Hyper-Rayleigh scattering study of η^5-monocyclopentadienyl–metal complexes for second order non-linear optical materials

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A series of ionic η^5-monocyclopentadienyl–metal compounds possessing p-substituted benzonitrile ligands has been studied by hyper-Rayleigh scattering at the fundamental wavelength of 1.064 μm. Upon systematic variation of the metal ion, the first hyperpolarizability β was found to increase along the sequence Co, Ni, Ru, Fe, with about a three-fold increase from Ru to Fe. This yields very high values for the iron complexes, $e.g.$, $\beta = 410 \times 10^{-30}$ esu for $[Fe(\eta^5-C_5H_5)(dppe)(p-NCC_6H_4NO_2)]^+[PF_6]^-$ dissolved in methanol. The high β values are attributed to π back-donation resulting in an extension of the conjugated π-system from the Fe^{II} organometallic fragment, acting as a good donor group, via the nitrile to the acceptor group NO$_2$. Complexes with single phenyl rings as conjugated chains perform better than their biphenyl analogues, which is explained in terms of non-planarity of the coordinated biphenyl ligands in solution. By comparing complexes with electron donor and acceptor substituted ligands it is demonstrated that the organometallic moiety can be used as an extremely effective donor group but not as a good acceptor group.

In the search for new materials for non-linear optical (NLO) applications many studies have focused on organic molecules containing highly polarizable conjugated backbones. For second order NLO an electron donor and an acceptor group are attached to both ends of this backbone to create an asymmetric 'push–pull' system.[1] More recently organometallic compounds have attracted considerable attention because of their enhanced NLO properties.[2–4] In these compounds the low energy charge transfer (metal to ligand or ligand to metal) which typically occurs in organometallic complexes is combined with the high mobility of π electrons in a conjugated organic ligand to obtain high hyperpolarizabilities. In this way the organometallic moiety forms an alternative type of donor or acceptor group for the traditional push–pull system. The energy of the charge transfer transition can be tuned by variation of the ligands and especially of the metal ion itself to optimise the hyperpolarizabilities by near resonant enhancement. Contrary to the ferrocene derivatives, which were the first organometallic compounds to be studied for their NLO properties, complexes containing a η^5-monocyclopentadienyl–metal fragment present the structural advantage of having the metal ion in the plane of the conjugated backbone (Fig. 1) which was expected to improve the non-linearity through a better coupling between the metal and the conjugated ligand.[3] In good agreement with this, we found encouraging NLO results in our earlier studies for $[Fe(\eta^5-C_5H_5)\{(+)-DIOP\}(p-NCC_6H_4NO_2)][PF_6]$ and $[Ru(\eta^5-C_5H_5)\{(+)-DIOP\}(p-NCC_6H_4NO_2)][CF_3SO_3]$, which were 38 and 10 times, respectively, more efficient than the urea standard in second harmonic generation (SHG) measured by the Kurtz powder technique.[5,6] Nevertheless, as Kurtz powder efficiencies depend strongly on packing arrangements in the crystal structure,

these results were difficult to interpret in terms of molecular structure–NLO property relationships.

For this reason, measurements of the molecular hyperpolarisabilities themselves are preferred. Because the usual EFISHG (electric field-induced second-harmonic generation) technique for determination of $\mu\beta$ is not applicable for these ionic compounds, the technique of hyper-Rayleigh scattering (HRS) in liquid solution was used. HRS is the scattering of second harmonic light, resulting from the incoherent addition of contributions from randomly oriented molecules in a disordered medium.[7] As this scattered intensity depends on an orientational average of the molecular β tensor,[8,9] it can be used to measure the molecular second order NLO response,[10] without the need to apply an electric field to break the macroscopic centrosymmetry of the medium. An additional advantage over the EFISHG technique is that it does not require the knowledge of the molecular dipole moment.

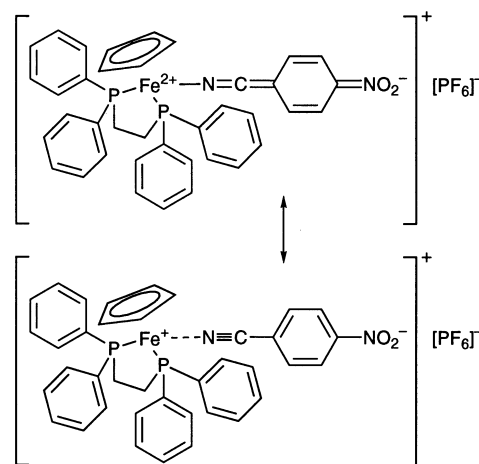In order to get a better understanding of the NLO structure–

