Nonlinear Optics

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Electrochemical Switching of the Cubic Nonlinear Optical Properties of an Aryldiethynyl-Linked Heterobimetallic Complex between Three Distinct States**

Marek Samoc, Nicolas Gauthier, Marie P. Cifuentes, Frédéric Paul,* Claude Lapinte, and Mark G. Humphrey**

Materials with nonlinear optical (NLO) properties are required in emerging photonics-based technologies for various applications, including processing of optical signals, optical data storage, nanophotonics, and biophotonics.[1–3]

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[*] Dr. M. Samoc
Laser Physics Centre
Research School of Physical Sciences and Engineering
Australian National University
Canberra, ACT 0200 (Australia)
Fax: (+61) 2-6125-0029
E-mail: marek.samoc@.anu.edu.au
N. Gauthier, Dr. F. Paul, Dr. C. Lapinte
Sciences Chimiques de Rennes
UMR CNRS 6226
Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex (France)
Fax: (+33) 2-2323-5637
E-mail: frederic.paul@univ-rennes1.fr
Dr. M. P. Cifuentes, Prof. M. G. Humphrey
Department of Chemistry
Australian National University
Canberra, ACT 0200 (Australia)
Fax: (+61) 2-6125-0760
E-mail: mark.humphrey@anu.edu.au

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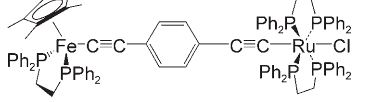
Although the focus was initially on the preparation of compounds with large nonlinearities, there has been significant recent interest in the reversible switching or modulation of NLO properties.[4–13] Switching of NLO properties has been achieved by protonation/deprotonation, oxidation/reduction, and photoisomerization sequences, but cubic NLO switchable systems have thus far been restricted to two NLO "states".[14] The coupling of two different ligated metal centers with well-separated redox potentials and distinct linear optical properties by an appropriate molecular linker could in principal permit switching between three redox states and, potentially, afford up to three linear-optical and NLO states. We report herein linear and nonlinear electrochromism of a mixed iron–ruthenium complex along with switching its NLO properties at more than one wavelength and between three distinct cubic NLO states.

The complex chosen for the current study (**1**) was prepared by an extension of standard procedures.[15] We have previously shown that the NLO properties of homometallic iron or ruthenium alkynyl complexes can be conveniently switched electrochemically through the reversible M^{II}/M^{III} couples.[7,9,10,12,13] The Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III} couples are far removed from one another, and, under electrochemical control, one can access the Fe^{II}/Ru^{II}, Fe^{III}/Ru^{II}, or Fe^{III}/Ru^{III} states (**1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$, respectively) by applying a potential of −0.6, 0, or +0.8 V (vs. Ag/AgCl).



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The UV/Vis/NIR spectra of **1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$ in CH_2Cl_2 are shown in Figure 1. Complex **1** is essentially transparent at wavelengths longer than 600 nm; oxidation to $\mathbf{1}^+$ affords an optical spectrum with a broad band centered at 1124 nm, and further oxidation to $\mathbf{1}^{2+}$ results in a decrease in intensity of this band and the appearance of strong bands centered at 706 and 914 nm. Cycling between the three oxidation states of the complex in solution in an optically transparent thin-layer electrochemical (OTTLE) cell can be achieved by applying the appropriate potentials; isosbestic points are observed in the UV/Vis/NIR spectra, which is consistent with fully reversible electrochemical conversions between the three forms.

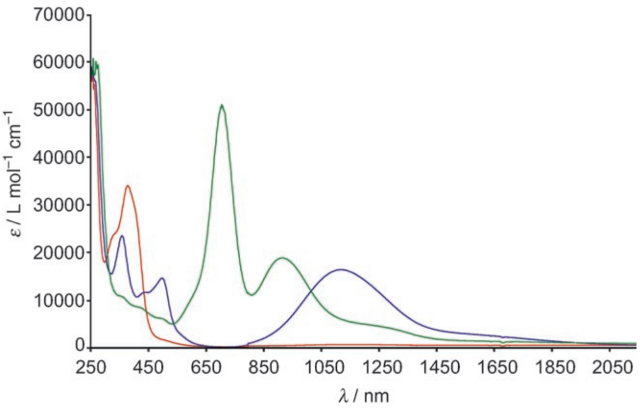

Figure 1. UV/Vis/NIR spectra of **1** (red trace), $\mathbf{1}^+$ (blue trace), and $\mathbf{1}^{2+}$ (green trace) in CH_2Cl_2.

A change in linear optical properties can be accompanied by a change in nonlinear properties, so the possibility of NLO switching was examined for solutions of the complex in CH_2Cl_2 in a specially modified OTTLE cell[7] at 790 and 1200 nm, wavelengths at which the $\mathbf{1}^{2+}$ and $\mathbf{1}^+$ forms, respectively, possess strong linear optical absorption, and which are therefore candidate wavelengths for NLO switching. The third-order NLO properties were assessed by a combination of open- and closed-aperture *Z*-scan experiments.

