Communication

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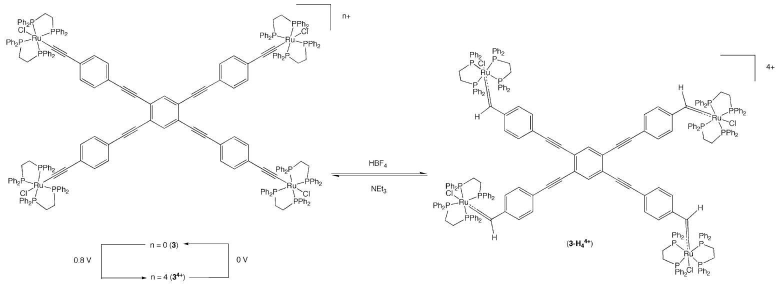

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Independent Switching of Cubic Nonlinear Optical Properties in a Ruthenium Alkynyl Cruciform Complex by Employing Protic and Electrochemical Stimuli[1]

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Materials with optimized nonlinear optical (NLO) properties are required for various applications, including processing of optical signals, optical data storage, nanophotonics, and biophotonics.[2−4] There has been significant recent interest in the reversible switching or modulation of NLO properties.[5−17] Specific procedures that have been employed to switch NLO properties include protonation/deprotonation, oxidation/reduction, and photoisomerization sequences, almost all reports considering two “states” only and providing data for a single wavelength only. Very recently, quadratic[15] and cubic[16] NLO properties have been switched between three distinct states for the first time. We have previously shown that the NLO properties of ruthenium alkynyl complexes can be conveniently switched electrochemically via the reversible $M^{II/III}$ couples.[8,10,11,13,14] We report herein synthesis of a quadrupolar ruthenium alkynyl cruciform complex, its reversible conversion to tetravinylidene complex or tetraruthenium(III) tetracationic complex forms by protonation or oxidation, linear and nonlinear proto- and electrochromism studies that reveal switching of NLO properties, cubic NLO wavelength-dependence studies for the alkynyl complex, its tetracation, and the vinylidene complex, and theoretical studies that shed light on the optical behavior.

The synthesis of the ruthenium alkynyl cruciform complex **3** is described in the Supporting Information. Its reversible conversion to the oxidized ($\mathbf{3}^{4+}$) and protonated ($\mathbf{3\text{-}H_4}^{4+}$) forms is shown in Scheme 1. The UV−vis−NIR spectra of **3**, $\mathbf{3}^{4+}$, and $\mathbf{3\text{-}H_4}^{4+}$ in CH_2Cl_2 are shown in Figure 1a. Complex **3** is essentially transparent at frequencies shorter than 17 000 cm^{-1}, oxidation to $\mathbf{3}^{4+}$ affording a linear optical spectrum with a broad band centered at 11 000 cm^{-1}. Cycling between the two oxidation states of the complex in solution in an optically transparent thin-layer electrochemical (OTTLE) cell can be achieved by applying the appropriate potentials; this results in isosbestic points in the UV−vis−NIR spectral progressions, consistent with fully reversible electrochemical conversions between the two forms. Similarly, facile and quantitative protonation of **3** to $\mathbf{3\text{-}H_4}^{4+}$ with HBF_4 and deprotonation to regenerate **3** is accompanied by significant changes in the UV−vis−NIR spectrum, with the protonated form transparent at frequencies below 20 000 cm^{-1}.

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] The third-order NLO properties were assessed by a combination of open- and closed-aperture Z-scan experiments. Figure 2 shows open-aperture Z-scans obtained on oxidation of **3** in the cell at 13 300 cm^{-1}. A minimum at $z = 0$ in the Z-scan trace of **3** indicates two-photon absorption; upon oxidation, this is replaced by a maximum, signifying the presence of saturable absorption in $\mathbf{3}^{4+}$.