Fig. 1 Chemical structure of the iron complex **F2** (see Table 2), depicting the charge transfer transition schematically

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property relationships we have synthesised a systematic series of compounds and measured their molecular first hyperpolarizability β by hyper-Rayleigh scattering in liquid solution. Each of the compounds consists of a transition metal center coordinated by an η^5-monocyclopentadienyl ring, a PPh_3 or dppe [1,2-bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$] ligand, and a conjugated nitrile ligand. The coordination through the $N\equiv C$ functional group permits interactions of the suitable metal d orbitals with the two sets of orthogonal π and π^* orbitals of the nitrile group (more localized on N and C atoms, respectively), leading consequently to an extension of the π-electron system between the metal and a donor/acceptor substituting group on the ligand. The donor/acceptor ability of a systematic series of metal fragments η^5-$C_5H_5M(PP)$ (M = Co^{III}, Ni^{II}, Fe^{II} or Ru^{II}; PP = phosphine ligand) was studied by combining them with the same set of conjugated ligands *para*-substituted with traditional acceptor/donor groups to form push–pull systems. Similar molybdenum and tungsten compounds have also been studied by the Kurtz powder SHG technique,[11] but they yielded very low SHG efficiencies, and because of the much more promising results on the iron and ruthenium compounds, they were not selected for further study. In all cases the possibility of using the organometallic fragment as a π-donor was investigated (in combination with a NO_2 group), while for the Ni and Co complexes also the possibility of using it as a (σ- or π-) acceptor was considered. The phosphine ligands used (PPh_3 and dppe) were selected for their good electron releasing properties, since chirality was not required here (unlike in our previous studies by means of the Kurtz powder technique, for which chiral phosphine ligands had to be used in order to obtain non-centrosymmetric crystals).[5,6]

The effect of different conjugated ligands, benzene *vs.* biphenyl derivatives, on the hyperpolarizability was also evaluated.

Experimental

Synthesis and characterization

All the experiments were carried out under vacuum or nitrogen atmosphere using standard Schlenk techniques, and solvents were dried following published methods.[12]

New complexes of Co^{III}, Ni^{II}, Ru^{II} and Fe^{II} were prepared by the general procedure of halide abstraction of the corresponding parent compound, in the presence of the required nitrile. In all cases PF_6^- was used as counter ion.

Compounds $[Co(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4C_6H_5)][PF_6]_2$ **C1** and $[Co(\eta^5\text{-}C_5H_5)(dppe)\{(p\text{-}NCC_6H_4N(CH_3)_2\}][PF_6]_2$ **C2** were synthesized in good yield by reaction of $[Co(\eta^5\text{-}C_5H_5)(CO)I_2]$[13] with dppe and $TlPF_6$ in the presence of a slight excess of the molar equivalent amount of the required nitrile. The reaction time depends on the nitrile ligand but in general takes several days. These new complexes were recrystallized from acetone–diethyl ether giving microcrystalline red–brown products which were fully characterized by elemental analysis, IR and ^1H, ^{13}C, ^{31}P NMR spectroscopies (Table 1). In addition, 10^{-3} M solutions of the compounds in nitromethane were found to present molar conductivities in agreement with values reported in the literature for 1:2 electrolytes.[14] Characteristic singlet signals from the η^5-C_5H_5 coordinated ligand were observed at δ 6.38 (in $[^2H_6]$acetone) for both complexes. In order to gain an understanding of the electronic flow, spectroscopic data of uncoordinated and coordinated nitrile ligands were compared. A general trend of shielding on *ortho* protons (relative to the NC group) in the benzene ring was observed accompanied by some deshielding on the other protons of the benzene rings. This effect might be attributed to electronic interactions in solution, as observed previously for a family of ruthenium analogues with a variety of counter ions,[6] since no evidence of π back-donation was found in the

present cases. In fact, a $30\,cm^{-1}$ positive shift for the ν_{NC} stretching vibration was observed, after coordination, in the IR spectra of both complexes, suggesting a normal metal–ligand σ coordination.

