Large second-order NLO properties of new conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine

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The NLO properties of a series of vinylenephenylene complexes with a pendant ferrocene and an end-capping pyridine have been evaluated by the HRS method. The NLO responses (β) are clearly dependent on both the nature of the electron-accepting fragment and the length of the conjugated chain. As seen in some previous works on other organometallic complexes, the spectroscopic properties and electrochemical behavior of our compounds provide efficient diagnostics for the nonlinear optical behavior.

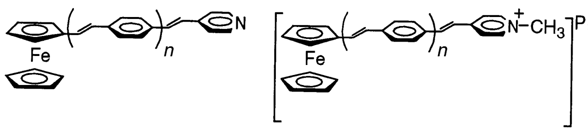
The increasing interest in the preparation of new chromophores suitable for electro-optical applications has initiated a search for new synthetic procedures leading to highly polarizable organometallic complexes. Many studies reporting nonlinear optical (NLO) properties of an enormous number of organic, inorganic and organometallic complexes have been published and some common structural features have been deduced. For example, in most cases the backbone of the chromophore consists of an electron-donating group connected to an electron-accepting group by a conjugated π-bridge. It is widely accepted that the NLO response of the chromophore is greatly increased upon chain lengthening of the conjugated π-bridge. On the other hand, it has been suggested that this increase gradually diminishes until an asymptotic or limiting situation is achieved, in which elongation of the chain does not lead to any further increase in the NLO response.[1]

We and other groups have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes.[2,3] Most of the problems regarding the synthesis of such complexes are encountered when trying to extend the conjugated chain in a multi-step synthetic procedure. In fact, the list of such long conjugated metal-based ligands used in nonlinear optics is still short, despite their high NLO responses.[3e,4] Since the electronic and optical responses of these materials seem to be highly influenced by the length of the conjugated chain connecting the electron-donating and electron-accepting termini of the molecule, we focused our efforts on obtaining long-chain oligomers with a pendant ferrocene fragment. We have recently reported the preparation and electronic properties of new conjugated ferrocenyl-based ligands based on end-capped nitrile,[2b] pyridine[5a] and nitro[5b] fragments with distances between the iron atom and the heteroatom of up to 27 Å.[5a] These complexes show interesting electronic and spectroscopic properties that make them good candidates for NLO measurements. Among all the compounds that we have already reported, we opted for pendant pyridines for several reasons: (i) there is a precedent[6] as extremely high NLO responses have been reported in the compound *E*-[CpFe(η^5-C_5H_4–CH=CH–$C_5H_4N^+$–CH_3)]I^-, (ii) the coordination properties of the pyridines allow us to obtain several complexes in which the electronic properties of the electron-accepting moiety can be fine-tuned, (iii) the lone pair on the nitrogen atom of the pyridine allows protonation and methylation, converting the compound into a cation with a positive charge located at the nitrogen atom and hence increasing the electron-accepting character of the ancillary ligand and (iv) the coplanarity observed in the molecular structures of the complexes,[5a] together with their redox and electronic properties, show efficient communication between the donor and acceptor groups.

Based on the above-mentioned premises, we have studied the NLO properties of several ferrocenyl oligomers with pyridine pendant groups and have shown their dependence upon chain lengthening, coordination capabilities and methylation of the pyridine groups. The NLO results obtained, together with the results obtained in our previous papers,[2a,5] allow us to confirm that spectroscopic and electrochemical data are an excellent way to qualitatively diagnosis NLO behavior.

Results and discussion

We recently reported the synthesis and characterization of new ferrocenyl oligomers connected to a pyridyl group through a π-conjugated bridge[5a] of the type CpFe(η^5-C_5H_4{CH=CHC_6H_4}$_n$CH=CHC_5H_4N) and [CpFe(η^5-C_5H_4-{CH=CHC_6H_4}$_n$CH=CH$C_5H_4NCH_3$)]PF_6 ($n = 0$, 1 and 2, Scheme 1). The molecular structures of these compounds show an almost perfect coplanarity of all the aromatic rings for the all-*E* conformation. This coplanarity suggests that the conjugated bridge is an effective electronic pathway between the ferrocenyl fragment and the pyridyl ring. Although it is difficult to relate solid state structures to those in solution, in the case of highly conjugated systems such as ours, a large



