Organometallics **2000,** *19,* 5235−5237

Nonlinear Optical Properties of Redox-Active Mono-, Bi-, and Trimetallic σ-Acetylide Complexes Connected through a Phenyl Ring in the Cp*(dppe)Fe Series. An Example of Electro-switchable NLO Response

Tania Weyland,[†] Isabelle Ledoux,[‡] Sophie Brasselet,[‡] Joseph Zyss,[‡] and Claude Lapinte*[,†]

Organométalliques et Catalyse Chimie et Electrochimie Moléculaire, UMR CNRS 6509, Campus de Beaulieu, 35042 Rennes Cedex, France, and Laboratoire de Photonique Quantique et Moléculaire, ENS Cachan, 61 Avenue du Président Wilson, 94235 Cachan, France

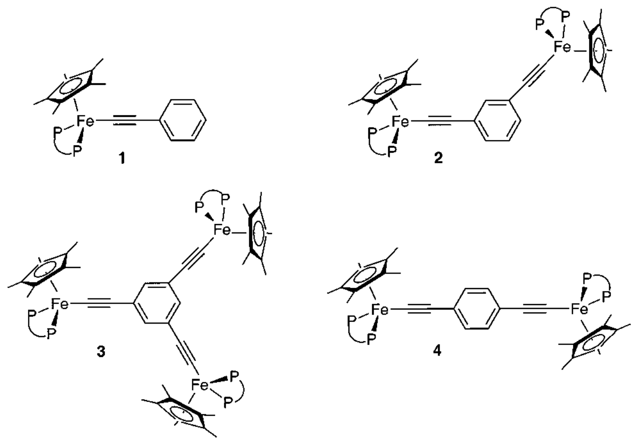
Received July 3, 2000

Summary: The first-order hyperpolarizabilities of a series of mono-, bi-, and trinuclear organometallic compounds were determined using Hyper-Rayleigh Scattering at 1.06 μm. The molecular nonlinear optical responses (NLO) were investigated for various combinations of iron(II) and iron(III), including mixed-valence iron(II)/iron(III) complexes. In the latter case, it is shown that the NLO activity can be controlled by one-electron redox processes.

Introduction

During the past decade, the interest in organometallics for the development of novel nonlinear optical (NLO) materials has considerably increased.[1−12] A special emphasis has been put on compounds made of metallocene or semisandwich-type moieties as electron-donating groups, conjugated with an electron-withdrawing group through a π-electron pathway.[13−15] Metal complexes of N-heterocyclic ligands (pyridines and oligopyridines) represent another class of interesting NLO molecules and offer a large variety of structures in terms of dimensionality and functionalization potential.[16] Moreover, it has been proposed that the incorporation of transition metals into the plane of the π-conjugated system should increase the molecular NLO response.[8] More recently, considerable interest has also been focused on NLO molecules[17] and especially organometallics that possess octupolar symmetry.[7,18]

Scheme 1



In a series of papers, we have described the synthesis and characterization of organometallic molecules containing one (**1**), two (**2**, **4**), and three (**3**) electron-rich Cp*(dppe)Fe units linked to a connecting arene group through an ethynyl spacer (Scheme 1).[19−22] Complex **1** can be viewed as the linear fragment of the dipolar complex **2** or octupolar derivative **3**. The binuclear complex **4** constitutes a reference model without octupolar symmetry and for which the dipolar moment is expected to be weak. Moreover, we have shown that all these compounds can be prepared and isolated with multiple oxidation states, since each metal center can

---

* Corresponding author. E-mail: lapinte@univ-rennes1.fr.

[†] Organométalliques et Catalyse Chimie et Electrochimie Moléculaire.

[‡] Laboratoire de Photonique Quantique et Moléculaire.

(1) Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349. Whitall, A. M.; McDonagh, M. G.; Humphrey, M.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.

(2) Marder, S. R. *Inorganic Compounds for NLO*; Marder, S. R., Ed.; Wiley-Interscience: Chichester, UK, 1992; p 115.

(3) Laidlaw, W. M.; Denning, R. G.; Verbiest, T.; Chauchard, E.; Persoons, A. *Nature* **1993**, *363*, 58.

(4) Zyss, J.; Dhenaut, C.; Chauvan, T.; Ledoux, I. *Chem. Phys. Lett.* **1993**, *206*, 409.

(5) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.

(6) Coe, B. J.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G. H.; Axon, T. L. *J. Chem. Soc., Dalton Trans.* **1995**, 673.

(7) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374*, 339.

(8) Di Bella, S.; Fragala, I.; Ledoux, I.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 9481.