Experimental data. $[Co(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4C_6H_5)]$ $[PF_6]_2$: reaction time, 120 h at r.t.; 70% yield (crude product); mp 185–187 °C (decomp.); molar conductivity = $186.5\,\Omega^{-1}\,cm^2\,mol^{-1}$; IR(KBr): $\nu_{CN} = 2265\,cm^{-1}$. Elemental analysis. Found (calc. for $C_{44}H_{38}CoF_{12}NP_4$): C, 49.7 (49.8); H, 3.9 (3.8); N, 1.5 (1.5%). $[Co(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6\text{-}H_4N(CH_3)_2)][PF_6]_2$: reaction time, 56 h at r.t. plus 70 h reflux; 96% yield (crude product); mp 185–187 °C (decomp.); molar conductivity = $165.4\,\Omega^{-1}\,cm^2\,mol^{-1}$; IR(KBr): ν_{CN} $2240\,cm^{-1}$. Elemental analysis. Found (calc. for $C_{40}H_{39}CoF_{12}N_2P_4$): C, 49.8 (50.1); H, 4.2 (4.1); N, 2.7 (2.9%).

Complexes $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(p\text{-}NCC_6H_4NO_2)]PF_6$ **N4** and $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(p\text{-}NCC_6H_4C_6H_4NO_2)]PF_6$ **N3** were prepared following the same procedure used for other compounds of this family.[15] Also for these compounds, both coordinated nitriles showed the same general behavior concerning spectroscopic data (Table 1), as was observed for the Co^{III} derivatives and again a $\Delta\nu_{NC} = 30\,cm^{-1}$ shift was found, suggesting the same normal metal–ligand σ coordination mode.

Experimental data. $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(NCC_6H_4NO_2)]$ PF_6: colour: brown; 65% yield; mp 162 °C (decomp.); molar conductivity = $75\,\Omega^{-1}\,cm^2\,mol^{-1}$; IR(KBr): ν_{CN} $2270\,cm^{-1}$; $\nu_{NO_2} = 1350$, $1530\,cm^{-1}$. Elemental analysis. Found (calc. for $C_{30}H_{24}F_6N_2NiO_2P_2$): C, 52.9 (53.1); H, 3.5 (3.6); N, 3.9 (4.1%). $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(NCC_6H_4C_6H_4NO_2)]PF_6$: color: brown–green; 55% yield; mp: 118–120 °C; molar conductivity = $78\,\Omega^{-1}\,cm^2\,mol^{-1}$; IR(KBr): ν_{CN} $2260\,cm^{-1}$; $\nu(NO_2) = 1350$, $1600\,cm^{-1}$. Elemental analysis. Found (calc. for $C_{36}H_{28}F_6N_2\text{-}NiO_2P_2$): C, 57.2 (57.2); H, 3.6 (3.7); N, 3.6 (3.7%). Experimental data relating to complexes $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(NCC_6H_4R)]PF_6$ [R = C_6H_5 (**N1**) and $N(CH_3)_2$ (**N2**)] are published elsewhere.[15]

The complexes $[Ru(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4NO_2)]PF_6$ **R2** and $[Ru(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4C_6H_4NO_2)]PF_6$ **R1** were synthesized by chloride abstraction of the parent compound $[Ru(\eta^5\text{-}C_5H_5)(dppe)Cl]$ and their characterization together with studies on their optical third harmonic generation (THG) were reported before.[16] Spectroscopic experimental data for these compounds suggest that π back-donation takes place, revealed by comparison of chemical shifts of the uncoordinated and coordinated ligands by ^1H and ^{13}C NMR spectroscopy, and also IR spectra presented the same value of ν_{NC} before and after coordination, this suggesting that the positive shift originating from the σ coordination is cancelled by the opposite effect of π back-donation.

The complexes $[Fe(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4NO_2)]$ $[PF_6]$ **F2** and $[Fe(\eta^5\text{-}C_5H_5)(dppe)(p\text{-}NCC_6H_4C_6H_4NO_2)]$ $[PF_6]$ **F1** were synthesized by iodine abstraction of the starting material $[Fe(\eta^5\text{-}C_5H_5)(dppe)I]$ following the same procedure used in the synthesis of analogous compounds.[5] Experimental data relative to these compounds are published elsewhere.[17] An important structural feature for these two compounds is the evidence of π back-donation revealed both by chemical shifts on ^1H and ^{13}C NMR spectra and by the negative shifts $\Delta\nu_{NC}$ of -20 to $-30\,cm^{-1}$ observed in IR spectra.

