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LETTERS

Organometallic Complexes for Nonlinear Optics. 24. Reversible Electrochemical Switching of Nonlinear Absorption

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The molecular inorganic compounds 1,3,5-{*trans*-[RuCl(dppe)$_2$]C≡C-4-C_6H_4C≡C}$_3C_6H_3$ (**1**), *trans*-[Ru(C≡C-4-C_6H_4C≡CPh)Cl(dppe)$_2$] (**2**), and *trans*-[Ru(C≡CPh)Cl(dppm)$_2$] (**3**) exhibit reversible oxidation in solution, assigned to the metal-centered $Ru^{II/III}$ processes. Complexes **1**−**3** are essentially transparent at frequencies below 20 × 10^3 cm^{-1}, whereas the green complexes $\mathbf{1}^+$−$\mathbf{3}^+$ have a strong absorption band centered near 11−12 × 10^3 cm^{-1}. These absorption bands have been utilized to demonstrate facile NLO switching utilizing an optically transparent thin-layer electrochemical cell, a procedure which has applicability to evaluating the switching capability of a range of materials. This procedure has been applied to switch cubic nonlinearities, the first electrochromic switching of molecular nonlinear absorption. Oxidation of the molecules results in changes, including changes of sign, of both the imaginary (absorptive) part of the third-order nonlinearity and the real (refractive) part. Cycling between the two forms of the molecules is facile. The sign of the nonlinearity is reversed on oxidation of **1** and **2**, whereas **3**, a complex with negligible third-order nonlinearity in the resting state, has third-order nonlinearity switched on upon oxidation to $\mathbf{3}^+$.

Introduction

New materials with desirable nonlinear optical (NLO) properties have been the subject of intense interest because these materials may provide an efficient means of controlling and processing signal-carrying light beams used in photonic technologies. Materials with significant quadratic and/or cubic NLO properties are therefore of considerable importance. Recently, the possibility of modifying molecular structure by external means and thereby switching the value of the nonlinearity has been noted. Attention has focused mainly on methods to reversibly modulate quadratic nonlinearities,[1] the most popular route involving photoexcitation to stimulate a structural change;[2] a photoinduced proton transfer in tautomeric nitrobenzyl pyridines results in 1−2 orders of magnitude variation in first hyperpolarizability.[3] Significantly less is known of switching third-order NLO response, a rare example being the photochromic *trans*−*cis* isomerization of polyimides with azo-containing side chains.[4]

Molecular inorganic complexes may be particularly well-suited to certain forms of switching. Inorganic complexes have been suggested to be far easier to switch magnetically than

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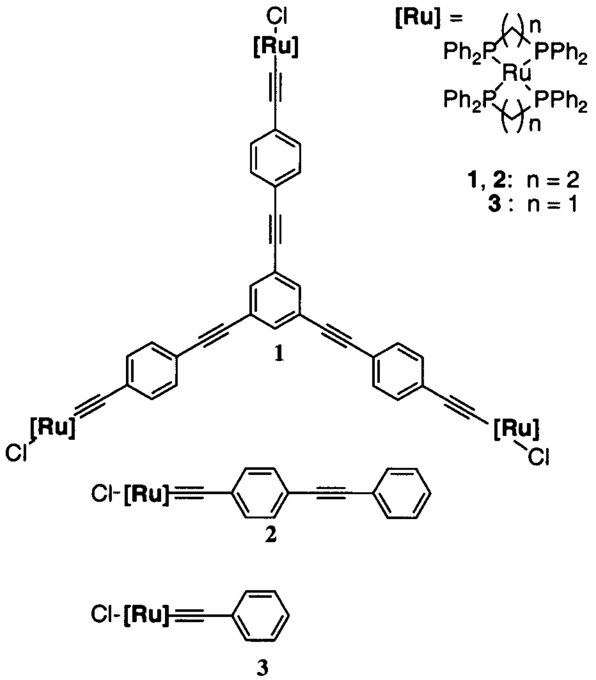

Figure 1. Molecular structures of the alkynylruthenium complexes examined in this work.

organic molecules,[5] although this has yet to be demonstrated. Attaching NLO-active ligands to metals can modulate the NLO response of the free ligand: metal coordination of Schiff bases has been employed to "switch on" quadratic nonlinearity,[6] but this is not reversible. The existence of facile reversible metal-centered redox processes suggests another approach. Indeed, modification *ex situ* by chemical oxidation and subsequent reduction of certain iron and ruthenium complexes has been demonstrated;[7] however, the chemical oxidation and reduction steps physically remote from the optical bench and the dilution procedures required prior to measurement suggest that this is a less than ideal approach to achieving redox-switched nonlinearity, particularly given that the practical goal should be "endless" repetitive cycling. We report herein (i) facile NLO switching utilizing an optically transparent thin-layer electrochemical (OTTLE) cell which has applicability to evaluating the switching capability of a range of materials, (ii) its application to switch cubic nonlinearities, the first electrochromic switching of molecular nonlinear absorption, and (iii) the identification of inorganic molecules with large two-photon absorption (TPA) cross-sections in the resting state and significant linear optical absorption in the oxidized form, an electrochemically accessible optical bistability of potential interest for *inter alia* logic gate applications. [TPA is an NLO process related to the imaginary component of the third-order nonlinearity. TPA materials have excited significant recent interest for applications in multiphoton microscopy, optical limiting, and optical data storage.]