(9) Whittall, I. R.; Humphrey, M. G. *Organometallics* **1995**, *14*, 5493.

(10) Whittall, I. R.; Humphrey, M.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1995**, *14*, 3970.

(11) Whittall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 1935.

(12) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, P. M.; Gimeno, J. *Organometallics* **1996**, *15*, 5266.

(13) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bondy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 660.

(14) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8205.

(15) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10338.

(16) Le Bozec, H.; Renouard, T. *Eur. J. Inorg. Chem.* **2000**, 229.

(17) Zyss, J. *J. Chem. Phys.* **1993**, *98*, 6583.

(18) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A. *J. Am. Chem. Soc.* **1999**, *121*, 1405.

(19) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634.

(20) Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. *Organometallics* **1997**, *16*, 2024.

(21) Weyland, T.; Costuas, K.; Mari, A.; Halet, J.-F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569.

(22) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J.-F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228−4239.

10.1021/om0005708 CCC: $19.00

Table 1. Wavelengh in nm (molar extinction coeficient, mol^{-1} cm^{-1}) of the UV−Vis Transitions[a] for 1^{n+}−4^{n+}

compd	$\pi \rightarrow \pi^*$	MLCT	LMCT	IVCT
1	245 (34000)	348 (12000)		
1$^+$	241 (34000) 267 (37000)		575 (2200), 663 (2900)	
2[b]	254 (28000)	349 (15000)		
2^{+}[b]	264 (47000)	359 (17000)	560 (2600), 650 (4000)	1805 (310)
2^{2+}[b]	285 (57000)	420 (12000)	574 (4500), 662 (5500)	
3[b]	283 (53000)	351 (35000)		
3^{+}[b]	282 (49000)	366 (22000)	600 (2300), 710 (4400)	1697 (440)
3^{2+}[b]	288 (56000)	410 (18000)	590 (4100), 688 (5500)	3174 (310), 1550 (250)
3^{3+}[b]	288 (56000)	425 (15000)	573 (5500), 662 (5500)	
4	242 (87000) 262 (63000)	413 (25000)		
4$^+$	246 (227000) 268 (229000)		546 (30000), 702 (6000)	2016 (5900)
4^{++}	277 (199000)		702 (55000)	

[a] At 77 K in CH_2Cl_2. [b] From ref 22.

be oxidized stepwise.[21,22] This property offers the unique opportunity to examine how the quadratic hyperpolarizability is modulated upon reversible electron transfer.

All first-order hyperpolarizabilities β were determined by using hyper-Rayleigh scaterring (HRS),[23] a technique suitable for the investigation of any kind of quadratic NLO species, including nonpolar and/or ionic molecules in solution. HRS measurements were performed at 1064 nm in dichloromethane, using a nanosecond Nd^{3+}:YAG laser operating at 10 Hz repetition rate. Due to strong absorption at 532 nm, very low concentrations (less than 10^{-4} M L^{-1} in some cases) were used. The UV−visible spectra of all the compounds of this series are summarized in Table 1. The UV spectra of the mononuclear, binuclear, and trinuclear complexes all display an intense absorption band in the range 250−290 nm. These high-energy transitions were assigned to a ligand-centered (LC) π−π^* electronic transition.[22] Stepwise oxidation of the metal centers produces a bathochromic shift of the band in the far UV, which indicates either stabilization of the empty ligand-based orbitals (π^*) or a destabilization of the occupied ones (π) upon oxidation. A second broad band is observed around 400 nm, which may be composed of several overlapping absorptions, as suggested by the presence of poorly resolved shoulders. This band is responsible for the orange color of the neutral compounds **2** and **3**, but also exists in the deeply colored oxidized forms. These absorptions should arise from metal-to-ligand charge transfer (MLCT) processes, since such transitions are usually observed for related complexes.[24,25] The spectra of the oxidized **2**$^+$, **2**$^{2+}$, **3**$^+$, **3**$^{2+}$, and **3**$^{3+}$ complexes contain a succession of two transitions above 550 nm. Despite their weaker intensity, these transitions explain the dark green or blue color of these salts in solution. They might be ascribed to ligand-to-metal charge transfer (LMCT) transitions.[21] Such transitions are likely to take place after creation of an electronic vacancy in the HOMO after the oxidation (SHOMO).[21,25] Moreover, the mixed-valence derivatives **2**$^+$, **3**$^+$, and **3**$^{2+}$ show an intervalence charge transfer in the NIR range.

