presumably most of these complexes crystallise in centrosymmetric space groups. The first examples of metal-bipyridine complexes possessing second-order polarisabilities were reported by Calabrese and Tam in 1987.[40] They studied the macroscopic SHG powder efficiencies by the Kurtz technique at 1.06 µm. The rhenium(I) complexes (bpy)Re$(CO)_3$X (**2**) [X = Cl, CF_3SO_3] were found to crystallise in a noncentrosymmetric space group and gave SHG efficiencies from 1.6 to 3 times that of urea. Other complexes such as (4-Y-pyridine)$_2$Re$(CO)_3$Br (**3**) [Y = H, styryl], (bpy)MCl_4 (**4**) [M = Pd, Pt] and (bpy)M$(CO)_4$ (**5**) [M = Cr, Mo, W] showed rather small SHG efficiencies ranging from 0.1 to 1.2 times that of urea (Figure 1). The first EFISH studies on metal pyridine and bipyridine (or phenanthroline) complexes were described by Cheng et al.[41][42] They measured the molecular hyperpolarisability β of (4-Y-pyridine)W$(CO)_5$ (**1a**), (4-Y-stilbazole)W$(CO)_5$ (**1b**) and (5-Y-1,10-phenanthroline)W$(CO)_5$ (**6**) (Figure 1). Their optical nonlinearities, ranging from -2 to -20×10^{-30} esu, were significantly enhanced relative to that of the free ligands. The negative values of β are consistent with the negative solvatochromism observed for such complexes by Wrighton and co-workers.[43] The use of 4-substituted pyridines with electron-acceptor groups led to a bathochromic shift of the MLCT transition energy and to larger β values. These trends can be explained by the lowering of the π*-acceptor orbital of the pyridine (phenanthroline) ligands and a decrease in the energy gap of the MLCT transition. Respectable nonlinearities were observed for complexes containing nitro-substituted ligands such as (4-NO_2-stilbazole)W$(CO)_4$ [$\beta = -20 \times 10^{-30}$ esu] and (5-Y-1,10-phenanthroline)W$(CO)_5$ [$\beta = -18 \times 10^{-30}$ esu].[41]

A ZINDO-SOS computational study of the related (4-Y-pyridine)Cr$(CO)_5$ (**1a**) and (4-Y-stilbazole)Cr$(CO)_5$ (**1b**) has more recently been described by Ratner, Marks and co-workers.[44] The computed molecular hyperpolarisabilities were in good agreement with the experimental values. These calculations also showed that the NLO response is dictated by the MLCT transition, that the pyridine ring is the primary charge acceptor and that the calculations also predicted the negative sign of β and an increase of the NLO response when electron-accepting groups are attached to the pyridine ring.

Thompson et al.[45] investigated the second-order NLO properties of iron(III) compounds Fe(SALEN)(4-Y-pyridyl)X (**7**), where X is a halide or an azide (Figure 2). The Kurtz powder test gave a sizeable SHG efficiency twice that of urea when X = N_3, whereas weak SHG intensities were found for the other complexes (0−0.2 × urea). The nonlinearity finds its origin in charge-transfer transitions in both the SALEN ligand and pyridyl-iron system. Attempts to measure the molecular hyperpolarisability β by EFISH in chloroform failed due to low solubility and dissociation of the pyridyl ligand. Thompson and co-workers also described the preparation of an interesting polymer chain **8** from the reaction of Mn(SALEN)Br and 4-pyridyl glycinate ligands or 4-(pyridylthio)acetic acid (Figure 2).[46] The polymers consisted of metal centres bridged by 4-pyridyl ligands. The crystal structures showed a head-to-tail alignment of adjacent dipoles along the polymer backbone. Unfortunately, adjacent polymer chains were antiparallel, so no NLO effects were observed.

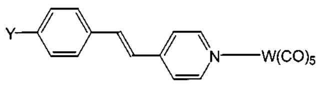
Large molecular hyperpolarisabilities have recently been observed by Coe et al.[47] in donor-acceptor ruthenium(II) complexes. They reported the synthesis of a series of *trans*-$[Ru(NH_3)_4(L^A)(L^B)]^{n+}$ complexes **9**, where L^A and L^D are acceptor/donor-substituted pyridyl ligands (Figure 2). All these complexes show highly solvatochromic low energy dπ(Ru) → π*(L^A) metal-to-ligand charge-transfer bands in the visible region. Using the HRS technique at 1.064 µm, large β values in the range $230-790 \times 10^{-30}$ esu were found, especially for complexes **9b−9d** containing *N*-meth-