HRS measurements

HRS measurements with a fundamental wavelength of $1.064\,\mu m$ were performed on dilute solutions (of the order of $1\,g\,l^{-1}$) in methanol or chloroform (depending on solubility and/or chemical stability). The solutions were systematically passed through 500 nm microporous filters. Laser pulses (energy *ca.* $20\,\mu J$, width = 70 ps, repetition rate = 2 kHz) from

Table 1 Selected ^1H and ^{13}C NMR data for complexes [CoCp(dppe)(*p*-NCR)][PF$_6$]$_2$ (in [$^2H_6$]acetone) and [NiCp(PPh$_3$)(*p*-NCR)]PF$_6$ (in [$^2H_1$]chloroform)
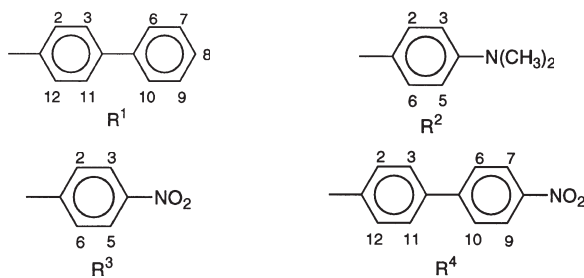
compound	δ (multiplicity, relative integral, assignment)
[CoCp(dppe)(*p*-NCR^1)][PF$_6$]$_2$	^1H 6.37 (s, 5H, η^5-C$_5$H$_5$), 7.03 (d, 2H, H^6,H^{10}), 7.46–7.54 (m, 4H, H^2,H^3,H^{11},H^{12}), 7.65–7.70 (m, 3H, H^7,H^8,H^9)
	^{13}C 94.86 (η^5-C$_5$H$_5$), 108.17 (C^1), 130.00 (C^3,C^{11}), 134.62 (C^2,C^{12}), 138.88 (CN), 148.55 (C^4)
[CoCp(dppe)(*p*-NCR^2)][PF$_6$]$_2$	^1H 3.06 [s, 6H, N(CH$_3$)$_2$], 6.31 (s, 5H, η^5-C$_5$H$_5$), 6.58 (d, 2H, H^3,H^5), 6.64 (d, 2H, H^2,H^6)
	^{13}C 39.89 [N(CH$_3$)$_2$], 92.75 (C^1), 94.46 (η^5-C$_5$H$_5$), 111.84 (C^3,C^5), 135.20 (C^2,C^6), 140.25 (CN), 155.1 (C^4)
[NiCp(PPh$_3$)(*p*-NCR^3)]PF$_6$	^1H 5.52 (s, 5H, η^5-C$_5$H$_5$), 7.36 (d, 2H, H^2,H^6), 8.13 (d, 2H, H^3,H^5)
	^{13}C 96.78 (η^5-C$_5$H$_5$), 115.32 (C^1), 123.95 (C^3,C^5), 134.61 (C^2,C^6), 150.46 (C^4)
[NiCp(PPh$_3$)(*p*-NCR^4)]PF$_6$	^1H 5.52 (s, 5H, η^5-C$_5$H$_5$), 7.27 (d, 2H, H^2,H^{12}), 7.58 (d, 2H, H^3,H^{11}), 7.66 (d, 2H, H^6,H^{10}), 8.29 (d, 2H, H^7,H^9)
	^{13}C 96.56 (η^5-C$_5$H$_5$), 109.52 (C^1), 124.34 (C^7,C^9), 128.00 (C^3,C^{11}), 128.22 (C^6,C^{10}), 133.84 (C^2,C^{12}), 144.56 (C^4), 144.85 (C^5), 148.02 (C^8)

a Nd : YAG regenerative amplifier were focused into a rectangular glass cell by a 100 mm lens (Fig. 2). The laser beam was expanded (*ca.* 2 cm width) first to minimize two-photon luminescence from the cut-off filter, which is used to eliminate any second harmonic light generated earlier on in the setup. The scattered harmonic light was collected at 90° and filtered by a monochromator with 1 nm bandwidth. Single photon pulses from a photomultiplier were detected in a 5 ns time gate around the laser pulse. The count rates were corrected for pile-up errors at increasing count rates and for losses due to absorption at 532 nm by the solution and due to the polarization dependent monochromator efficiency. Systematic scanning of an 8 nm wide region around 532 nm allows for correction for any two photon luminescence background, which is approximated to be linear over this narrow region. This correction is accomplished by integrating the signal over the inner 4 nm wide interval and subtracting a background based on a linear fit of the remaining two outer regions. A
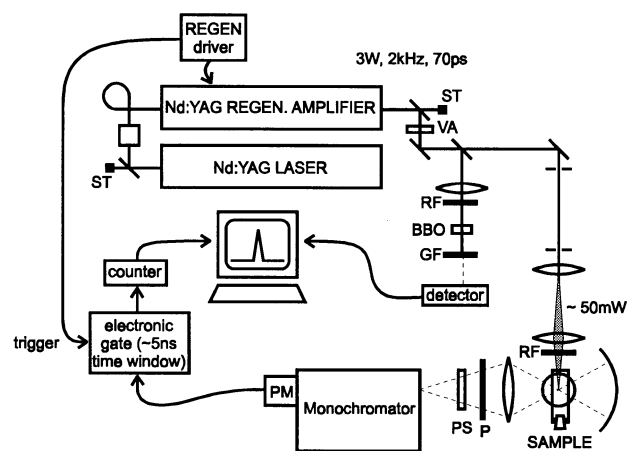