In the case of one-dimensional intramolecular charge transfer molecules, for which a single absorption band is generally observed in the UV−visible range, a correction for resonance enhancement can be made using the two-level dispersion model for β, as previously proposed:[26,27] static β_{EFISH} (0) values can then be inferred from the experimental $\beta_{\mathrm{EFISH}}(\omega)$ data according to the classical off-resonance expression (eq 1).[27]

$$\beta_{\mathrm{EFISH}}(\omega) = \beta_{\mathrm{EFISH}}(0)\,\frac{W^4}{(W^2 - (\hbar\omega)^2)(W^2 - (2\hbar\omega)^2)} \quad (1)$$

For organometallic compounds, which contain multiple electronic transitions, the determination of the static hyperpolarizability β_0 is not obvious. Considering that besides the $\pi \rightarrow \pi^*$ transition of the organic ligands located in the far UV, the four neutral compounds **1**−**4** have a unique metal−ligand charge transfer (MLCT) band in the visible or near-UV range, it was decided to use this band to calculate the β_0. Since this band is the closest to the harmonic frequency, it should be kept in mind that the calculated β_0 parameter will only be an estimated value, since the molecules have a stronger absorption band at higher energy. However, similar treatments were previously reported for transition metal complexes, and the good correlations found between β_0 and the wavelength of maximal absorption ($\lambda_{\max}$) apparently justify this procedure.[28] In other words, the MLCT transition seems to be the main contributor to β. Importantly, the neutral complexes have absorption bands far from the second harmonic wavelength of 532 nm, permitting assessment of the impact of the structural variation on quadratic NLO response.

Complex **1** constitutes the elemental structure of the series. It shows a weak NLO response (Table 2), which compares well in intensity with other organometallics of similar structure.[12,18] Progressing from **1** to the binuclear compounds **2** and **3** results in a 3- or 4-fold increase in the quadratic NLO response with little loss of optical transparency. The enhancement of the NLO response is similar for these two complexes, but its origin is quite different. In complex **2**, the 1,3-connection of two Cp*(dppe)Fe units on the central arene is supposed to enhance the dipole moment of the molecule,

---

(23) Terhune, R. W.; Maker, P. D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *61*, 681.

(24) Wu, I. Y.; Lin, J. T.; Luo, J.; Sun, S.-S.; Li, C.-S.; Lin, K. J.; Tsai, C.; Hsu, C.-C.; Lin, J.-L. *Organometallics* **1997**, *16*, 2038.

(25) Le Stang, S.; Paul, F.; Lapinte, C. *Inorg. Chim. Acta* **1999**, *291*, 403.

(26) Oudar, J.-L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(27) Oudar, J.-L. *J. Chem. Phys.* **1977**, *67*, 446.

(28) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

(29) Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 366.

(30) Coe, B. J. *Chem. Eur. J.* **1999**, *5*, 2464.

Table 2. Quadratic Hyperpolarizabilities[a] and Absorptions for Complexes 1^{n+}–4^{n+}

compd	β [a] (10^{-30} esu)	β_0 (10^{-30} esu)	ϵ_{1064} ($M^{-1}\,cm^{-1}$)	ϵ_{532} ($M^{-1}\,cm^{-1}$)
1	52	24	0	100
$\mathbf{1}^{+}$	80		0	1900
2	210	98	0	600
$\mathbf{2}^{+}$	150		150 ± 20	2500
$\mathbf{2}^{2+}$	200		0	3800
3	175	87	0	1000
$\mathbf{3}^{+}$	190		120 ± 20	2700
$\mathbf{3}^{2+}$	170		150 ± 20	3900
$\mathbf{3}^{3+}$	53		0	5200
4	180	60	0	100
$\mathbf{4}^{+}$	400		600	23000
$\mathbf{4}^{2+}$	200		100	6300

[a] Hyper-Rayleigh scattering measurements β (10% error). All measurements have been performed in CH_2Cl_2 at 20 °C and 1064 nm.

whereas in the case of the trinuclear complex **3** the octupolar irreducible tensor distribution is expected to be the major contribution in the NLO activity. Most of the data evaluating the quadratic NLO properties of organometallic octupolar compounds are reported in ref 16. In that respect, it is interesting to note that complex **3** constitutes a novel template, its NLO response being of the same order of magnitude as those of other classes of octupolar organometallic complexes. Moreover, a significant enhancement factor was also reported between the mononuclear fragment and the octupolar molecules. The quadratic NLO activity of the binuclear complex **4** is more surprising. Indeed, despite an apparent C_2 symmetry, this complex is at least twice as active as the mononuclear complex **1**. This behavior was not expected for a compound in which two identical electron-donor moieties are linked on an arene ring in the 1,4-positions.[31]