1a

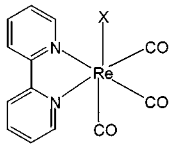
M = Cr, Mo, W

Y = H, CHO, COMe, CN, COC_6H_5



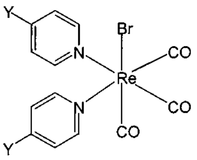
1b

Y = H, CHO, NO_2



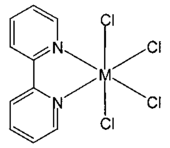
2

X = Br, CF_3SO_3



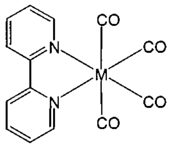
3

Y = H, Ph-CH=CH-



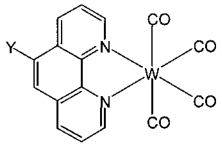
4

M = Pd, Pt



5

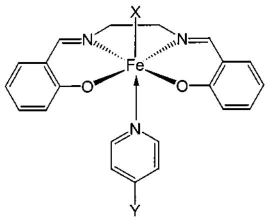
M = Cr, Mo, W



6

Y = H, NO_2

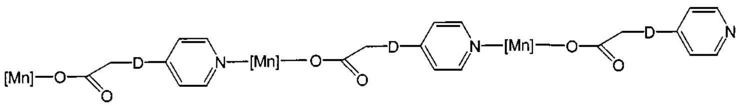
Figure 1. Dipolar complexes with MLCT transitions



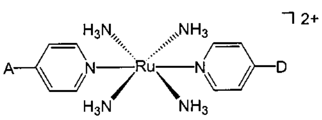
7

X = Cl, Br, I, N_3

Y = H, NH_2, NMe_2



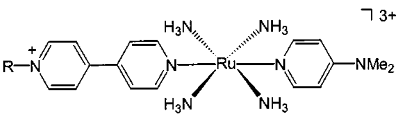
8 [Mn] = (SALEN)Mn ; D = NH, S



9a

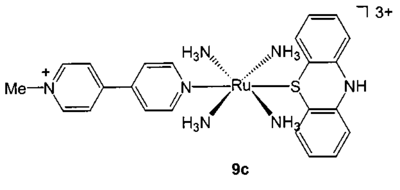
A = COMe, CHO, CO_2Et

D = NMe_2

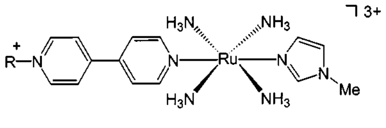


9b

R = Me, Ph



9c



9d

R = Me, Ph

Figure 2. Dipolar complexes with MLCT transitions

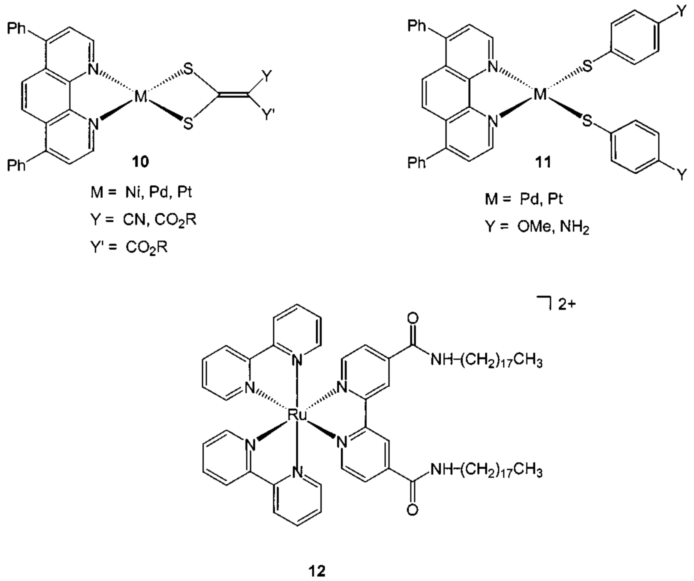


Figure 3. Dipolar diimine metal complexes with MLCT transitions

yl- and *N*-phenyl-4,4′-bipyridinium (MQ^+) as electron-acceptor ligands. As these complexes absorb in the region of the second harmonic (0.532 μm), the large β values were attributed in part to resonance enhancement. Static hyperpolarisabilities $\beta(0)$ were also calculated and ranged from 10 to 266×10^{-30} esu.

Eisenberg and co-workers[48] prepared a series of mixed-ligand transition-metal diimine dithiolate complexes **10−11** (diimine = phenanthrolines, bipyridines; metal = Ni, Pd, Pt) and studied their NLO properties by EFISH at 1.91 μm. Some examples of complexes are displayed in Figure 3. Their lowest-energy excited states involve a HOMO which is a mixture of M(d)- and dithiolate-orbital character and a LUMO which is a π* orbital of the diimine ligands. This transition has been termed by the authors as "charge-transfer-to-diimine."[49][50] The role of the metal ion, dithiolate and diimine ligands in the tuning of the optical and nonlinear optical properties was investigated. Negative β values in the range 0 to -40×10^{-30} esu were found. Larger values of β were observed with Pt^{II} metal ions and dithiolate ligands containing electron-donating substituents such as in **11**. In contrast, complexes **10** with dithiolate ligands containing electron-withdrawing groups exhibited reduced β values: a decrease of the electron-donating strength of the dithiolate and the presence of another charge-transfer-to-dithiolate, which is vectorially opposed to the charge-transfer-to-diimine, were proposed to explain the lowering of the molecular hyperpolarisability.

