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Molecular Switches

Switching the Cubic Nonlinear Optical Properties of an Electro-, Halo-, and Photochromic Ruthenium Alkynyl Complex Across Six States[**]

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The impending breakdown in Moore's law has prompted the search for molecule-based information-processing components such as molecular switches and logic gates.[1] Bistable molecules that afford states possessing distinct linear optical properties (absorbance, fluorescence) and that can be interconverted by chemical, redox, magnetic, or photonic stimuli have attracted considerable interest for Boolean logic operations.[2] In principle, molecular computing could exploit ternary or higher-order digit representations, which would permit smaller device components. "Switchable" molecular properties are also of intense interest for sensor applications. Despite this interest, molecules that can exist in more than two stable and independently addressable states, which could be employed for complex and higher-order logic functions, have been explored significantly less than two-state molecules. One potentially very important procedure to exploit molecular switches is to utilize their cubic nonlinear optical (NLO) properties,[3] and in particular their nonlinear absorption.[4] However, this avenue is also poorly explored and is to date restricted to switching between three states at most,[5,6] although such switching offers 1) the prospect of broadening the available spectral range (and in particular utilizing telecommunications-relevant wavelengths) and 2) the possibility of enhanced spatial control (compared to linear optical switching) because of the higher-order dependence on the intensity of the incident light. Herein we show that a specific binuclear metal alkynyl complex[7] incorporating a functionalized 5,5′-dithienylperfluorocyclopentene (DTE) bridge[8] can afford six stable and switchable states that possess distinct cubic NLO properties. The complex is comprised of independently addressable modules that respond orthogonally to protic (alkynyl ligand⇄vinylidene ligand), electrochemical (metal-centered redox: $\mathrm{Ru^{II}} \rightleftarrows \mathrm{Ru^{III}}$), and photochemical (DTE ring-opening⇄ring-closing) stimuli. The six states are interconverted along seven pathways, all of which result in distinct changes to cubic nonlinearity for specific regions of the spectrum. Our results demonstrate that complexes of this type have the potential to be used, among other things, in the construction of multi-input logic gates responding to diverse stimuli across a broad spectral range.

The synthesis of the dinuclear ruthenium alkynyl complex **oa(II)** is depicted in Figure S1 in the Supporting Information. The DTE unit is obtained in the "open" form as its 5,5′-diethynyl derivative; the open DTE is thermally stable, and this open form persists through the preparative steps that ultimately afford **oa(II)**. Complete synthetic and characterization details are given in the Supporting Information. Complex **oa(II)** can be reversibly protonated to the di(vinylidene) complex **ov(II)**, reversibly oxidized to the $\mathrm{Ru^{III}}$ complex dication **oa(III)**, and photoisomerized with UV light to the closed alkynyl complex **ca(II)**. Complex **ca(II)** can be reversibly protonated to **cv(II)** and reversibly oxidized to **ca(III)** and undergoes photoreversion to **oa(II)** on irradiation with red light. The vinylidene forms and the oxidized forms undergo reversible photoisomerization under analogous irradiation conditions. Note that oxidation of ruthenium vinylidene complexes with these coligands is an irreversible process, as assessed by cyclic voltammetry,[9] so there is a maximum of six switchable states for this complex.[10] The interconversions of the six stable states of the complex are depicted in Scheme 1, and key spectral data are tabulated in the Supporting Information (Table S1). Cyclic voltammograms and UV/Vis/NIR spectral progressions for the redox processes, the latter acquired with an optically transparent thin-layer spectroelectrochemical (OTTLE) cell and demonstrating stable isosbestic points, are given in the Supporting Information, together with NMR spectra demonstrating spectroscopically complete 1) photoisomerization between the open and closed forms and 2) protonation/deprotonation to afford the vinylidene and alkynyl complex forms, and IR spectra demonstrating spectroscopically complete oxidation from the $\mathrm{Ru^{II}}$ to the $\mathrm{Ru^{III}}$ form.

Several organometallic alkyne-functionalized DTE complexes have been reported, and the effect of oxidation state on photochromic behavior has been probed, although there was no assessment of the effect of protonation/deprotonation on photochromism. $[\mathrm{CpFe}(\eta^5\text{-}\mathrm{C_5H_4C{\equiv}C{-}DTE{-}C{\equiv}C}\text{-}\eta^5\text{-}\mathrm{C_5H_4})\mathrm{FeCp}]$[11] and $[(\mathrm{dppe})\mathrm{Cp^*Fe}(\mathrm{C{\equiv}C{-}DTE{-}C{\equiv}C})\mathrm{FeCp^*}$-