1, $n = 0$
2, $n = 1$
3, $n = 2$

1-CH_3, $n = 0$
2-CH_3, $n = 1$
3-CH_3, $n = 2$

Scheme 1

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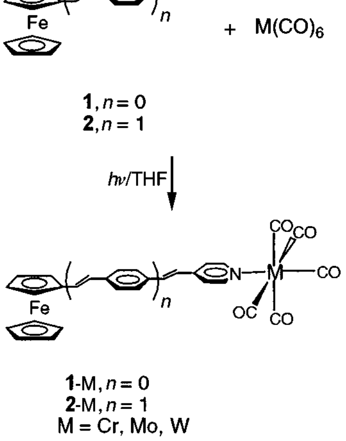
contribution from the coplanar structure is expected as a consequence of the effective overlap of the carbon p_z orbitals to form the extended π system. This is confirmed by other physical properties of the compounds such as the electrochemical behavior and the electronic spectra.[5a]

The coordination capabilities of pyridine allow us to obtain a series of group 6 carbonyl compounds, which have proved to act as a very effective electron-accepting moiety in several NLO chromophores. Scheme 2 shows the general procedure to obtain such complexes in the case of $n = 1$. The NLO behavior of some of these complexes ($n = 0$) was reported simultaneously to our results[2a] by Lee *et al.*,[3d] who found β values significantly different from ours, probably because they used a different solvent for their measurements.

Physical properties of the complexes

Table 1 shows the physical properties of the complexes under study. Regarding the spectroscopic data, in general, the electronic absorption spectra of the neutral compounds show one prominent band between 300 and 400 nm assigned to the π–π* transitions, according to the reported data in the literature for monosubstituted ferrocenyl compounds.[3d,g,h,7a,e] The weaker band at about 450–500 nm is assigned to a ferrocenyl-based MLCT band. Another weak band at higher wavelengths (about 500 nm), assigned to a d–d transition, is only discernible in some cases as a shoulder on the other MLCT band and is not listed in Table 1. In our pyridine-based compounds, the MLCT band is strongly influenced by the nature of the ancillary ligand, showing a hypsochromic shift upon lengthening the conjugated chain. It has been shown that this band gains in oscillator strength as the electron-accepting capabilities of the ancillary ligand are increased.[3d] In our case, the hypsochromic shift is difficult to justify without any further theoretical MO studies, but it may imply that this band contributes less to β. We have observed the same tendency for –CN–M(CO)$_5$ (M = Cr, Mo, W) terminated complexes,[2b] and other examples have been reported in which this trend is also observed.[3e] In other similar complexes reported by us, terminated by –CN[2b] and –NO$_2$[5b], we observed a bathochromic shift; this is the opposite variation upon chain lengthening, so it is difficult to establish a clear correlation between band energy and effective conjugation when using the MLCT band. Much more informative are the data derived from the more intense π–π* band, which in all the cases that we[2b,5b] and others[3a,e,g,4e] have reported, shows a clear bathochromic shift when elongating the conjugation chain, which most likely lowers the energy of the π* orbital. In all the complexes that we have studied, the addition of one vinylenephenylene unit when going from $n = 1$ to $n = 2$ results in a positive shift of 40–60 nm. Addition of one vinylenephenylene unit when going from $n = 2$ to $n = 3$ (**2**-CH$_3$ to **3**-CH$_3$), results in a much smaller bathochromic shift (20 nm).



Scheme 2

Electrochemistry offers the possibility to examine trends in LUMO energies. Addition of an electron-accepting fragment to ferrocene results in an increase in the redox potential compared to that of unsubstituted ferrocene (445 mV). This effect is clearly seen in our pyridine complexes and agrees with the general trend observed for our other related oligomers.[2,5] The effect has been studied in detail by Barlow *et al.*[8] Chain lengthening promotes a decrease in the redox potential, due to the stabilization of the positive charge of the oxidized species along the conjugated chain. According to our present and previous results,[2,5] the addition of each vinylenephenylene unit leads to a linear decrease in the redox potential of 50–90 mV for all the py, –CN, –CHO, M(CO)$_5$ (M = Cr, Mo, W) and NO$_2$ terminated complexes. This correlation is not observed for the cationic complexes **1**-CH$_3$, **2**-CH$_3$ and **3**-CH$_3$, for which a very large decrease is observed when going from **1**-CH$_3$ to **2**-CH$_3$ (190 mV) and much smaller from **2**-CH$_3$ to **3**-CH$_3$ (30 mV). This, together with the spectroscopic results described before, suggests that for these complexes, conjugation may be reaching a limiting effective length.[1,5a]