Matsuo and co-workers[51] studied the second-harmonic generation of the amphiphilic tris(2,2′-bipyridyl)ruthenium(II) complex **12** in a Langmuir-Blodgett film (Figure 3). Amide groups were introduced at the 4,4′-position of one bipyridine ligand in order to increase the vectorial properties of the MLCT. The absorption spectrum of the LB film showed a typical MLCT band at 450 nm and another at 480 nm which was assigned to the MLCT transition to the 4,4′-diamide-2,2′-bipyridine ligand. The β value was estimated to be 70×10^{-30} esu. Second harmonic generation was also observed from ultrathin polyvinyl chloride films impregnated with the same tris(bipyridyl)ruthenium(II) complex.[52]

3.2 Dipolar Complexes with Intraligand Charge-Transfer Transitions

In the first phase of our work on bipyridyl metal complexes for nonlinear optics, we developed the synthesis of the 4-alkenyl-2,2′-bipyridines **13−14** bearing π-donor substituents (Figure 4).[53][54] These ligands are easily available from 4,4′-dimethyl-2,2′-bipyridine.[55] The optical UV/Vis absorption spectra of **13** showed a characteristically intense solvatochromic intramolecular charge-transfer transition, whereas that of the metallocenylvinyl bipyridines **14** exhibited two less intense bands assigned to MLCT and π−π* transitions, respectively.[28b,56] The EFISH measurements of **13** and **14** at 1.34 μm[57] indicated moderate β values ranging from 4 to 14×10^{-30} esu; the most efficient donor group was, as expected, dibutylaminophenyl [$4\text{-}Bu_2N{-}C_6H_4\text{-} >> 4\text{-}RO{-}C_6H_4\text{-} \approx (C_5H_5)Fe(C_5H_4\text{-}) > (C_5H_5)Ru(C_5H_4\text{-})$]. These ligands were coordinated to acceptor organometallic fragments, and two types of complexes were prepared: octahedral rhenium(I) carbonyl complexes of general formula *fac*-(bpy)$Re(CO)_3X$ (**15**) and tetrahedral zinc and mercury complexes of general formula (bpy)MX_2 (**16**) (Figure 4).[53][57] A selection of optical and nonlinear optical data are displayed in Table 1. We observed a red shift of the ILCT transition (Δλ ≈ 40−70 nm) which was sensitive to the nature of both the organometallic moiety and the conjugated donor group. For a given donor group (for example Bu_2N), the relative ordering of the acceptor strength was: $Re(CO)_3Br > ZnCl_2 > Zn(OAc)_2 >$