The effect of applied potential on the open-aperture signal (from which the imaginary component of the nonlinearity is available) is shown in Figures 2 and 3. Cation $\mathbf{1}^+$ was found to be an efficient two-photon absorber at 790 nm. Scans in which the potential applied to the working electrode was negative indicated that the neutral form **1** exhibits a negligible nonlinear absorption and that the doubly oxidized form $\mathbf{1}^{2+}$, obtained by switching to positive potential, is a one-photon absorber and a saturable absorber at 790 nm. These changes of the imaginary part of the third-order polarizability γ were also accompanied by changes in the real part of the hyperpolarizability that were assessed by closed-aperture *Z*-scan, but it could only be established that the real part of γ for $\mathbf{1}^+$ is negative and that the real part of γ for **1** and $\mathbf{1}^{2+}$ could not

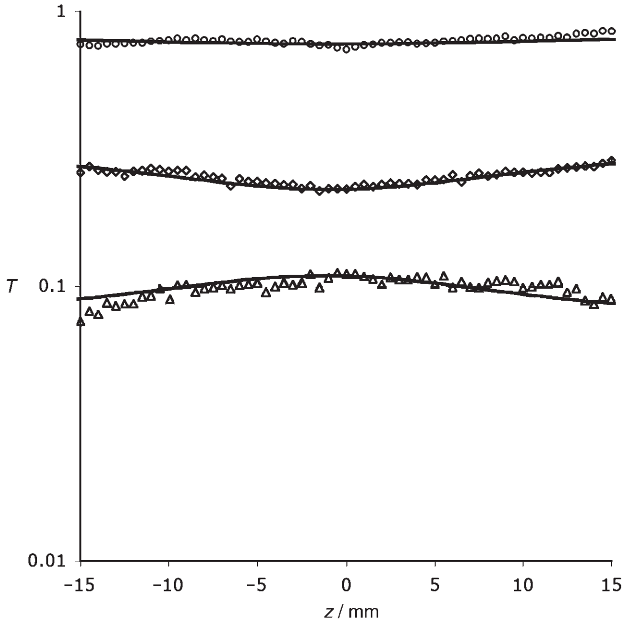

Figure 2. Open-aperture scans at 790 nm at an applied potential of 0 V (diamonds, $\mathbf{1}^+$), −0.6 V (circles, **1**), and +0.8 V (triangles, $\mathbf{1}^{2+}$). Lines denote theoretically computed *Z*-scans. The complex is a two-photon absorber at 0 V, shows almost no nonlinear absorption at the negative potential, and is a saturable absorber at the positive potential. *T* = open-aperture transmittance.

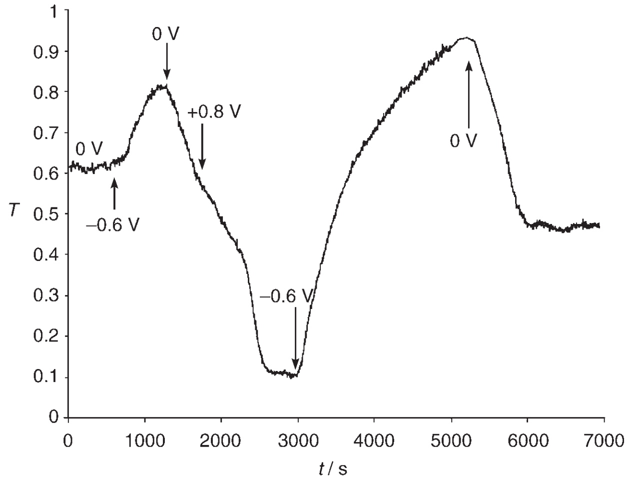

Figure 3. The $z=0$ open-aperture Z-scan signal at 790 nm as a function of time and potential. Arrows show application of the electrochemical potentials.

be reliably determined. Table 1 summarizes the data at 790 nm.

Table 1: Experimental cubic nonlinear optical response parameters.

Cmpd[a]	γ_{real}[b]	γ_{imag}[b]	$\lvert\gamma\rvert$[b]	σ_2[c]
1	<100	<100	ca. 0	ca. 0
$\mathbf{1}^{+}$	-450 ± 100	1600 ± 200	1700 ± 250	420 ± 50
$\mathbf{1}^{2+}$	<300	-970 ± 200	1000 ± 300	-250 ± 50

[a] Conditions: measurements were carried out in CH_2Cl_2 at 790 nm; values are referenced to the nonlinear refractive index of silica $n_2=3\times10^{-16}\ \text{cm}^2\text{W}^{-1}$. [b] 10^{-36} esu. [c] $10^{-50}\ \text{cm}^4\text{s}$ (= Goeppert–Mayer unit).

