Synthesis and Second-order Nonlinear Optical Properties of New Bipyridyl Metal Complexes

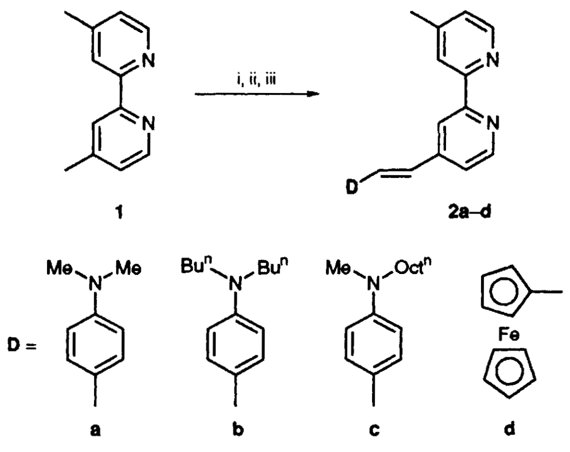
M. Bourgault,[a] C. Mountassir,[a] H. Le Bozec,*[a] I. Ledoux,[b] G. Pucetti[b] and J. Zyss*[b]

[a] *Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France*

[b] *CNET, France Telecom, Laboratoire de Bagneux, Centre Paris B, URA CNRS 250, 196 Avenue Henri Ravera, 92220 Bagneux, France*

The synthesis and characterisation of a series of new π-donor substituted vinyl bipyridines and their rhenium, zinc and mercury complexes {donore = 4-R_2N–C_6H_4– [R_2N = Me_2N, $Bu^n{}_2N$, (Me)(Oct^nN)]; (η^5-C_5H_5)Fe(η^5-C_5H_4–)} with large nonlinear optical properties are presented; EFISH experiments at 1.34 μm show that complexation leads to a strong enhancement (by a factor of 3 to 9) of the molecular hyperpolarisability β(0).

The search for new materials possessing large optical nonlinearities is of considerable interest. To date numerous conjugated π-donor–acceptor organic molecules have been shown to display large second-order polarisabilities.[1–3] More recently the use of transition metal–organic compounds in nonlinear optical (NLO) materials has received growing attention.[4–10] Many organometallic complexes are known to act as strong electron donor or electron acceptor species depending on the nature of the metal, its oxidation state and the ligand environment. Organometallic complexes are also interesting candidates in the new field of 'octapolar molecular engineering,' which emphasizes the advantages of non-polar octupolar systems over more classical dipolar ones, in terms of optimization of the non linearity–transparency trade-off.[11] For these reasons the design and preparation of new organometallic compounds for NLO appears to be attractive. Recent work has shown that metal–2,2′-bipyridine complexes are capable of generating second-harmonic radiation; this study, restricted to the Kurtz powder technique, gave powder second-harmonic radiation (SHG) efficiencies of 0.1 to 3 times that of urea.[6a] In order to tune or to modify the NLO properties of such complexes, we have investigated the synthesis of donor–acceptor organometallic molecules containing 4,4′-unsymmetrical substituted 2,2′-bipyridine ligands linked to a conjugated donor group and coordinated to an organometallic electron acceptor moiety. Here we report (*i*) the synthesis and characterization of some new 4-alkenyl-4′-methyl-2,2′-bipyridine complexes of rhenium, zinc and mercury, in which the alkenyl fragment bears a π-donor group such as dialkylaminophenyl or ferrocenyl, and (*ii*) preliminary solution electric field-induced second-harmonic generation (EFISH) studies, which show a strong enhancement of the second-order molecular hyperpolarisability (β) upon complexation.



Scheme 1 *Reagents*: i, $Pr^i{}_2NLi$, ii, D–CHO; iii, $(MeCO)_2O$

Bipyridyl ligands **2a–d**† were prepared easily from commercially available 4,4′-dimethyl-2,2′-bipyridine;[12] monolithiation with 1 equiv. of lithium diisopropylamide, followed by addition of the appropriate aldehyde and dehydration of the resulting alcohol in refluxing acetic anhydride, yielded exclusively the (*E*)-vinyl substituted bipyridines **2** in 60–95% yield (Scheme 1). The absorption spectra for the luminescent yellow compounds **2a–c** are characterised by an intense intramolecular charge transfer transition (ICT) at λ_{max} = 380 or 390 nm (ε *ca.* 21000), whereas that of the red ferrocenyl compound **2d** exhibits in the visible region two typical bands at λ_{max} = 472 and 375 nm, which are also attributed to CT transitions.[5b,c]