Results and Discussion

The molecular inorganic compounds (Figure 1) comprise 1,3,5-$\{trans\text{-}[RuCl(dppe)_2]C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C\}_3C_6H_3$ (**1**), its linear "component" $trans\text{-}[Ru(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CPh)Cl(dppe)_2]$ (**2**), and $trans\text{-}[Ru(C{\equiv}CPh)Cl(dppm)_2]$ (**3**) (**3** is related to **2** by conceptual removal of one phenylethynyl unit, i.e., a "π-chain shortening", as well as bidentate co-ligand variation). The syntheses of **1**[8] and **3**[9] have been described elsewhere, and **2** was prepared analogously.

Cyclic voltammetry reveals that **1**−**3** undergo reversible oxidation in solution, assigned to the metal-centered $Ru^{II/III}$ processes. The electrochromic behavior of all three complexes, identified by UV−visible spectroelectrochemistry, is broadly similar and in accord with their virtually identical coordination spheres; a representative progression (for conversion of **1** to $\mathbf{1}^+$) is depicted in Figure 2, whereas relevant spectroscopic data for all three complexes and their oxidized forms ($\mathbf{1}^+$−$\mathbf{3}^+$) are collected in Table 1. [N.B. ($\mathbf{1}^+$) is triply charged overall, whereas ($\mathbf{2}^+$) and ($\mathbf{3}^+$) are monocationic.] Complexes **1**−**3** are essentially transparent at frequencies below 20×10^3 cm^{-1}, whereas the green complexes $\mathbf{1}^+$−$\mathbf{3}^+$ have a strong absorption band centered near $11-12 \times 10^3$ cm^{-1}; we assign this band to acetylide-to-Ru^{III} charge transfer. Thus, oxidation of **1**−**3** "switches on" a transition which has appreciable intensity at the frequency of our mode-locked Ti−sapphire laser.

In the present studies, we employed a Z-scan experiment with an incident wavelength of 800 nm, examining the materials in solution in an OTTLE cell with a switching potential of 0.8 V. The results are listed in Table 1, and Z-scan plots of a representative example (**1**) are displayed in Figure 3. Octopolar complexes such as **1**, and chemically related dendrimers, possess significant TPA cross sections σ_2 at 800 nm.[10] The sign of the imaginary part of the third-order nonlinearity is positive for TPA, but under strong one-photon absorption conditions in the oxidized form, an absorption saturation effect is possible; it should therefore be possible to reverse the sign of the nonlinearity on oxidation of **1** and **2**. Equally, a complex with negligible third-order nonlinearity in the resting state (such as **3**) will simply have third-order nonlinearity switched on upon oxidation to $\mathbf{3}^+$: see Table 1. Oxidation of the molecules results in changes (including changes of sign) of both the imaginary

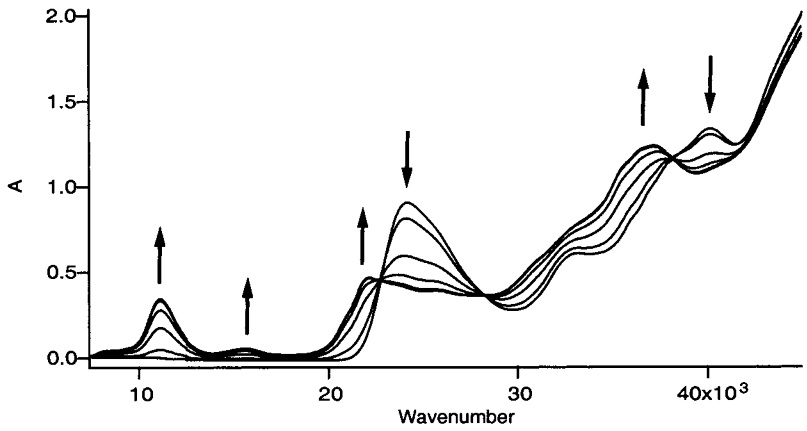

Figure 2. UV−vis−NIR spectra of a CH_2Cl_2 solution of **1** in an OTTLE cell: path length 0.5 mm, during oxidation at $E_{appl} \approx 0.80$ V at 248 K.