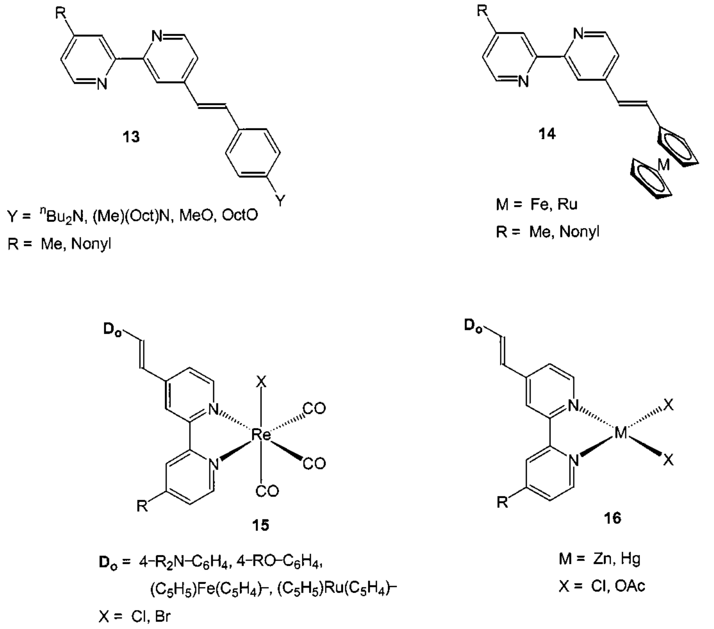


Figure 4. Dipolar bipyridine metal complexes with ILCT transitions

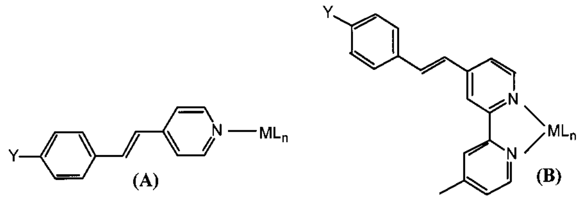
$HgCl_2 > Hg(OAc)_2$. In addition to the ILCT band, each of the rhenium complexes also exhibited a less intense absorption near 380 nm, which was assigned to a $d\pi(Re) \rightarrow \pi^*$ (bpy) transition. Upon coordination, the β values were found to increase by a factor ranging from 2 to 11 (Table 1). The inductive acceptor strength of the ML_n fragment contributes mainly to the enhancement of the NLO response. A conformational change of the bipyridine ligand upon chelation [trans → cis] could also play a non negligible role. The ordering of the β values followed that found for the relative energies of the ILCT bands, with the exception of the rhenium complexes **15** which were less efficient than the corresponding zinc complexes **16**: The presence of two vectorially opposed charge-transfer axes (MLCT and ILCT) in **15** could contribute to the decrease in β. The largest static response was found for compound **16** with dibutylaminophenyl as the electron donor and zinc dichloride as the electron acceptor [$\beta(0) = 71 \times 10^{-30}$ esu]; its molecular nonlinearity $\mu{\cdot}\beta(0)$ [$\mu{\cdot}\beta(0) = 831 \times 10^{-48}$ esu], which is the relevant parameter for poled polymer applications, compared well with that of the prototypical chromophore disperse red 1 [$\mu{\cdot}\beta(0) = 450 \times 10^{-48}$ esu].[58]

Molecular quadratic hyperpolarisabilities of donor-substituted stilbazole complexes have also been recently studied by several groups. Bruce and Thornton[59] prepared mesogenic 4-alkoxystilbazole complexes of Rh^I and Ir^I **17** (Figure 5). A chiral alkoxy chain such as (*S*)-(+)-2-methylbutoxy was used in order to promote noncentrosymmetric packing in the solid state. A bathochromic shift ($\Delta\lambda \approx 20-30$ nm) was observed upon complexation of the ligand to the $[MCl(CO)_2]$ fragment. The complexation also resulted in enhanced values of μ by a factor of ca. 2, and $\beta(0)$ by a factor of ca. 1.5 (Table 1). Ratner, Marks and co-workers[44] studied the experimental and computed NLO properties of [4-(dimethylamino)stilbazole]$M(CO)_5$ complexes **18** (M = Cr, W). The EFISH studies at 1.064 μm indicated an increase in β of two times the organic stilbazole ligand. The calculated β [65×10^{-30} esu] was in excellent agreement with the observed experimental molecular hyperpolarisability [61×10^{-30} esu]. It is noteworthy that this response is larger and of an opposite sign to the (4-acceptorstilbazole)$M(CO)_5$ derivatives **1b**. As for the donor substituted bipyridine metal complexes **15**, the NLO response is here dictated by an ILCT transition and the role of the metal fragment is that of an inductive acceptor. ZINDO calculations were used to study the difference in electronic populations between ground state and excited state: The study showed that the MLCT excitation is of secondary importance since only 0.14 electrons are transferred from $M(CO)_5$.[44]

Marder et al.[60] have recently examined the NLO properties of the same 4-donorstilbazoles and their Lewis acidic borane adducts **19** (Figure 5). The β values of the free stilbazole ligands were found to be larger than those of the related 4-alkoxy- or 4-aminostyryl-2,2′-bipyridine (**13**) (Table 1).[57] This difference could be explained by the transoid conformation of the bipyridine ligands and thus to the presence of opposed charge-transfer excited states which are expected to reduce the magnitude of β. The red shift ($\Delta\lambda \approx 40-90$ nm) of the intramolecular charge-transfer transition upon coordination of the Lewis acidic boranes was more pronounced than when the same ligands were complexed to $W(CO)_5$[44] or $[M(CO)_2Cl]$.[59] Enhanced molecular hyperpolarisabilities β by a factor > 2 were found in all cases. The largest value was found for the dimethylaminostilbazole adduct with $B(C_6F_5)_3$. Its molecular nonlinearity $\mu{\cdot}\beta(0)$ [724×10^{-48} esu] was found to be similar to that of our bipyridine zinc complexes **16** (Table 1).

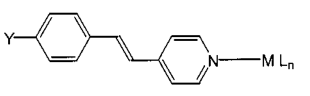
The NLO properties of several donor-vinylpyridine metal complexes, containing an organometallic fragment as the donor group, have recently been reported in the literature.

Table 1. Selected linear and nonlinear optical data for 4-donor-substituted stilbazoles, styrylbipyridines and complexes