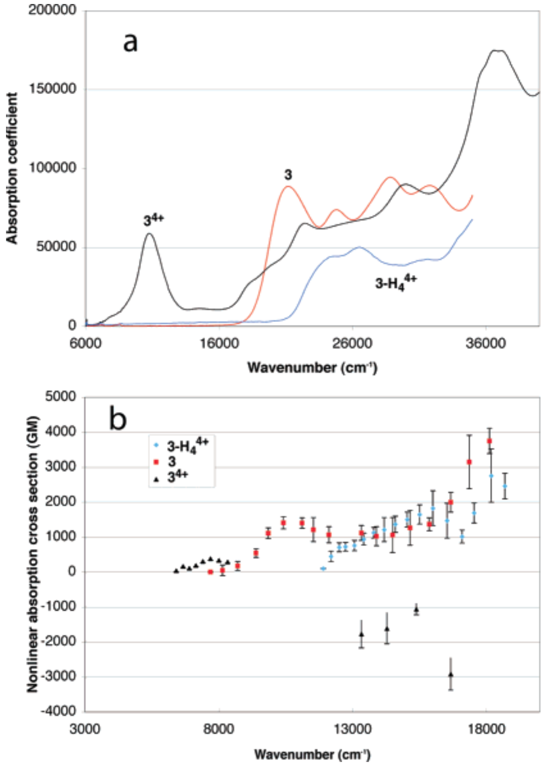

Figure 1. (a) UV/vis/NIR spectra of **3**, $\mathbf{3}^{4+}$, and $\mathbf{3\text{-}H_4}^{4+}$ in CH_2Cl_2. (b) Comparison of nonlinear absorption spectra for **3**, $\mathbf{3}^{4+}$, and $\mathbf{3\text{-}H_4}^{4+}$.

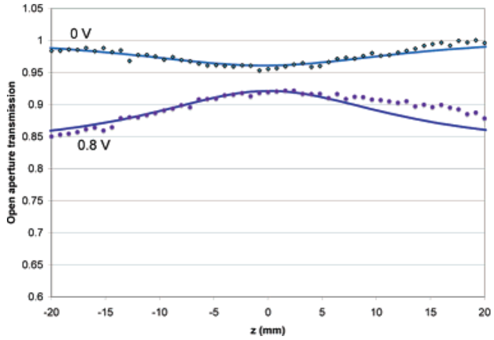

Figure 2. In situ open-aperture Z-scans at 13 300 cm^{-1} illustrating switching the nonlinearity between **3** and $\mathbf{3}^{4+}$. Lines are theoretical fits of the Z-scan curves.

We have carried out detailed studies of the dispersion of the cubic NLO properties of all three compounds. The absorptive nonlinearity results are shown in Figure 1b. Comparison of these

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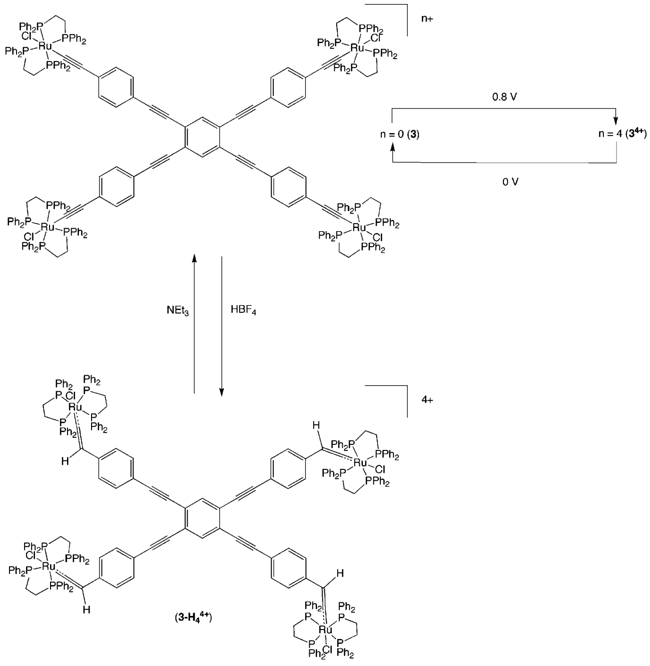