Nonlinear optical properties of the complexes

All the compounds were analysed by the hyper-Rayleigh scattering (HRS) technique.[9] The hyperpolarizabilities β for the pyridine-based compounds are reported in Table 1. The neutral compounds were measured in chloroform, while

Table 1 Experimental nonlinear response and electrochemical properties of the conjugated oligomers with a pendant ferrocenyl and an end-capped pyridine

	λ_{max}/nm			$E_{1/2}$/mV (ΔE_p/mV)	
Compound	π–π*	MLCT	β[a]	Ferrocene-based	M-based
Ferroceno				445 (105)[b] 450 (100)[c]	
1	315	468	21[d]	500 (70)[b]	—
2	386	459	146[d]	440 (65)[b]	—
1-CH$_3$	359	553	40[c]	595 (85)[c]	—
2-CH$_3$	399	503	197[c]	385 (80)[c]	—
3-CH$_3$	417	462	458[c]	355 (65)[c]	—
1-Cr[e]	330	477	63[d]	520 (75)[b]	930 (75)
1-Mo[e]	345	487	95[d]	520 (85)[b]	1110[f]
1-W[e]	362	491	101[d]	530 (75)[b]	1125[f]
2-Cr	374	462	369[d]	440 (75)[b]	906 (70)
2-Mo	389	476	448[d]	450 (75)[b]	1120[f]
2-W	405	487	535[d]	440 (70)[b]	1125[f]

[a] All β values are in 10^{-30} e.s.u. and the experimental error is ±15% of the value. [b] Measured in CH$_2$Cl$_2$. [c] Measured in Acetone. [d] Measured in CHCl$_3$. [e] Values are taken from ref. 2(*a*). [f] Irreversible peak, measured at 100 mV s^{-1}.

acetone was used for the ionic methylpyridinium compounds due to their low solubility in the former solvent. In order to compare the NLO results in the same solvent, we also tried to measure the neutral compounds **1**-M and **2**-M (M = Cr, Mo, W) in acetone, but found that they decomposed, probably because of replacement of the pyridine ligand by acetone in the metal carbonyl fragments. It has been shown that both the MLCT and the π–π* transitions lead to changes in β,[7] so a two-level model may not be appropriate when considering metallocenes, therefore we have not estimated the static hyperpolarizability values.

Some important structure–property relationships can be derived from the NLO values. As expected, the increase in the conjugation length by *n* multiple bonds results in a rather dramatic increase in the β values, as seen for the methylpyridinium compounds **1**-CH_3, **2**-CH_3 and **3**-CH_3 (Table 1). A similar trend is observed for the neutral pyridyl complexes and from our previously reported data on NO_2 terminated complexes,[5b] although different increases in the β values are observed for each vinylenephenylene unit added in the three series of complexes [–py, –py–M(CO)$_5$ and –NO_2]. The metal carbonyl moieties enhance the push–pull character as compared to the uncoordinated pyridyl species and even to the methylpyridinium compounds, as reflected by the higher β values observed. However, this point has to be considered as a crude estimate, since first hyperpolarizabilities of organometallic push–pull complexes often exhibit a significant solvent polarity dependence, which enhances β when the polarity increases. In this sense, it is observed that the stronger acceptor (cationic –CH_3 terminated complexes) does not lead to the largest nonlinearities. This observation is rather surprising, although it has been pointed out that long π-chain complexes with better acceptors do not necessarily show higher nonlinear responses.[7a]

According to theoretical calculations, a linear dependence between β and the length of the conjugated chain must not be expected.[7b,c] In extended conjugated systems, the number of excited states contributing to β increases upon chain lengthening.[7d] In an effort to quantify the NLO dependence on the chain length, Jayaprakash *et al.* found that the equation $\beta = an^b$ (where *a* and *b* are constants and *n* the number of double bonds),[3e] gives a good correlation for their compounds. Although a limited amount of data is available for our compounds, we compared the different *b* values obtained using the same relationship. We found that the exponent *b* is 2.27 for the methylpyridinium complexes and 2.8 for the uncoordinated neutral pyridyl ones. For the metal carbonyl substituted compounds, the values are 2.6, 2.2 and 2.4 for Cr, Mo and W, respectively. For the NO_2 terminated complexes reported in our previous paper,[5b] *b* is 3.6. These values are considerably higher than those obtained by Jayaprakash *et al.* in their study,[3e] showing that they seem to be highly dependent on the nature of the electron-accepting fragment, although in an apparently random manner.