	Y	ML_n	λ_{max} [nm]	μ [D]	β [10^{-30} esu]	$\beta(0)$ [10^{-30} esu]	$\mu\cdot\beta(0)$ [10^{-48} esu]	Ref.
(A)	OMe		326	6	24[a]	17.2	103	[60]
	$OCH_2CH(Et)(Me)$		335	3.8	15.8[b]	13.4	51	[59]
	NMe_2		368	10	45[a]	29	291	[60]
	OMe	BF_3	364	7.3	48[a]	31.3	229	[60]
	OMe	$B(C_6F_5)_3$	376	6.4	48[a]	30.3	195	[60]
	$OCH_2CH(Et)(Me)$	$Rh(CO)_2Cl$	355	7.4	20.1[b]	16.7	124	[59]
	$OCH_2CH(Et)(Me)$	$Rh(CO)_2Br$	357	7.7	23.9[b]	19.8	153	[59]
	$OCH_2CH(Et)(Me)$	$Ir(CO)_2Cl$	364	6.9	24.4[b]	20.0	138	[60]
	NMe_2	$W(CO)_5$	421	14.9[c]	61[d]	19.2	286	[44]
	NMe_2	BF_3	438	11.8	129[a]	66	721	[60]
	NMe_2	$B(C_6F_5)_3$	458	10	155[a]	72.5	724	[60]
(B)	OOct		329	6.5	4[a]	3	20	[57]
	NBu_2		388	5.1	14[a]	8	41	[57]
	OOct	$Re(CO)_3Br$	367	11.6	11[a]	7	81	[57]
	OOct	$Hg(OAc)_2$	360	10.4	18[a]	12	125	[57]
	OOct	$HgCl_2$	361	10.7	18[a]	12	128	[57]
	OOct	$Zn(OAc)_2$	358	10	19[a]	13	130	[57]
	NBu_2	$Re(CO)_3Br$	475	9.9	71[a]	31	307	[57]
	NBu_2	$HgCl_2$	442	11.7	65[a]	32	374	[57]
	NBu_2	$Zn(OAc)_2$	447	7.9	116[a]	57	450	[57]
	NBu_2	$ZnCl_2$	160	11.7	152[a]	71	831	[57]

[a] EFISH at 1.34 µm in $CHCl_3$. – [b] EFISH at 1.907 µm in $CHCl_3$. – [c] Calculated. – [d] EFISH at 1.064 µm in dioxane.



17 Y = $OCH_2CH(Me)(Et)$; M L_n = $Rh(CO)_2Cl$, $Ir(CO)_2Cl$

18 Y = NMe_2 ; M L_n = $Cr(CO)_5$, $W(CO)_5$

19 Y = OMe, NMe_2 ; M L_n = BF_3, $B(C_6F_5)_3$

Figure 5. 4-Donor stilbazole complexes

The heterobimetallic ferrocenyl(vinylpyridine)ML_n compounds **20** were simultaneously prepared by Mata et al.[61] and by Lee et al.,[62] and their NLO responses measured by the HRS technique at 1.064 µm (Figure 6). Quite different β values were found for identical complexes by the two groups [for example, ML_n = $W(CO)_5$: $\beta = 101 \times 10^{-30}$ esu[61] and 282×10^{-30} esu[62]]. Surprisingly, large β values were obtained, especially for cationic complexes [ML_n = $Re(CO)_5{}^+$, $\beta_{1.06}$ (HRS) = 712×10^{-30} esu[62]], in comparison with that for our heterobimetallic ferrocenyl-bipyridine rhenium complexes **15** [$\beta_{1.34}$ (EFISH) = 17×10^{-30} esu]. However, since they absorbed relatively close to the frequency doubled scattered light (λ/2 = 532 mm), these values were substantially resonance enhanced. Gimeno, Persoons and co-workers[63] described the synthesis and HRS measurements of the novel enynylruthenium(II)–chromium(0) or –tungsten(0) bimetallic complexes **21** (Figure 6). The efficiencies of the half sandwich indenylbis(triphenylphosphane)ruthenium–alkynyl donor moiety was demonstrated by large hyperpolarisabilities, particularly when the pyridine ligand was coordinated to $W(CO)_5$ [λ_{max} = 462 nm; $\beta_{1.06} = 535 \times 10^{-30}$ esu; $\beta(0) = 71 \times 10^{-30}$ esu].

4. Non-Dipolar Complexes

4.1 Octupolar Complexes with Metal-to-Ligand Charge-Transfer Transitions

The quadratic nonlinear susceptibility of octupolar metal complexes was first demonstrated by Zyss et al[64] for the tris(bipyridine)- and tris(phenanthroline)ruthenium(II) cations **22** and **23** (Figure 7). These complexes have attracted intense interest over the past twenty years due to their luminescence properties and capacity for electron- and energy-transfer processes.[65] They possess D_3 symmetry and exhibit intense absorption transitions near 450 nm assigned to dπ(Ru) → π*(bpy or phen) MLCT transitions. Large β_{HRS} values of 210×10^{-30} and 170×10^{-30} esu were found at 1.064 mm for **22** and **23**, respectively. However, the first hyperpolarisability of $Ru(bpy)_3{}^{2+}$ **22** was recently reexamined by Morrison et al,[66] and estimated to be 25×10^{-30} esu. The large β value appeared to be mainly due to a two-photon excited luminescence, and a typical red emission with a luminescence lifetime of 210 ns was observed by exciting with the harmonic frequency at 532 nm.

