Organometallic Complexes for Nonlinear Optics. 33.[1] Electrochemical Switching of the Third-Order Nonlinearity Observed by Simultaneous Femtosecond Degenerate Four-Wave Mixing and Pump−Probe Measurements

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The molecular inorganic compound 1,3,5-{*trans*-[RuCl(dppe)$_2$]C≡C-4-C$_6$H$_4$C≡C}$_3$C$_6$H$_3$ (**1**) is reversibly oxidized in solution using an optically transparent thin-layer electrochemical (OTTLE) cell, the oxidation to **1**$^{3+}$ resulting in the appearance of a strong absorption band at 11 200 cm^{-1} in contrast to **1**, which is optically transparent at frequencies below 20 000 cm^{-1}. This linear electrochromic behavior is accompanied by third-order nonlinear optical electrochromic behavior, which has been probed by a combination of femtosecond degenerate four-wave mixing (DFWM) and pump−probe experiments at 12 500 cm^{-1}. DFWM studies of **1** and **1**$^{3+}$ reveal an order of magnitude increase in the hyperpolarizability, $|\gamma|$, upon oxidation with $|\gamma|$ values of 2000×10^{-36} esu and $20\,000 \times 10^{-36}$ esu, respectively; the DFWM signal of the latter is dominated by a delayed response (relaxation time ca. 1 ps). The transient absorption (TA) data for **1** reveal efficient two-photon absorption ($\sigma_2 \approx 10^3$ GM), whereas the TA data for **1**$^{3+}$ reveal saturable absorption (decay time ca. 1 ps). The switching of third-order nonlinearity in the **1**/**1**$^{3+}$ pair represents the first demonstration of femtosecond time-scale processes being responsible for nonlinear electrochromism.

Introduction

Materials with optimized nonlinear optical (NLO) properties are required for the control and processing of signal-carrying light beams in the emerging photonics-based technologies. As a consequence, considerable effort has been expended in successfully developing molecular structure−NLO activity relationships for both quadratic and cubic NLO merit. Recently, attention has turned to the possibility of modulating the values of the optical nonlinearities in molecules. Reversibly modulating (i.e., “switching”) the quadratic NLO properties of molecules by modifying their molecular structure has commanded significant recent interest, typical procedures to achieve such switching including protonation/deprotonation, chemical oxidation/reduction, or photoisomerization sequences.[2−7] Switching cubic NLO properties is equally interesting but is thus far little studied. We recently reported initial observations of the electrochemical switching of the third-order nonlinearity in organometallics.[8−10] This new effect is, in principle, a nonlinear analogue of electrochromism, for which an electrically (electrochemically) induced change of a molecule (e.g., oxidation of a metal complex) brings about changes in the linear optical properties of the molecule. Specifically, we accomplished switching between an octopolar alkynylruthenium complex and its tricationic oxidized form (Figure 1); the former is a two-photon absorber (a positive value of the nonlinear absorption coefficient) and shows a negative real part of the third-order polarizability, γ (i.e., self-defocusing behavior), whereas the latter is a saturable absorber (a negative value of the nonlinear absorption coefficient) and has a positive real part of γ (self-focusing behavior). These results were obtained using in-situ Z-scan at 800 nm with 100 fs laser pulses. Z-scan is a technique in which one investigates both a spatial distortion of a laser beam and the changes in its total intensity. It is therefore a convenient technique for the determination of both the real part (the refractive part) and the imaginary part (the absorptive part) of the third-order nonlinearity of various substances, but there can be some uncertainties about the mechanisms of the nonlinear processes since, despite the use of very short laser pulses, information on temporal changes of the refractive and absorptive properties of a sample is not available from ordinary Z-scan experiments. We have therefore resorted to a combination of two time-resolved techniques—probing this nonlinear optical electrochromic effect using a combination of degenerate four-wave mixing (DFWM) and pump−probe techniques not only allows one to confirm the magnitudes of the effects seen previously but, more importantly, provides critical information on the temporal nature of the nonlinear processes.