In general, we have observed that electrochemical and spectroscopic studies give a good idea of the trends in NLO behavior in a series of similar complexes. In this sense, we always observe that while maintaining the same electron-accepting and electron-donating groups, chain lengthening promotes a bathochromic shift of the π–π* band, reduction of the redox potential, and an enhancement of the NLO response. These results confirm that the ferrocenyl derivatives follow the same qualitative design rules that have evolved for π-electron organic chromophores. However, our attempts to make quantitative predictions or good correlations between these physical properties and the hyperpolarizability values failed, probably due to the increase in the number of excited states contributing to β upon chain lengthening, thus making simple models to interpret the experimental data (such as the two-level model) poor approximations.

Experimental

General details

NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using $CDCl_3$ as solvent, unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR from NaCl pellets. Electronic absorption spectra were obtained on a UV-1603 Shimadzu spectrophotometer. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are not corrected for the junction potential. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument, using CH_3CH_2OH as the mobile phase solvent. The samples were added to give a mobile phase of approximate concentration 0.1 mM. The synthesis and characterization of the ferrocenyl derivatives with a pendant end-capped pyridine is described in our previous works.[5]

NLO measurements

Details of the HRS set-up have been discussed previously.[9] All measurements are performed in chloroform and the known hyperpolarizability of *para*-nitroaniline ($\beta = 23 \times 10^{-30}$ esu in chloroform)[10] is used as an external reference. The samples were passed through a 0.45 µm filter, since contaminated samples often produce spurious signals, and were checked for multiphoton fluorescence that can interfere with the HRS signal.[11] IR laser pulses generated with an injection seeded, Q-switched Nd : YAG laser (Quanta-Ray GCR-5, 1064 nm, 10 ns pulses, 10 Hz) were focused into a cylindrical cell containing the solution (7 ml). The fundamental intensity was altered by rotation of a half-wave plate placed between crossed polarizers, and measured with a photodiode. An efficient condenser system was used to collect the light scattered at the harmonic frequency (532 nm), which was detected by a photomultiplier. Discrimination of the second-harmonic light from the fundamental light was accomplished by a low-pass filter and a 532 nm interference filter. Actual values for the intensities were retrieved by using gated integrators. In all experiments the incident light was vertically polarized along the *z* axis.

Synthesis

[(*E*,*E*)-(η^5-C_5H_5)Fe{η^5-C_5H_4CH=CHC_6H_4CH=CHC_5H_4N-Cr(CO)$_5$}], 2-Cr. Chromium hexacarbonyl (220 mg, 1.0 mmol) was dissolved in dry THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **2** (200 mg, 0.5 mmol) was added to the yellow solution formed upon irradiation in order to obtain **2**-Cr. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solution was concentrated under reduced pressure. Purification by column chromatography on neutral alumina with CH_2Cl_2–hexane (1 : 1) afforded pure **2**-Cr. Yield 45%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.48 (d, 2H, $^3J_{H-H} = 5.0$, C_5H_4N); 7.26 (m, 2H, C_5H_4N); 7.51 (d, 2H, $^3J_{H-H} = 8.0$, C_6H_4); 7.47 (d, 2H, $^3J_{H-H} = 8.0$, C_6H_4); 7.31 (d, 1H, $^3J_{H-H} = 16.5$, CH=CH); 6.95 (m, 1H, CH=CH); 6.95 (m, 1H, CH=CH); 6.71 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 4.50 (s, 2H, C_5H_4); 4.36 (s, 2H, C_5H_4); 4.16 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.8, 70.1 (4C, C_5H_4); 70.0 (5C, C_5H_5); 83.5 (1Cq, C_5H_4); 122.1, 123.7, 125.6, 126.8, 128.4, 129.2, 135.8, 155.9 (12C, CH=CH and C_6H_4); 139.8, 146.7 (2Cq, C_6H_4); 214.9

(4Cq, CO); 221.3 (1Cq, CO). IR (ν/cm^{-1}): 2071 (s), 1976 (s), 1885 (vs). Elem. anal. calc. for **2**-Cr: $C_{30}H_{21}FeCrNO_5$, M_w = 583.34: C, 61.8; H, 3.63; N, 2.4; found; C, 61.6; H, 3.62; N, 2.4%. Electrospray MS (cone 70 V) *m*/*z* (fragment): 584 $[M]^+$; 392 $[M - Cr(CO)_5]^+$