To achieve enhanced optical nonlinearities by extension of the π-electron system and introduction of strong ac-

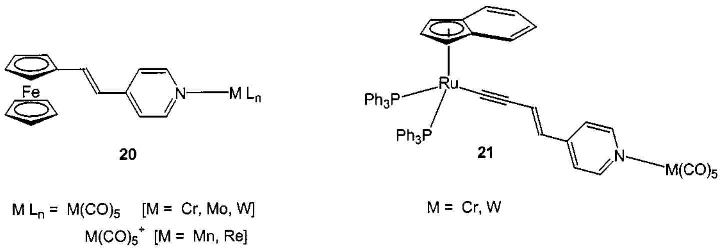


Figure 6. Dipolar heterobimetallic complexes

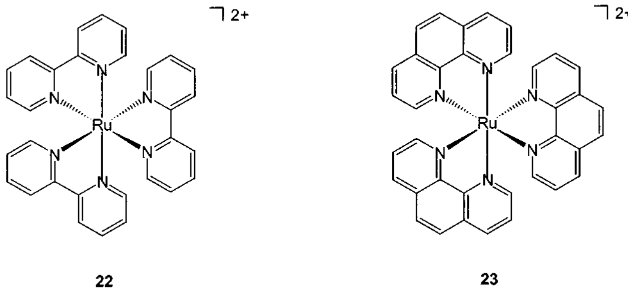


Figure 7. Octupolar diimine complexes with MLCT transitions

ceptor groups, we prepared the 4,4′-dialkenyl-2,2′-bipyridines **25a**,**b** containing nitrophenyl and nitrothienyl substituents.[67] To this end we have developed a convenient method for the preparation of the precursor 4,4′-diformyl-2,2′-bipyridine (**24**), based on the enamination of 4,4′-dimethyl-2,2′-bipyridine. Ligands **25a**,**b** were readily obtained from **24** by a classical Wittig-Horner reaction (Figure 8). The synthesis of tris(bipyridyl)ruthenium(II) (**26b**) was achieved by treating **25b** with ruthenium trichloride (Figure 8).[68] As expected from the presence of strong acceptors, the MLCT transition [λ_{max} (acetone) = 508 nm] was significantly red-shifted with respect to Ru(bpy)$_3^{2+}$. Unfortunately, very poor solubility precluded its β measurement by the HRS technique.

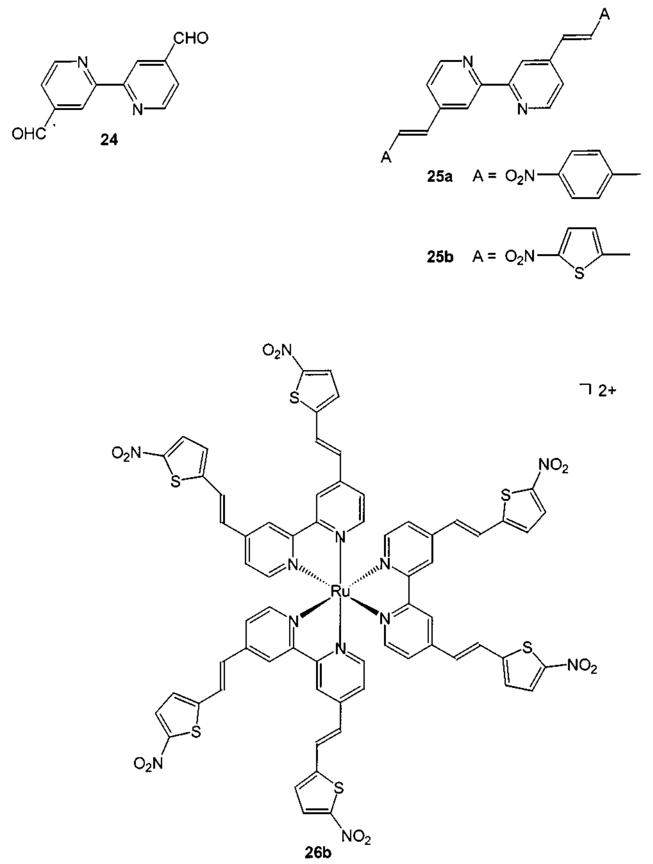


Figure 8. 4,4′-Dialkenyl-2,2′-bipyridines containing acceptor substituents, and corresponding octupolar ruthenium complexes