The rhenium complexes **3a–d** were obtained in almost quantitative yields by heating ligands **2a–d** with $Re(CO)_5Br$ in toluene. Zinc complexes **4b** and **4′b** were prepared by the reaction of **2b** with 1 equiv. of zinc chloride and zinc acetate, respectively, in dichloromethane at room temperature. The same procedure was used to prepare the corresponding mercury compounds **5b** and **5′b**, Scheme 2.† The UV–VIS spectra of **3a–d** are characterised by intense broad CT bands (ε *ca.* 28000), which are 70–90 nm red-shifted in comparison with those of the free bipyridines. In addition, a less intense absorption is observed at higher energy (λ *ca.* 375 nm), which can be assigned to a MLCT transition dπ (Re) → π* (bpy).[13]

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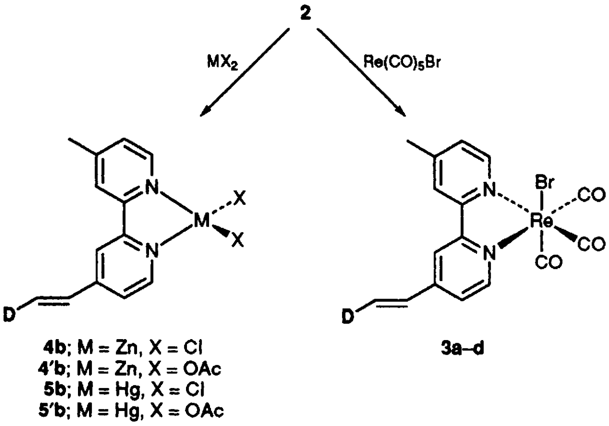
† All compounds gave satisfactory elemental analyses. *Selected spectroscopic data*: **2b**: ^1H NMR (300.12 MHz, CD_2Cl_2, 297 K) δ 8.51 (d, 1H, 6-PyH, *J* 5.2 Hz), 8.50 (d, 1H, 6′-PyH, *J* 4.4 Hz), 8.43 (d, 1H, 3-PyH, *J* 1.7 Hz), 8.24 (s, 1H, 3′-PyH), 7.40 (d, 2H, ArH, *J* 9.0 Hz), 7.35 (d, 1H, =CH, *J* 16.4 Hz), 7.31 (d, 1H, 5-PyH, *J* 5.2 and 1.4 Hz), 7.13 (dd, 1H, 5′-PyH, *J* 4.4 and 1.0 Hz), 6.87 (d, 1H, =CH, *J* 16.4 Hz), 6.62 (d, 2H, ArH, *J* 9.0 Hz), 3.29 (t, 4H, NCH_2, *J* 7.8 Hz), 2.41 (s, 3H, $PyCH_3$), 1.57 (m, 4H, –CH_2–), 1.35 (m, 4H, –CH_2–) and 0.95 (t, 6H, CH_3, *J* 7.3 Hz).

2d: ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K) δ 8.53 (d, 1H, 6-PyH, *J* 5.4 Hz), 8.52 (d, 1H, 6′-PyH, *J* 5.4 Hz), 8.45 (d, 1H, 3-PyH, *J* 1.6 Hz), 8.27 (s, 1H, 3′-PyH), 7.29 (dd, 1H, 5-PyH, *J* 5.2 and 1.8 Hz), 7.28 (d, 1H, =CH, *J* 16.1 Hz), 7.15 (dd, 1H, 5′-PyH, *J* 4.9 and 1.6 Hz), 6.73 (d, 1H, =CH, *J* 16.1 Hz), 4.53 (2H, t, α,α′-FcH, *J* 1.8 Hz), 4.35 (t, 2H, β,β′-FcH, *J* 1.8 Hz), 4.14 (s, 5H, C_5H_5) and 2.43 (3H, s, $PyCH_3$).

3b: IR (KBr) ν/cm^{-1} 2017, 1911 and 1887 (CO); ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K) δ 8.70 (d, 1H, 6-PyH, *J* 5.6 Hz), 8.61 (d, 1H, 6′-PyH, *J* 5.8 Hz), 8.07 (s, 1H, 3-PyH), 8.04 (s, 1H, 3′-PyH), 7.51 (d, 2H, ArH, *J* 8.3 Hz), 7.35 (d, 1H, =CH, *J* 16.0 Hz), 7.17 (dd, 1H, 5-PyH, *J* 5.9 and 1.5 Hz), 7.11 (dd, 1H, 5′-PyH, *J* 5.6 and 0.8 Hz), 6.67 (d, 1H, =CH, *J* 16.0 Hz), 6.67 (d, 2H, ArH, *J* 8.3 Hz), 3.33 (t, 4H, NCH_2, *J* 7.5 Hz), 2.34 (s, 3H, $PyCH_3$), 1.59 (m, 4H, –CH_2–), 1.37 (m, 4H, –CH_2–) and 0.96 (t, 6H, CH_3, *J* 7.3 Hz).