Fig. 2 Experimental setup for hyper-Rayleigh scattering measurements. VA: variable attenuator; RF: long wavelength pass filter; GF: short wavelength pass filter; P: polarizer; ST: beam stop; dashed lines: frequency doubled light.

significant photoluminescence background was only observed for the Co compounds, where the luminescence signal, integrated over 4 nm, was about 1 to 2.5 times the actual HRS signal. Hyper-Rayleigh scattering from the glass walls of the cell is eliminated by imaging this part outside the entrance slit of the monochromator. In a reference arm a fraction of the laser light was frequency-doubled and this intensity was used to correct for fluctuations of the laser intensity and pulse shape. Using the internal reference method[18] we obtain the ratio β_{HRS}/β_{HRS}(solvent), where β_{HRS} is given in terms of the orientational averages $\langle\beta_{IJK}^2\rangle$ of the molecular hyperpolarizability by $(\langle\beta_{ZZZ}^2\rangle+\langle\beta_{XZZ}^2\rangle)^{1/2}$. The β tensors of chloroform and of methanol are treated as if they were also dominated by β_{zzz}, using values $\beta_{CHCl_3}=0.49\times10^{-30}$ esu (EFISHG, from ref. 19) and $\beta_{MeOH}=0.23\times10^{-30}$ esu respectively, the β value for the solute ($=|\beta_{zzz}|$) was determined. Alhough for MeOH and CHCl$_3$ off-diagonal components may be expected to be significant, additional assumptions on the β tensor components would be needed to improve on this analysis. The reference value for MeOH was measured by HRS relative to CHCl$_3$ by external reference, using the usual Lorentz local field factors and correcting for the different focusing in solvents with different refractive indices. In these external reference measurements the incident average power had to be reduced to less than 20 mW in order to minimize thermal self-defocusing in MeOH and obtain a reliable ratio $\beta_{MeOH}/\beta_{CHCl_3}$.

Results and Discussion

The chemical structures of the compounds studied and the experimental results are summarized in Table 2. For comparison the experiments were also performed on the free nitrile ligands **L1–L4**. The Co and Ni complexes **C1**, **C2**, **N1** and **N2**, in which the organometallic moiety was expected to act as an electron acceptor, show rather low hyperpolarizabilities. In fact, the β values of the Ni complexes are comparable to those of the free nitrile ligands. Moreover, as the Co complexes were chemically too unstable in methanol solution to allow accurate measurements before significant decomposition took place, and as the decomposition products showed higher β values

Table 2 Experimental hyperpolarizabilities and spectroscopic data measured in chloroform and in methanol solution

compound	λ_{max}/nm MeOH	λ_{max}/nm CHCl$_3$	λ_{eg}^{a}/nm	ε_{max}/ l mol^{-1} cm^{-1}	β/10^{-30} esu MeOH	β/10^{-30} esu CHCl$_3$	ν_{CN} ($\Delta\nu$)/cm^{-1}
free ligand							
L1 p-NCC$_6$H$_4$Ph	269			19 000[b]	8.7		2230
L2 p-NCC$_6$H$_4$N(CH$_3$)$_2$	293			27 000[b]	18.5		2220
L3 p-NCC$_6$H$_4$C$_6$H$_4$NO$_2$	294	298		21 500[b]	14.6	11	2230
L4 p-NCC$_6$H$_4$NO$_2$	257			14 000[b]	4.4		2240
complex							
C1 [CoCp(dppe)(**L1**)]$^{2+}$	298			31 000[b]	<25		2265 (+35)
C2 [CoCp(dppe)(**L2**)]$^{2+}$	332			60 000[b]	<40		2240 (+20)
C3 [CoCp(dppe)(**L3**)]$^{2+}$		420[c]	511[c]	650[c]	≈35		2270[d] (+40)
C4 [CoCp(dppe)(**L4**)]$^{2+}$	419	416[c]	507[c]	1700[c]	≈45		2275[d] (+35)
N1 [NiCp(PPh$_3$)(**L1**)]$^{+}$	267	282		30 000[b]	17	18	2275[d] (+45)
N2 [NiCp(PPh$_3$)(**L2**)]$^{+}$	291	298		27 000[b]	18.4	14	2240[e] (+20)
N3 [NiCp(PPh$_3$)(**L3**)]$^{+}$	293	299	453	38 000[f]		45	2260 (+30)
N4 [NiCp(PPh$_3$)(**L4**)]$^{+}$		419	419	4000[f]		93	2270 (+30)
R1 [RuCp(dppe)(**L3**)]$^{+}$	288	293	401	17 000[f]	96	85	2230[g] (0)
R2 [RuCp(dppe)(**L4**)]$^{+}$	358	358	435	8000[b]	138	126	2230[g] (−10)
F1 [FeCp(dppe)(**L3**)]$^{+}$	375	372	431	8000[f]	276	240	2210[h] (−20)
F2 [FeCp(dppe)(**L4**)]$^{+}$	468	460	457	5700[b]	410	375	2210[h] (−30)