TABLE 1: Electrochemical, Linear Optical, and Nonlinear Optical Response Parameters[a]

complex	$E_{1/2}$ (V) ($Ru^{II/III}$)	ν_{max} (cm^{-1})	ϵ (10^4 M^{-1} cm^{-1})	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	$\lvert\gamma\rvert$ (10^{-36} esu)	σ_2 (10^{-50} cm^4 s)
1 $[Ru^{II}]_3$	0.51	24 200	20.1	-330 ± 100	2200 ± 500	2200 ± 600	530 ± 120
$\mathbf{1}^+$ $[Ru^{III}]_3$		11 200	7.8	13500 ± 3000	-4700 ± 500	14000 ± 3000	-1200 ± 100
2 $[Ru^{II}]$	0.55	25 800	3.6	-100 ± 100	450 ± 200	460 ± 200	110 ± 50
$\mathbf{2}^+$ $[Ru^{III}]$		11 200	2.0	2900 ± 1000	-1200 ± 600	3100 ± 1000	-300 ± 70
3 $[Ru^{II}]$	0.55	31 400	2.3	<300	<200	$\cong 0$	$\cong 0$
$\mathbf{3}^+$ $[Ru^{III}]$		12 000	1.0	1300 ± 500	-2200 ± 1000	2600 ± 1000	-540 ± 200

[a] All measurements in CH_2Cl_2 solvent. All γ results are referenced to the nonlinear refractive index of silica $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1}. $E_{1/2}$ measurements are referenced to Ag/AgCl (against which the ferrocene/ferrocenium couple is found at 0.56 V). σ_2 values are calculated using the equation $\sigma_2 = h\omega\beta/(2\pi N)$, where β is the two-photon absorption coefficient. $\mathbf{1}^+$ is triply charged overall, unlike $\mathbf{2}^+$ and $\mathbf{3}^+$: see text.

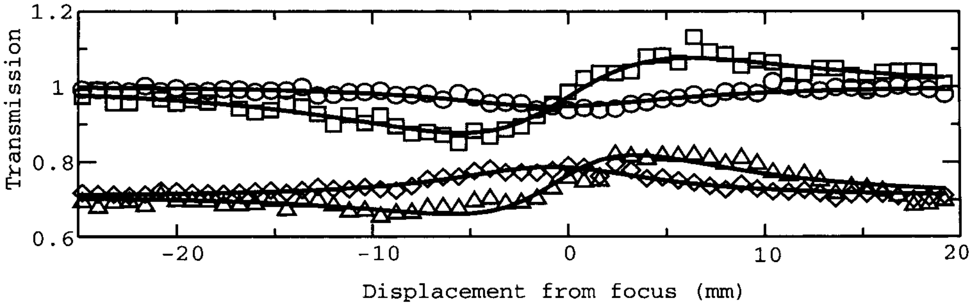

Figure 3. Closed and open aperture Z-scan traces for **1** and $\mathbf{1}^+$, at 800 nm using 100 fs pulses. Closed aperture **1** (squares), open aperture **1** (circles), closed aperture $\mathbf{1}^+$ (triangles), open aperture $\mathbf{1}^+$ (diamonds). Theoretical curves assume a thin sample approximation.

(absorptive) part of the third-order nonlinearity and the real (refractive) part. Cycling between the two forms of the molecules is facile.

The photochromic switching described earlier[4] suffers from the back reaction proceeding thermally over hundreds of seconds, too long to be useful. In contrast, the rate of reversible electrochemical switching is diffusion controlled, and unlike the photochromic switching, the back reaction proceeds at essentially the same rapid rate as the forward process. Very fast switching is therefore possible by electrochromic means.

Significant absorption at 12 500 cm^{-1} (corresponding to our laser irradiation wavelength of 800 nm) is seen in complexes $\mathbf{1}^+-\mathbf{3}^+$ with a tervalent *trans*-$[Ru(C{\equiv}CR)Cl(L_2)_2]$ (L_2 = bidentate phosphine) composition. This is of potential interest as most biological materials, such as tissue, have maximum transparency at this wavelength. The NIR absorption maximum of the oxidized form and, hence, the frequency at which switching the absorptive nonlinearity can occur is tunable in complexes such as these by appropriate molecular modification. Replacing the chloride with a second alkynyl ligand to afford *trans*-$[Ru(C{\equiv}CR)(C{\equiv}CR')(L_2)_2]$ results not only in complexes with enhanced σ_2[10] but also in complexes where the absorption maximum in the oxidized form is at ca. 7700 cm^{-1}, ie., 1300 nm. This is a wavelength at which silica has optimal transparency, affording the prospect of electrochromic switching devices at telecommunications-relevant wavelengths.

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Supporting Information Available: Experimental procedures for synthesis and characterization of **2**, electrochemical and nonlinear optical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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