Scheme 1. Syntheses of **3**, **3^{4+}**, and **3-H_4^{4+}**

Table 1. Intense Low-Energy Absorption Features of the Computational Model and Laboratory Cruciform Complexes

species	calcd (PBE)/cm^{-1}	*f* (PBE)/au	obs/cm^{-1}
3	18100	2.33	21200
3-H_4^{4+}	19700	2.57	24400
3^{4+}	8400	3.65	10800

results with Figure 1a indicates similarities in the location of one-photon and two-photon absorption bands for **3** and **3-H_4^{4+}**. The nonlinear absorption spectrum of **3^{4+}** contains a region dominated by two-photon absorption that peaks at 7700 cm^{-1} and a region of absorption saturation between 16 700 and 12 500 cm^{-1}. Strong one-photon absorption between 12 500 and 9100 cm^{-1} rendered it impossible to obtain NLO data in that range. The NLO spectra in Figure 1b reveal several possibilities for switching between the three forms of the cruciform leading to a strong two-photon absorber, a saturable absorber, or negligible nonlinear absorption for different laser wavelength ranges.

The linear and nonlinear absorption spectra of the complexes can be rationalized from DFT computations that have been performed on D_{2h} symmetry models of **3**, **3^{4+}**, and **3-H_4^{4+}**. All three of the model structures have been optimized in the singlet state; additional optimizations on triplet and quintet state models of **3^{4+}** determined the latter configurations are slightly higher in energy than the singlet model of **3^{4+}**. Further details of the optimizations are described in the Supporting Information. Time-dependent DFT (TD-DFT) calculations on these models identify a plethora of electronic transitions with excitation energies less than 25 000 cm^{-1}. Of the dipole-allowed transitions, those with substantially the highest calculated oscillator strength for the models of **3**, **3^{4+}**, and **3-H_4^{4+}** (Table 1) correspond fairly well with the lowest-energy peaks in the spectra shown in Figure 1a.

The computed PBE/TZP results in each case underestimate the observed features by a few thousand wavenumbers. Nonetheless, these calculations replicate the experimental difference between low-frequency peaks for **3** and **3^{4+}**, as well as the blue-shifted onset of absorption for **3-H_4^{4+}** compared to **3**. For **3** and **3-H_4^{4+}**, the intense single-photon absorption features in Table 1 involve excitation from $^{17}b_{1g}$ (HOMO) to $^{19}b_{3u}$, while for **3^{4+}**, the excitation is from $^{17}b_{3u}$ to $^{17}b_{1g}$. In all three species, the $^{17}b_{1g}$ orbital is π-bonding on the C_2 units of the organic acetylene and organometallic alkynyl (or vinylidene) moieties of the cruciform, while for **3** and **3-H_4^{4+}**, $^{19}b_{3u}$ confers cumulenic character to the C(arm-aryl)C_2C(central-aryl) units. For **3^{4+}**, the $^{17}b_{3u}$ orbital is dominated by alkynyl π-bonding character. In all instances, the ground-state orbital has significantly greater electron density at the alkynyl group than does the excited-state orbital. Although interpretation of the two-photon spectra is more difficult, our calculations do show that several forbidden transitions are a close energetic match (and involve excitations of similar local bonding or antibonding character) to the intense transitions for each form of **3**, consistent with experimental results for which two-photon transitions match the energies of dipole-allowed transitions.

Quadrupolar molecules have attracted significant interest as TPA materials. Metal-containing examples are little explored, although the presence of transition metals and organic ligands can impart important functionality; the present studies have shown that appropriately designed complexes can act as NLO molecular switches when one employs "orthogonal stimuli" (the fully reversible oxidation/reduction and protonation/deprotonation procedures are independent of one another).

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Supporting Information Available: Preparation, spectroscopic, and analytical data for **3** and its precursor compounds, the nonlinear optical measurements, and the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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