4.2 Octupolar Complexes with Intraligand Charge-Transfer Transitions

4.2.1. Octahedral Complexes

To design octupolar tris(bipyridyl)ruthenium(II) with a multidirectional intraligand charge-transfer as the main transition responsible for the NLO response, we developed the synthesis of a series of 4,4′-dialkenyl-2,2′-bipyridine ligands **27** bearing π-donor substituents (dialkylaminophenyl and alkoxyphenyl) by the same route employed for the preparation of bipyridines **19** (Figure 9).[54] The corresponding complex [Ru(**27**)$_3$](PF$_6$)$_2$ (**28**) showed characteristically intense charge-transitions ($\varepsilon \approx 120000-150000$) which were sensitive to the nature of the donor group.[68][69] For complexes **28a**,**b** [D = NBu$_2$, N(Me)(Oct)], a very broad ILCT band was observed at ca. 500−510 nm; the MLCT transition, expected at ca. 450−480 nm, was hidden by the more intense ILCT band. For **28c** (D = OOct) two maxima could be easily identified, the main ILCT transition at 380 nm and the less intense MLCT transition at 482 nm. The first HRS measurement of **28a** at 1.34 μm in chloroform gave an exceptionally high β value of 2200×10^{-30} esu.[69] This value was recently found to be overestimated due to some two-photon excited luminescence, and new measurements gave reduced, but still high, hyperpolarisabilities [**28a**: $\beta_{HRS} = 1130 \times 10^{-30}$ esu; **28b**: $\beta_{HRS} = 1000 \times 10^{-30}$ esu[70]]. The alkoxy derivative **28c** gave a smaller β value [$\beta_{HRS} = 490 \times 10^{-30}$ esu] but displayed a better nonlinearity-transparency trade-off. The ordering of the β values was the same as that found from the relative energies of the ILCT bands i.e. **28a** > **28b** >> **28c**.

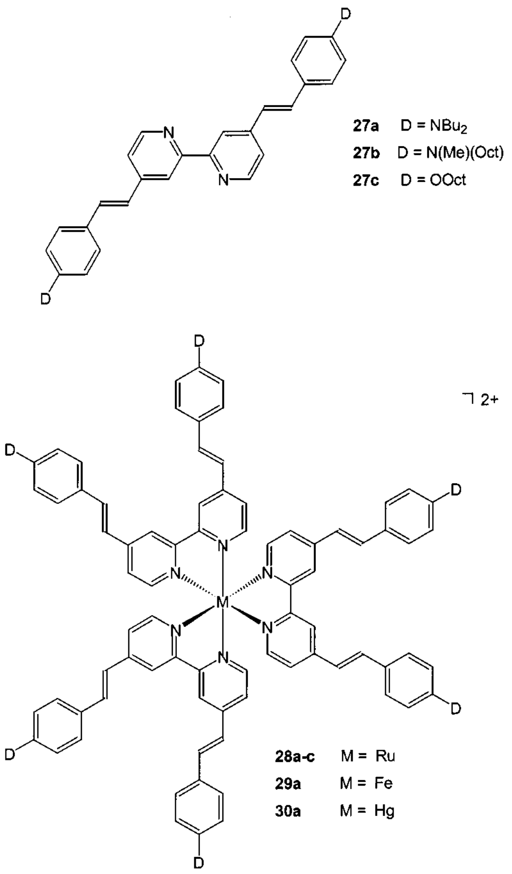


Figure 9. 4,4′-Dialkenyl-2,2′-bipyridines bearing π-donor substituents and corresponding octahedral complexes

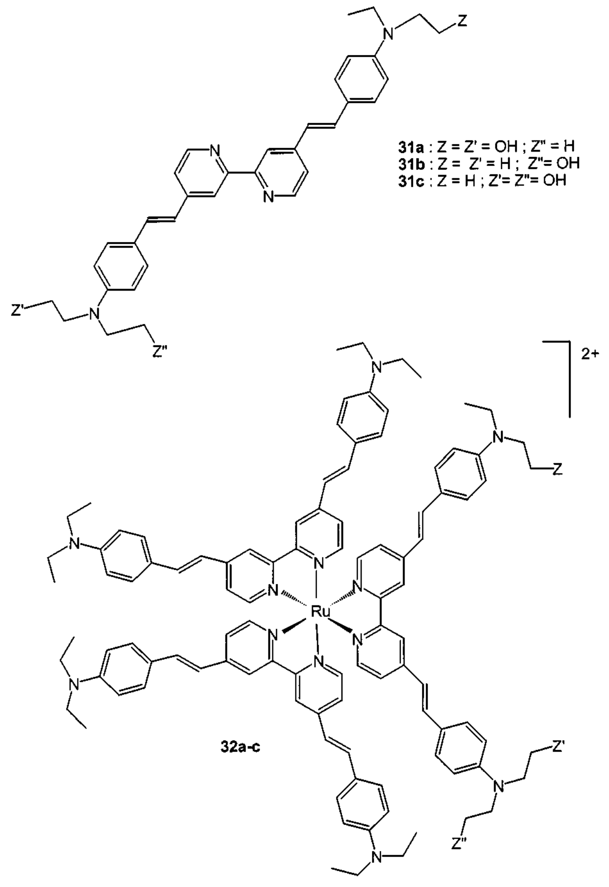


Figure 10. Hydroxy-functionalised bipyridines and corresponding octahedral complexes

The influence of the metal on the linear and nonlinear optical properties was also investigated.[68] For example, the iron derivative **29a** exhibited two absorption bands, the more intense ILCT transition blue-shifted with respect to the ruthenium derivative **28a** [λ_{max} = 467 nm] and the less intense blue-shifted MLCT transition [λ_{max} = 593 nm]. The mercury(II) derivative **30a** showed only the absorption band at λ_{max} = 438 nm, attributable to the ILCT transition, and the antagonist MLCT transition was nonexistent as expected from the high third ionisation potential of mercury. Smaller β values were obtained for such complexes [**29a**: $\beta_{HRS} = 260 \times 10^{-30}$ esu; **30a**: $\beta_{HRS} = 515 \times 10^{-30}$ esu], showing that the nonlinearity-transparency compromise can be fine-tuned by changing the metallic centre.