[a] λ_{eg} is the position of the longest wavelength absorption band obtained from a Gaussian fit and used for the two-level model. [b] In methanol. [c] In dichloromethane. [d] This work. [e] Ref. 15. [f] In chloroform. [g] Ref. 16. [h] Ref. 17.

than the original complexes, the experimental error on β for the Co complexes **C3** and **C4** is quite large (estimated at *ca.* 30%) and for the two other Co complexes (**C1** and **C2**) only an upper limit of β could be determined. Chemical decomposition was also accompanied by the appearance/increase of a two-photon luminescence background.

The β values for the Ni complexes **N1** and **N2** are comparable to those of the free nitrile ligands, while for the Ni complexes with acceptor-substituted ligands significantly larger β values are obtained, which seems to suggest that Ni acts as a (π-)donor rather than an (σ- or π-)acceptor. These results might be somewhat surprising, considering that the Ni fragment behaves as an acceptor group, according to our spectroscopic data for both p-NCC$_6$H$_4$NMe$_2$ and p-NCC$_6$H$_4$NO$_2$ coordinated nitriles. One reasonable explanation for this was found in our theoretical calculations by the extended Hückel method,[15] which suggest that the frontier π molecular orbitals are not totally delocalized from nickel to the end-group. Moreover, they also show that C and N atoms of the functional nitrile group do not contribute to these frontier π molecular orbitals, this making the N≡C group act as a spacer between the Ni fragment and the π system of the ligand aromatic ring. Therefore, the low values found for these nickel derivatives can be understood on the basis of the mentioned theoretical calculations. The trend found in the present work for the hyperpolarizabilities, [NiCp(PPh$_3$)-(p-NCC$_6$H$_4$NO$_2$)]$^{+}$ > [NiCp(PPh$_3$)(p-NCC$_6$H$_4$C$_6$H$_4$NO$_2$)]$^{+}$ > [NiCp(PPh$_3$)(p-NCC$_6$H$_4$C$_6$H$_5$)]$^{+}$ > [NiCp(PPh$_3$)(p-NC-C$_6$H$_4$NMe$_2$)]$^{+}$, is explained by the increase of the HOMO–LUMO gap, which is one of the factors that determine the hyperpolarizability (as can be seen from the two-level model; see eqn. (1), below). In fact, our theoretical calculations by the extended Hückel method have yielded for the model compounds [NiCp(PH$_3$)(p-NCC$_6$H$_4$NO$_2$)]$^{+}$, [NiCp(PH$_3$)(p-NCC$_6$H$_4$C$_6$H$_5$)]$^{+}$ and [NiCp(PH$_3$)(p-NCC$_6$H$_4$NH$_2$)]$^{+}$ values for the HOMO–LUMO gap of 0.4, 1.5 and 3.0 eV, respectively.[15] Of course these calculated values are only expected to predict the general trend: the extended Hückel method does not give realistic absolute values for the energies. However, the lowest value of 0.4 eV would make the nitro derivative the best candidate for NLO properties in this family of nickel compounds, as was found experimentally in the present work.

The Ru and especially Fe complexes show even higher β values. This supports the idea that the Ru or Fe organometallic moiety forms a good electron donor and that d–π* back-donation takes place extending the conjugation from the metal *via* the nitrile to the acceptor group NO$_2$, as expected on the basis of NMR and IR studies.[5,6,16] Indeed, the increase in hyperpolarizability along the series Co, Ni, Ru, Fe is perfectly consistent with the occurrence of π back-donation in the Ru and Fe complexes as reflected in the decrease in vibration frequency of the C≡N group upon coordination: $\Delta\nu$ is of the order of +30 cm^{-1} for the Ni and Co complexes, 0 to −10 cm^{-1} for the Ru complexes and up to −30 cm^{-1} for the Fe complexes.