Experimental Section

The molecular inorganic compound 1,3,5-{*trans*-[RuCl(dppe)$_2$]C≡C-4-C$_6$H$_4$C≡C}$_3$C$_6$H$_3$ (**1**) was prepared as previously described.[11] The time-resolved experiments were carried out using an amplified laser system comprising a Coherent Verdi-pumped Coherent Mira 900D femtosecond oscillator and a regenerative chirped pulse Ti−sapphire amplifier pumped at 30 Hz with the frequency-doubled output of a Spectra Physics GCR Q-switched Nd:YAG laser. The sample was a 0.3% w/w solution of **1** in dichloromethane, with ~0.3 M NBu$^n{}_4$PF$_6$ as supporting electrolyte to provide sufficient conductivity for the

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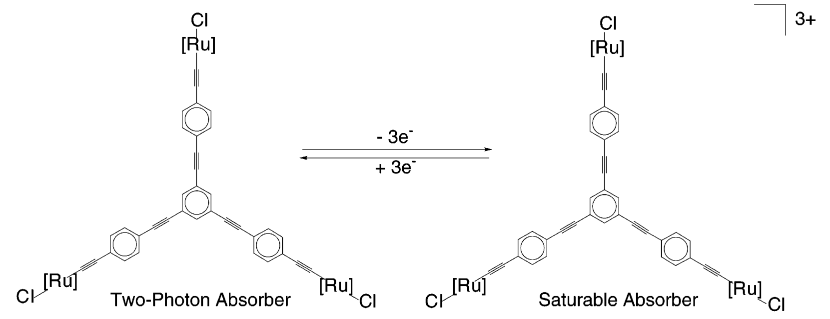

λ_{max}	24 200	11 200	(cm^{-1})
ε	10.4	7.8	(10^4 M^{-1} cm^{-1})
γ_{real}	-330 ± 100	13 500 ± 3000	(10^{-36} esu)
γ_{imag}	2200 ± 500	-4700 ± 500	(10^{-36} esu)
$\lvert\gamma\rvert$	2200 ± 600	14 000 ± 3000	(10^{-36} esu)

Figure 1. Reversible electrochemical switching of 1,3,5-{*trans*-[RuCl(dppe)$_2$]C≡C-4-C_6H_4C≡C}$_3C_6H_3$ (**1**) and its effect on the cubic nonlinear optical properties determined by the Z-scan technique.[8]