A current approach for the design of NLO materials is the covalent attachment of NLO-phores to a polymer backbone. As this approach usually requires the introduction of appropriate reactive functionalities at the electron-donating site of the chromophore, we have performed the synthesis of the mono- and dihydroxy-substituted 4,4′-bis(dialkylaminostyryl)-2,2′-bipyridines (**31**) (Figure 10).[71] The synthetic methodology for the preparation of the corresponding ruthenium complexes **32** was based on the sequential coordination of the "parent" 4,4′-bis(*p*-diethylaminostyryl)-2,2′-bipyridine and of the appropriate hydroxy-functionalised bipyridine **31**. Thus, macroscopic organisation of such octupoles in noncentrosymmetric assemblies can be envisaged from the new optical poling method.[72]

4.2.2. Tetrahedral Complexes

In comparison to D_{3h} and D_3 compounds, only a few examples of nondipolar tetrahedral chromophores have been investigated for nonlinear optics.[72–75] Bipyridine- or phenanthrolinecopper(I) complexes with substituents α to the nitrogen atoms are known to give stable tetrahedral molecules of D_{2d} symmetry.[76] Thus, we designed the new 4,4′-diaminostyryl-6,6′-dimethyl-2,2′-bipyridines (**33**); the corresponding copper(I) complexes **34** were simply obtained by treatment of the ligand with $Cu(CH_3CN)_4^+$ (Figure 11).[77] The UV/Vis spectra displayed the characteristic ILCT transition at $\lambda_{max} \approx 420$ nm, which was considerably blue-shifted relative to the corresponding ruthenium(II) complexes **28**. The MLCT transition was typically observed at ca. 480 nm as a shoulder of the more intense ILCT band.

Their molecular hyperpolarisabilities, measured by means of the HRS technique at 1.34 μm, revealed large β values, especially with the most effective electron-donating dialkylamino group [NRR′ = N*n*Bu$_2$ $\beta_{HRS} = 144 \times 10^{-30}$ esu]. Compared to the octahedral tris(bipyridyl)ruthenium(II) complex **28a**, the copper(I) derivatives **32** showed reduced values, as expected from the higher energy of the ILCT ex-

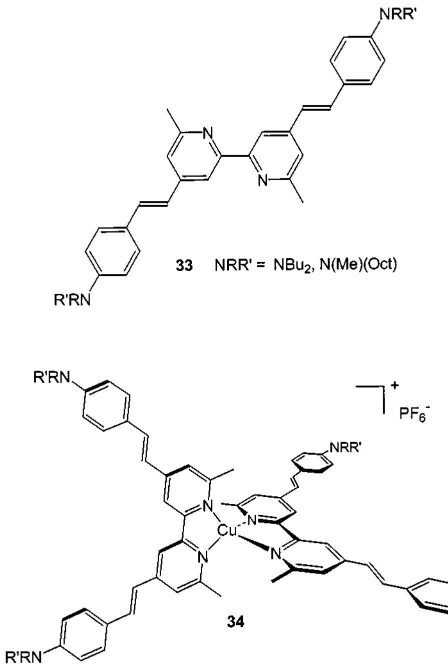


Figure 11. Tetrahedral octupolar copper(I) complexes

cited state. However, these complexes represent a new class of nondipolar NLO organometallic chromophores combining good transparencies and large nonlinearities.

5. Concluding Remarks

Studies on pyridyl- and bipyridylmetal complexes for nonlinear optics have been extensively developed since the first report of Frazier in 1986.[39] In such complexes, the NLO response can be dictated by either a MLCT or ILCT transition and the pyridine ring plays the role of the primary acceptor. Many strategies have emerged that allow access to new NLO chromophores. The most widely studied systems are still dipolar compounds, and versatile synthetic methodologies allow the design and synthesis of efficient second-order nonlinear materials. Octupolar bipyridyl metal complexes remain an emerging field of research. However, as the geometry can be imposed by the nature of the metallic centre and its oxidation state, many other polypyridyl metal derivatives can be potentially used in the construction of NLO compounds with the required 3D octupolar symmetry. Finally, the ability to substitute the pyridine rings with various functional groups offers the possibility of easily incorporating such types of chromophores into polymers. Development of these polymetallic materials will be an interesting challenge in the forthcoming years.

The experimental work reported from our group was performed by Manuel Bourgault, Thierry Renouard, Thomas Le Bouder, Barbara Lognoné, Philippe Dupau and Philippe Massiot. The EFISH and HRS studies were performed by Dr. Zyss's group (ENS Cachan). We are grateful to all of them.

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