For all compounds, both complexes and free nitrile ligands, a depolarization ratio of 0.20±0.02 was found in HRS, as for a linear molecule with only one (diagonal) β tensor component.[9,20] This, together with the dramatic ligand dependence of the hyperpolarizability, confirms that the latter originates mainly in the essentially linear conjugated path from metal to nitrile ligand, and not, for example, in the phosphine ligand. This is further supported by the fact that the separate (halogen substituted) organometallic fragments without conjugated ligands show no significant absorption features in the visible range,[16] as observed for the nitrile complexes. It is therefore remarkable to obtain a β value which is so much larger (410 × 10^{-30} esu) than that of Me$_2$N—N=CC$_6$H$_4$NO$_2$ (β_{EFISHG}^{1064nm} = 63 × 10^{-30} esu,§ from ref. 21), while using a similar, very short, conjugated chain, and using the same traditional acceptor group. This means that the Fe(η^5-C$_5$H$_5$)(dppe) moiety forms an extremely effective donor group for second order NLO push–pull systems. A recent study by Whittall *et al.*[22] has demonstrated for comparable Ru complexes that by using slightly longer conjugated ligands indeed very high hyperpolarizabilities can be obtained. Extrapolating our present results, a further improvement by a factor of three could be expected for their compounds upon replacement of Ru by Fe. It is also interesting to compare the β value of 93 × 10^{-30} esu for compound **N4** with that of 221 × 10^{-30} esu reported by Whittall *et al.*[23] for the completely analogous Ni complex with a C≡C linkage instead of N≡C. In as far as these results obtained under different experimental conditions and with a different calibration standard can be directly compared, they seem to indicate that the C≡C linkage leads to a more efficient π back-donation.

§ In ref. 21 a different definition of β was used. Here, we use the power series definition, and this literature value was converted accordingly, as indicated in Table 1 of this reference.
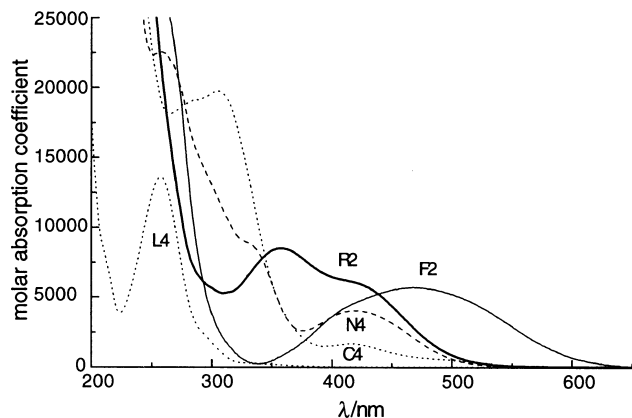
Fig. 3 Absorption spectra of the free $NCC_6H_4NO_2$ ligand (**L4**) and the corresponding metal complexes, labeled as in Table 2

Note that the Ni, Ru and Fe compounds with the $NC(C_6H_4)_2NO_2$ ligand have lower β values than the corresponding compounds with the shorter $NC(C_6H_4)NO_2$ ligand. This is quite a surprising result, which can be explained by a breaking of the conjugation if we assume there is a significant torsion angle between the two phenyl rings, when the compound is in solution, conversely to what happens in the solid state, for which X-ray diffraction results show an almost planar structure of the biphenyl ligand (dihedral angle *ca.* 11°). This difference in dihedral angle between the solid state and solution structure is not so surprising as it is well known that the energy barrier for rotation of a biphenyl linkage is quite low. Also, similar differences in torsion angle between solid state ($\leqslant 10°$) and liquid (30°) or gas phase structure (40°) have been reported for pure biphenyl.[24] Earlier THG studies (at 1064 nm) in PMMA films, however, have shown a higher γ for compound **R1** than for **R2**.[16] So either we have to assume that in polymer solution the torsion angle is much smaller, as it is in the crystal structure, or that the higher γ of compound **R1** is caused by a three-photon resonance, rather than by the larger conjugation length assumed in ref. 16. Indeed the third harmonic wavelength (355 nm) is within a series of absorption bands (*ca.* 350 and 400 nm for both compounds and also *ca.* 300 nm for **R1**; see Fig. 2 of ref. 16 and Fig. 3), and therefore a complicated process involving several near-resonant enhanced contributions may be responsible for the observed γ_{THG} values.