4′b: ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K) δ 8.69 (d, 1H, 6-PyH, *J* 5.2 Hz), 8.63 (d, 1H, 6′-PyH, *J* 5.2 Hz), 8.08 (s, 1H, 3-PyH), 8.04 (s, 1H, 3′-PyH), 7.48 (d, 1H, 5-PyH, *J* 5.2 Hz), 7.43 (d, 2H, ArH, *J* 9.0 Hz), 7.42 (d, 1H, =CH, *J* 16.2 Hz), 7.36 (d, 1H, 5′-PyH, *J* 4.9 Hz), 6.77 (d, 1H, =CH, *J* 16.2 Hz), 6.59 (d, 2H, ArH, *J* 8.9 Hz), 3.25 (t, 2H, NCH_2, *J* 7.7 Hz), 2.45 (s, 3H, $PyCH_3$), 1.88 [s, 6H, C(O)–CH_3], 1.52 (m, 2H, –CH_2–), 1.30 (m, 2H, –CH_2–) and 0.90 (t, 3H, CH_3, *J* 7.3 Hz).



Scheme 2

The low energy spectra of the zinc and mercury complexes **4,4′** and **5,5′** are also dominated by strong ICT transitions between 420 and 460 nm. The energy of this ICT band is sensitive to the nature of the organometallic fragment, providing a relative ordering of the acceptor strength. With a given donor group (for example Bu^n_2N), the ordering is: $ZnCl_2 > Zn(OAc)_2 > HgCl_2 > Hg(OAc)_2$ (Table 1).

Preliminary NLO solution measurements were performed by using the well known EFISH technique at 1.34 μm.[14] The values of β and β(0) obtained in chloroform for compounds containing the dibutylamino group, as well as their dipole moments, are reported in Table 1. This technique allows determination of $\gamma + \mu\cdot\beta/5kT$ where γ is the third-order polarizability of the molecule, μ its dipole moment, β the vector part of the first hyperpolarisability tensor, and T the temperature. In the case of molecules with a strong ICT and large dipole moment μ, γ may be neglected with respect of $\mu\cdot\beta/5kT$. As the EFISH technique gives only the scalar product μ·β, the ground state dipole moment has to be measured independently by a classical method based on the Guggenheim law. The angle θ between the directions of β and μ is assumed to be approximately the same for all compounds **3b**, **4b**, **4′b**, **5b** and **5′b**, so that comparison of β values of these molecules is relevant. Owing to metal complexation, this angle θ is somewhat different from that of the pure ligand; however assuming that the main contribution to the ICT is oriented along the axis separating the donor **D** from the nitrogen atom of the first pyridinium ring, this difference should not significantly affect the value of the scalar μ·β. The value of the zero-frequency β(0) is deduced from the experimental β value by considering the expression (1) for β

$$\beta(-2\omega;\omega,\omega) = \frac{W^4}{[W^2-(\hbar\omega)^2][W^2-(2\hbar\omega)^2]}\beta(0) \qquad (1)$$

for a two-level system where W is the energy of the ICT transition and ω the fundamental frequency.[14] Table 1 clearly shows the large increase of β and β(0) values by a factor of 3 to 9 upon complexation; the efficiency of the '$Re(CO)_3X$' moiety [$\beta(0) = 31 \times 10^{-30}$ esu] is found to be comparable to that of HgX_2[$\beta(0) = 25$–32×10^{-30} esu] whereas, as expected, the enhancement factor is much larger with the stronger Lewis acids ZnX_2[$\beta(0) = 57$–71×10^{-30} esu] than for the mercury analogues. In addition, halogeno complexes **4b** and **5b** display larger β values than acetato derivatives **4′b** and **5′b**. The electronegativity of the other ligands plays a non-negligible role in the nonlinear response of the molecule, and the ordering of the β values for zinc and mercury complexes is the same as that found from the relative energies of the ICT band.

Table 1 Spectroscopic and nonlinear optical (NLO) properties of 4-(*p*-dibutylaminostyryl)-4′-methyl-2,2′-bipyridine ligand and complexes

Compd	ML_n	λ_{max}/ nm[a]	μ^b/ Debye	β^b/ 10^{-30} esu	$\beta_0{}^b$/ 10^{-30} esu
2b	—	388	5.1	13.7	8.0
3b	$Re(CO)_3Br$	474	9.9	70.8	31.0
4b	$ZnCl_2$	460	11.6	152.0	71.0
4′b	$Zn(OAc)_2$	447	8.9	116.0	57.2
5b	$HgCl_2$	444	11.7	65.0	32.0
5′b	$Hg(OAc)_2$	441	9.8	50.0	25.0

[a] In CH_2Cl_2 solution. [b] In $CHCl_3$ solution. 1 Debye = 3.336×10^{-30} C m.

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