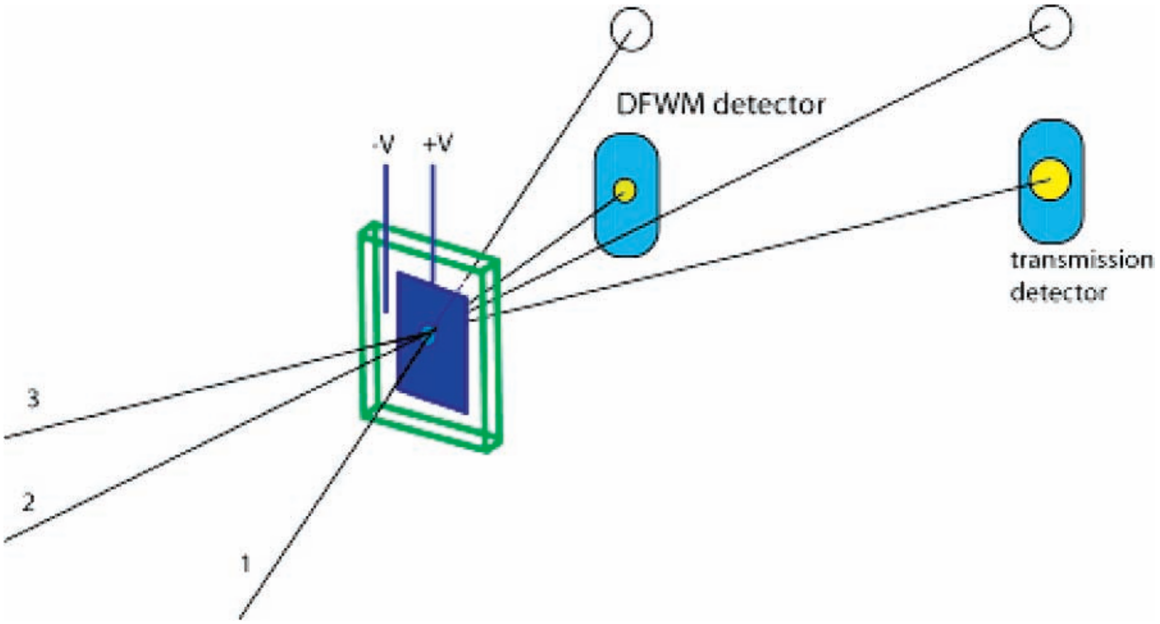

Figure 2. Diagram of the simultaneous DFWM and pump−probe experiments for in-situ measurements of electrochemical switching of third-order nonlinearity. Beams 1 and 2 were timed to arrive at the sample (a hole in the Pt electrode) simultaneously, while the delay of beam 3 was scanned with a computer-controlled delay line. The phase-matched DFWM signal appearing in the fourth corner of the rectangle defined by the three incident beams was monitored as a function of the beam 3 delay. The intensity of beam 3 transmitted through the sample was also monitored; this provided a pump−probe (transient absorption, TA) signal where beams 1 and 2 were pumps and beam 3 was the probe monitoring transmission changes induced by the pumps.

electrochemical experiments. The solution was purged and maintained under argon and placed in a homemade 0.5 mm path length optically transparent thin-layer electrochemical (OTTLE) cell,[12] incorporating platinum auxiliary and Ag−AgCl reference electrodes but modified by replacing the platinum gauze working electrode with a platinum sheet electrode with a 1.5 mm diameter hole to allow passage of the laser beam. A potentiostat supplied the electrogeneration potential of 0.8 V.

The NLO measurements were performed at 12 500 cm^{-1} in a forward (i.e., BOXCARS) DFWM geometry[13] with the output beam from the laser system split into three beams, which were aligned so as to overlap on the sample (spot size ca. 150 μm). The beams were timed with optical delay lines in such a way that two of the beams (1 and 2 in Figure 2) arrived at the sample at the same time, while the delay of beam 3 was scanned between negative values (corresponding to beam 3 arriving at the sample before the pump beams 1 and 2) and positive values (corresponding to beam 3 arriving at the sample after the pump beams). Two detectors were employed, one of them monitoring the phase-matched DFWM signal appearing in the fourth corner of the rectangle formed by the three interacting beams and the other one monitoring the intensity of the probe beam (beam 3) after the sample. With this arrangement, the DFWM signal originating from the formation of a transient grating and the transient absorption (TA) signal originating from modification of the sample absorptivity by the presence of high-intensity pump beams could be measured simultaneously. The results were referenced to those of a 1 mm thick silica glass plate, for which the nonlinear index $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} was assumed.

Results and Discussion

As we reported previously, complex **1** undergoes reversible oxidation in solution (assigned to the metal-centered $Ru^{II/III}$

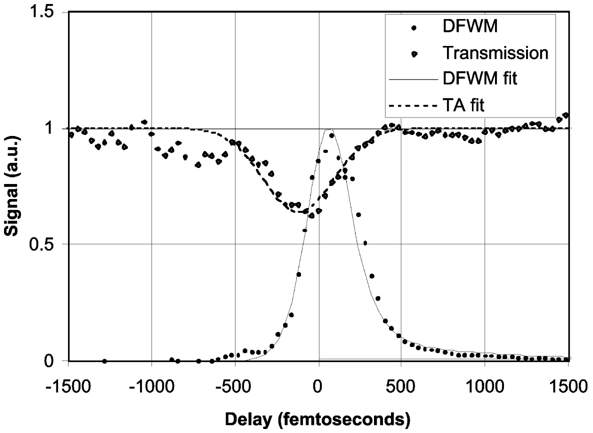

Figure 3. Simultaneous DFWM and pump−probe measurements on a solution of **1** (0.3% w/w in CH_2Cl_2) in an electrochemical cell before oxidation.