Compounds with larger β values clearly show absorption bands extending further into the visible range (Fig. 3). This observation can be examined quantitatively by applying the two-level model, according to which β is given by[25]

$$\beta(-2\omega;\omega,\omega) = \frac{3e^2}{2\hbar m} \frac{\omega_{eg} f \Delta\mu}{(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2)} \quad (1)$$

Most of the absorption spectra consist of several poorly resolved bands, so we fitted them with a series of Gaussian bands. Assuming that the lowest energy band is the main charge transfer band contributing to β, we can then enter the position ω_{eg} (see Table 2) and the integrated intensity (proportional to the oscillator strength f) of this band into eqn. (1). This two-level model obviously is a rather crude simplification of the complicated electronic structure of these compounds, but by comparing the absorption spectra with those of the free conjugated ligands and with those of similar (Cl substituted) organometallic fragments without conjugated ligands (see Fig. 2 of ref. 16), several of the higher energy bands can be assigned to excitations localized within the conjugated ligands and with d–d transitions of the metal center, respectively, and are therefore not expected to give a substantial contribution to β. As the dipole moment difference $\Delta\mu$ between the ground state and excited state is unknown, we plotted the experimental β *vs.* the factor $\omega_{eg} f/(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2)$ in

Fig. 4 (for the complexes with NO_2 groups). A very clear correlation is found and especially the trend between complexes of the same metal when replacing biphenyl with phenyl ligands is very systematic. Some deviations occur for the less hyperpolarizable compounds, but it should be noted that for some of these (**R1** and **N3**) the lowest energy band used in the two level model is only a shoulder on a much stronger band which is also well below the energy of the free ligand absorption bands, and it is therefore not clear in these cases which is the charge transfer band giving the main contribution to β. Finally, $\Delta\mu$, which was not taken into account, might also differ significantly among compounds, especially as the metal is changed. Note that, in this model, the increase in hyperpolarizability of the Ru compounds with respect to the corresponding Ni compounds should be attributed entirely to this difference in $\Delta\mu$.

Conclusions

By measuring the first optical hyperpolarizability in a systematic series of complexes with varying metal ions and with both donor and acceptor substituted ligands, we found that metal–cyclopentadienyl groups can act as extremely good electron donor groups, but not as acceptor groups. Cyclopentadienyl groups with ruthenium and especially iron are much more efficient electron donors than the traditional donor groups (such as alkyl substituted amine groups) for second order NLO molecules. The first hyperpolarizabilities are found to increase along the series Co, Ni, Ru, Fe, with iron complexes showing three times higher non-linearities than the analogous ruthenium compounds. These results are in perfect agreement with the spectroscopic evidence for d–π* back-donation taking place in the Ru and especially Fe complexes. As the complexes studied here contain only conjugated chains of moderate length, we expect that important further improvements of the first hyperpolarizability will be obtained by optimization of this π system. Based on the good correspondence with the two-level model, we assigned the low energy transitions observed in the optical absorption spectra to the metal to ligand charge transfer which is responsible for the high hyperpolarizabilities. The lower hyperpolarizabilities observed for complexes with biphenyl derived ligands are attributed to the possible non-planarity of these ligands.
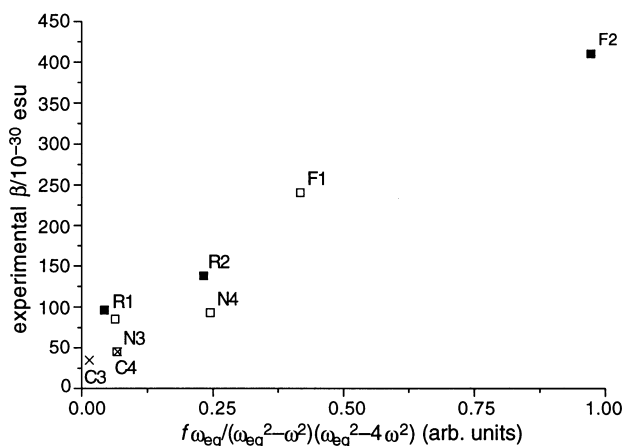
Fig. 4 Correlation of β from HRS with the truncated expression from the two-level model based on the lowest energy transition in the absorption spectra. The Ni, Ru and Fe complexes (squares) are measured in $CHCl_3$ ($\square$) or MeOH ($\blacksquare$) solution, while for the Co complexes ($\times$), HRS data in MeOH solution were combined with absorption data in CH_2Cl_2.

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