[(*E*,*E*)-(η^5-C_5H_5)Fe{η^5-$C_5H_4CH{=}CHC_6H_4CH{=}CHC_5H_4N$-$Mo(CO)_5$}], 2-Mo. This compound was obtained following the general procedure described for **2**-Cr using molybdenum hexacarbonyl (264 mg, 1.0 mmol) instead of chromium hexacarbonyl. Purification was achieved by column chromatography on neutral alumina using hexane–CH_2Cl_2 (3 : 2) as eluent. Yield: 55%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.55 (d, 2H, $^3J_{H-H}$ = 6.3, C_5H_4N); 7.30 (m, 2H, C_5H_4N); 7.53 (d, 2H, $^3J_{H-H}$ = 7.0, C_6H_4); 7.47 (d, 2H, $^3J_{H-H}$ = 8.4, C_6H_4); 7.30 (m, 1H, CH=CH); 7.00 (m, 1H, CH=CH); 7.00 (m, 1H, CH=CH); 6.72 (d, 1H, $^3J_{H-H}$ = 15.9 Hz, CH=CH); 4.50 (s, 2H, C_5H_4); 4.34 (s, 2H, C_5H_4); 4.17 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.8, 70.1 (4C, C_5H_4); 70.0 (5C, C_5H_5); 83.5 (1Cq, C_5H_4); 122.1, 123.8, 125.7, 126.8, 128.4, 129.3, 136.0, 155.3 (12C, CH=CH and C_6H_4); 134.3, 139.9, 146.9 (3Cq, C_6H_4); 204.8 (4Cq, CO); 214.5 (1Cq, CO). IR (ν/cm^{-1}): 2070 (s), 1977 (s), 1900 (vs). Elem. anal. calc. for **2**-Mo: $C_{30}H_{21}FeMoNO_5$, M_w = 627.29: C, 57.4; H, 3.37; N, 2.2; found: C, 57.5; H, 3.36; N, 2.2%. Electrospray MS (cone 60 V) *m*/*z* (fragment): 628 $[M]^+$; 392 $[M - Mo(CO)_5]^+$

[(*E*,*E*)-(η^5-C_5H_5)Fe{η^5-$C_5H_4CH{=}CHC_6H_4CH{=}CHC_5H_4N$-$W(CO)_5$}], 2-W. This compound was obtained following the general procedure described for **2**-Cr using tungsten hexacarbonyl (352 mg, 1.0 mmol) instead of chromium hexacarbonyl. The purification was achieved by column chromatography on neutral alumina using hexane–CH_2Cl_2 (1 : 1) as eluent. Yield: 60%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.71 (d, 2H, $^3J_{H-H}$ = 6.5, C_5H_4N); 7.30 (d, 2H, $^3J_{H-H}$ = 6.5 C_5H_4N); 7.53 (d, 2H, $^3J_{H-H}$ = 8.0, C_6H_4); 7.48 (d, 2H, $^3J_{H-H}$ = 8.0, C_6H_4); 7.36 (d, 1H, $^3J_{H-H}$ = 16.0, CH=CH); 6.99 (m, 1H, CH=CH); 6.99 (m, 1H, CH=CH); 6.72 (d, 1H, $^3J_{H-H}$ = 16.0 Hz, CH=CH); 4.50 (s, 2H, C_5H_4); 4.34 (s, 2H, C_5H_4); 4.17 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.8, 70.1 (4C, C_5H_4); 70.0 (5C, C_5H_5); 83.5 (1Cq, C_5H_4); 122.7, 123.6, 125.6, 126.8, 128.5, 129.4, 136.3, 156.4 (12C, CH=CH and C_6H_4); 134.2, 140.0, 146.8 (3Cq, C_6H_4); 199.3 (4Cq, CO); 202.9 (1Cq, CO). IR (ν/cm^{-1}): 2069 (s), 1969 (s), 1895 (vs). Elem. anal. calc. for **2**-W: $C_{30}H_{21}FeWNO_5$, M_w = 715.21: C, 50.4; H, 2.96; N, 1.9; found: C, 50.2; H, 2.97; N, 1.9%. Electrospray MS, (cone 70 V) *m*/*z* (fragment): 715 $[M]^+$; 392 $[M - W(CO)_5]^+$.

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