The mono-, bi-, and trinuclear iron(III) radical cations $\mathbf{1}^{+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{3+}$ together with the mixed-valence complexes $\mathbf{2}^{+}$, $\mathbf{3}^{+}$, and $\mathbf{3}^{2+}$ show quadratic NLO tensors similar to those of their respective iron(II) homologues (Table 1). In the case of the radical cations the discussion of the β values is not straightforward. Indeed, these compounds present absorption bands (corresponding to LMCT transitions) located very close or even beyond the second harmonic wavelength. In such cases, the use of the two-level model does not make any sense and the static hyperpolarizability (β_0) parameters cannot be calculated. Furthermore, the maximum of absorption of the LMCT bands is not far from the second harmonic, leading to underestimated β values. Taken as a whole, our results indicate that the radicals have a second-order NLO activity. Moreover, as a significant loss of optical transparency is observed for these complexes at 532 nm, it cannot be excluded that the intrinsic NLO activity of the radical cations might be larger than that of the neutral homologues.

The mixed-valence complex $\mathbf{4}^{+}$ deserves special attention. Despite a strong absorption at the second harmonic wavelength, this complex shows a β tensor twice those of the neutral complex **4** and the diradical $\mathbf{4}^{2+}$. Complex $\mathbf{4}^{+}$ is a class II mixed-valence complex, retaining charge localization, but with enough electronic coupling between the redox centers to permit intense intervalence charge transfer transitions.[19] The energy of this transition is weakly sensitive to the solvent (λ_{max} = 2016 nm in CH_2Cl_2 and λ_{max} = 1997 nm in methanol). As the redox systems $\mathbf{4}/\mathbf{4}^{+}$ and $\mathbf{4}^{+}/\mathbf{4}^{2+}$ are fully reversible, this system constitutes a reversible electronic switch of the molecular NLO response. To our knowledge, such a system has been achieved in only one documented case, the β switch being based on a redox-active ruthenium complex.[29,30] In the case of the compounds $\mathbf{4}^{n+}$, we have a family of three stable and well-defined molecules for which the intermediate redox state gives a larger NLO response that the extreme oxidation states. Therefore, the electro-switch can be activated in either oxidation or reduction modes. This compound constitutes a model of an NLO molecular switch with a remarkable reversibility. Such an approach has obvious potential for extension to the switching of bulk NLO effects in electrode-deposited films. However, strategies for the molecular engineering of such potentially useful switchable NLO materials require the design of redox-active molecules with a better optical transparency.

Experimental Section

The preparation of the neutral,[20] fully oxidized,[21] and mixed-valence complexes[22] has been described elsewhere.

Typical Procedure for the Measurement of the β Values. The solutions of the NLO molecules in dichloromethane were placed into a 4 cm long fluorimetric cell, after being carefully filtered through a 0.2 μm filter in order to eliminate the white light noise resulting from microburning of the remaining dust particles by the incoming laser beam. β measurements were carried out using the harmonic light scattering technique (also named Hyper-Rayleigh) in chloroform solutions. The fundamental wave at 1.064 μm was provided by a nanosecond homemade Q-switched Nd3+:YAG laser operating in the 10 Hz repetition range. The scattered second harmonic signal is collected at 90° with respect to the direction of the incoming laser beam, using a high-aperture lens. The harmonic photons are detected by a Hamamatsu R 2228 photomultiplier, sampled by a Stanford Research box car, and processed by a computer. The fundamental intensity was varied by rotating a half-wave plate between two crossed Glan polarizers. The scattered second harmonic intensity is recorded as a function of a "reference" harmonic signal emitted by a NPP powder illuminated by a small fraction of the fundamental wave taken from the incident beam using a glass plate at 45° incidence angle. From the slope of the resulting line we infer the mean $\langle\beta^2\rangle$ value of the β tensor of the NLO molecules.

Acknowledgment. We are grateful to Dr. H. Le Bozec (Rennes) for helpful discussions and to the Laboratoires Standa (Caen, France) for financial support to T.W.

OM0005708

---

(31) An unexpected and significant signal was observed for the two centrosymmetric compounds **4** and $\mathbf{4}^{2+}$, resulting in nonnegligible "apparent" β values. This signal may be ascribed to a two-photon fluorescence emission, which competes, in some cases, with second harmonic generation. For the other molecules, we have checked that this two-photon fluorescence contribution is negligible, by filtering out the scattered visible light with several interference filters centered at various wavelengths that are different from the second harmonic one and located in the green-yellow spectral range. In the case of **4** and $\mathbf{4}^{2+}$, two-photon transitions from the ground state to an excited state with the same parity is allowed, resulting in a significant two-photon broadband emission that encompasses the harmonic frequency of the incident fundamental wave.