process), UV−vis−NIR spectroelectrochemistry in the OTTLE cell revealing that oxidation “switches on” an intense transition centered on 11 200 cm^{-1} with appreciable intensity at 12 500 cm^{-1}.[8] Typical DFWM and TA at 12 500 cm^{-1} scans recorded on a pristine sample of a solution of **1** in the same electrochemical cell are presented in Figure 3. The DFWM curve is somewhat unsymmetrical with a slight “tail” for positive delays. The magnitude of the response of the sample of **1** (ca. 22 times that of 1 mm silica) was used to estimate an approximate value of n_2 of the solution and $|\gamma|$ for the solute, the value $|\gamma| \approx 2000 \times 10^{-36}$ esu being obtained, in good agreement with that from previous Z-scan results ($(2200 \pm 600) \times 10^{-36}$ esu).[11] The changes of transmission (a dip at the delay time close to zero) seen in the pump−probe signal in Figure 3 are consistent with our previous results, indicating efficient two-photon absorption in **1**. The dip depth affords the two-photon absorption coefficient $\beta = 0.05$ cm GW^{-1} for the 0.3% w/w solution, leading to $\sigma_2 \approx 10^{-47}$ cm^4 W^{-1} (10^3 GM units), again in reasonable agreement with $\sigma_2 = 0.53 \times 10^{-47}$ cm^4 W^{-1}, which we determined in our previous studies from γ_{imag} obtained from Z-scan.[8]

We then carried out oxidation and reduction cycles in the electrochemical cell, while monitoring both the transmission signal and the DFWM signal. Oxidizing the 0.3% w/w solution of **1** to the oxidized state $\mathbf{1}^{3+}$ caused the transmission at 800 nm to decrease to about 10% of that before oxidation, while the DFWM signal increased to about 1.4 times its intensity before oxidation. Figure 4 shows the time-resolved signals obtained on the sample in the oxidized state. Two major differences are seen compared to the signals in Figure 3: the DFWM signal is now dominated by a delayed response with a characteristic time of about 1 ps, and the TA signal is now positive (indicating absorption saturation effects) with a decay time that is also on the order of 1 ps. From the magnitude of the DFWM signal after oxidation (and taking into account a suitable absorption correction), we calculate the value of $|\gamma|$ of **1** after oxidation to be ca. 20×10^{-33} esu, about 10 times larger than that for the neutral molecule, and once again in good agreement with the Z-scan result reported previously ($(14\,000 \pm 3000) \times 10^{-36}$ esu).[8] The change of the character of the TA signal also confirms the change of sign of γ_{imag}.

Our present results conclusively prove that the switching of the third-order nonlinearity reported by us previously represents the first demonstrable example of nonlinear electrochromism originating in femtosecond scale processes. It is clearly of interest to investigate in more detail the temporal characteristics of the relaxation of the transient absorption and DFWM signals: the fast relaxation may be due to efficient energy transfer from the excited complex molecules and to solution interactions (including fast reorientation of molecules). Further studies directed to these ends are currently underway.

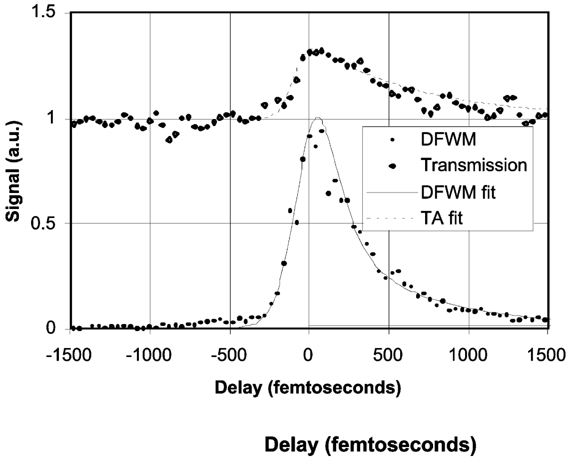

Figure 4. Simultaneous DFWM and pump−probe measurements on a solution of **1** (0.3% w/w in CH_2Cl_2) in an electrochemical cell after oxidation.

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Note Added after ASAP Posting

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