Measurements carried out at 1200 nm reveal behavior that differs from that at 790 nm (Table 2), and the open-aperture traces are displayed in Figure 4. The magnitudes of the parameters for the nonlinear effects at 1200 nm cannot be readily determined quantitatively because the open-aperture scans cannot be accurately fitted with the approximation that was used at 790 nm, namely, that absorption saturation is a negative analogue of two-photon absorption (i.e., the absorption coefficient is approximated as $\alpha=\alpha_0-\beta I$, whereby I is the intensity and β is the nonlinear absorption coefficient). This approximation is known to fail in the case of strong absorption-saturation effects.[16]

Table 2: Nonlinear absorption behavior of **1**, $\mathbf{1}^{+}$, and $\mathbf{1}^{2+}$ at 790 and 1200 nm.

Cmpd	790 nm	1200 nm
1	negligible	negligible
$\mathbf{1}^{+}$	two-photon absorber	saturable absorber
$\mathbf{1}^{2+}$	saturable absorber	saturable absorber

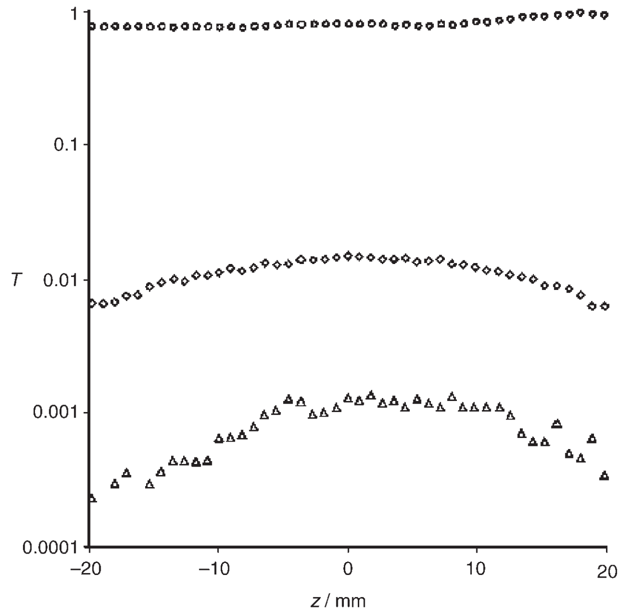

Figure 4. Open-aperture Z-scans at 1200 nm (0 V: diamonds, −0.6 V: circles, +0.8 V: triangles). The presence of maxima in scans at 0 and +0.8 V indicates saturable absorption.

In conclusion, oxidation processes in this heterobimetallic complex "switch on" optical transitions at long wavelength, and these linear electrochromic effects are accompanied by modifications in the NLO properties. To the best of our knowledge, the effect observed at 790 nm constitutes the first example of cubic NLO switching between three states (nonlinearity "off", and two forms of nonlinearity "on", namely, two-photon absorber and saturable absorber, which correspond to differences in sign of the imaginary component of the third-order nonlinearity). The switching phenomenon is not restricted to this wavelength range; a system corresponding to nonlinearity "off" in the neutral complex and "on" in the oxidized forms is observed at the longer wavelength.

Experimental Section

Complex **1** was prepared by standard procedures.[15] Third-order nonlinearities of **1**, $\mathbf{1}^{+}$, and $\mathbf{1}^{2+}$ were investigated by Z-scan measurements at 790 and 1200 nm. Complex **1** was examined in an OTTLE cell by using a laser system with a Clark-MXR regenerative amplifier pumping a light-conversion TOPAS optical parametric amplifier. The measurements at 790 nm were performed with the doubled idler from the TOPAS and the measurements at 1200 nm used the signal from the TOPAS. The repetition rate of the regenerative amplifier was set to 82 Hz to reduce problems with thermal nonlinearity and the possibility of material photodecomposition. The pulse duration was about 150 fs. The Z-scan system used a focused spot with $w_0=65\ \mu\text{m}$ at 790 nm and $w_0=80\ \mu\text{m}$ at 1200 nm, as was found from numerical fitting of closed-aperture scans for fused silica samples. Measurements on silica also served for calibration of the light intensities and therefore magnitudes of the nonlinearities. It was assumed that the nonlinear index of silica was $n_2=3\times10^{-16}\ \text{cm}^2\text{W}^{-1}$.

Solutions of **1** (concentration = 0.896 % w/w for measurements at 790 nm and 0.9 % w/w for measurements at 1200 nm) in dichloromethane were placed in a glass (0.5-mm path length) electrochemical cell equipped with a large-area platinum working electrode with a 1.5-mm-diameter round hole. The Z-scan experiments were carried out by passing the focused beam through that hole. Electrochemically induced linear and nonlinear optical property changes were investigated either by recording the transmission through the hole at a fixed position of the electrochemical cell (see Figure 3) or by performing scans in which the z coordinate (i.e., the distance of the sample from the focal plane of the lens) was scanned between $z = -20$ and 20 mm (see Figure 2 for open-aperture scans).

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