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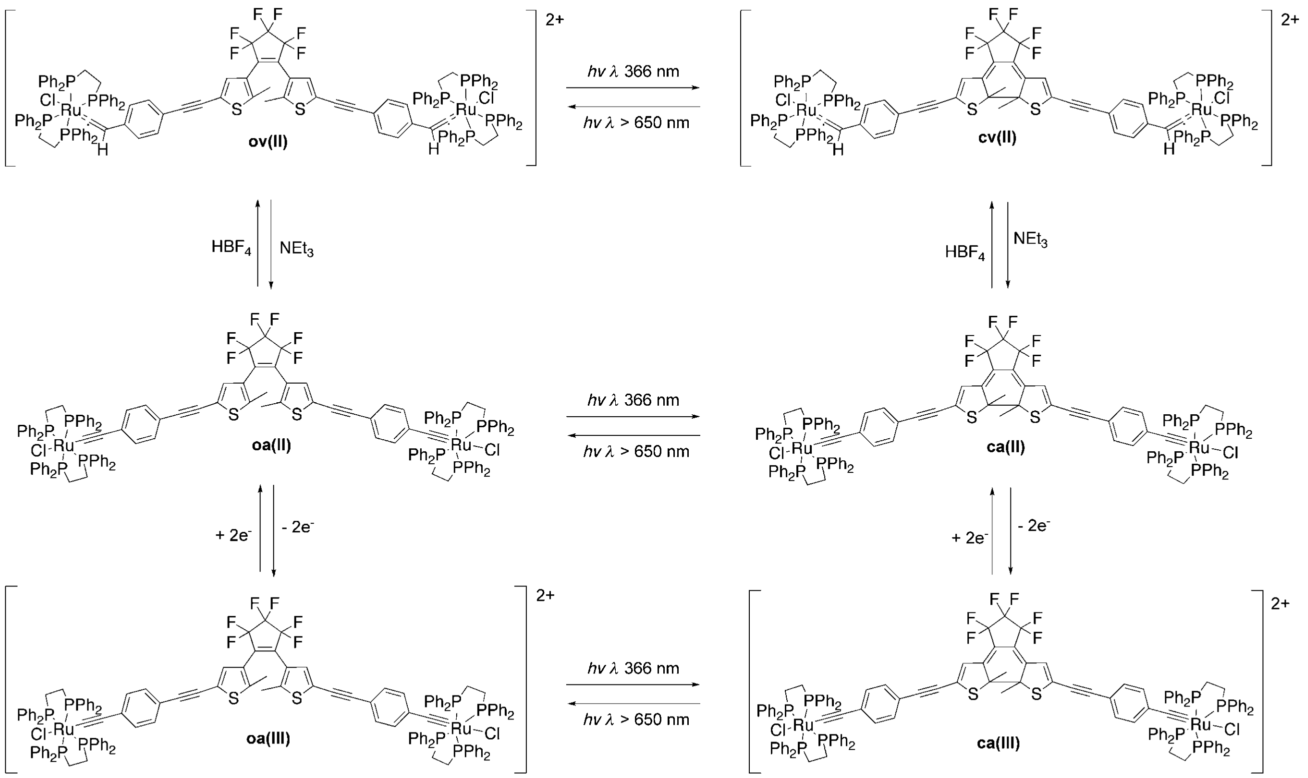

Scheme 1. Interconversions of **oa(II)**, **ov(II)**, **oa(III)**, **ca(II)**, **cv(II)**, and **ca(III)**. **o** = open DTE, **c** = closed DTE, **a** = alkynyl, **v** = vinylidene, **II/III** = (formal) metal-centered oxidation states.

(dppe)][12] ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$, dppe = 1,2-bis(diphenylphosphino)ethane) undergo ring opening of the closed form on oxidation, with the latter undergoing decomposition on ring closing of the oxidized open form, whereas oxidation of the open form of [*trans*-Cl(dppe)$_2$Ru(C$\equiv$C−DTE−C$\equiv$C)-*trans*-RuCl(dppe)$_2$] results in ring closing.[13] In stark contrast, the present complex cleanly photoisomerizes in both the resting state and the oxidized forms, with all seven interconversions affording bistable molecular switches.

The cubic NLO properties of the six states were assessed by femtosecond Z scan over a broad spectral range. Note that a complete spectral dependence study of each state typically requires many hours, thus demonstrating the stability of the oxidized species **oa(III)** and **ca(III)**. The marked differences in absorptive nonlinearities for the six states of the complex afford the possibility of NLO switching. This situation is illustrated in Figure 1 (which depicts the two-photon absorption cross-sections), with (a) and (b) corresponding to oxidation/reduction and (c) corresponding to photoisomerization. Note that there are broad ranges of the nonlinear spectra in which the behavior of the different forms of the complex is dramatically different. In the range 600–1000 nm, the open forms of the complex comprise a two-photon absorber (**oa(II)**), a saturable absorber (**oa(III)**), and an inactive nonlinear absorber (**ov(II)**), corresponding to positive, negative, and near-zero values of the imaginary component of the cubic nonlinearity. The two vinylidene complex forms are inactive (**ov(II)**) and a two-photon absorber (**cv(II)**) over the spectral range 750–1600 nm, while the two alkynyl complex forms are inactive (**oa(II)**) and a two-photon absorber (**ca(II)**) over the range 1100–1600 nm.

The orthogonal switching that is possible with the alkynyl complex forms affords the possibility of two-input logic gates corresponding to 1) pH and *hν* input or 2) V and *hν* input, which can be interrogated through their nonlinear absorption. For example, Table 1 illustrates this for (1) with a NOR gate, while Table 2 illustrates this for (2) with an INH gate.[14]

Our results demonstrate an "orthogonal" extension of the concept of photochromism into the nonlinear optics domain, similar to that which we have previously demonstrated with

Table 1: NOR gate from vinylidene (**v**)/alkynyl (**a**) and open (**o**)/closed (**c**) switching of two-photon absorption at 900 nm.

Complex	**v** = 0, **a** = 1	**o** = 0, **c** = 1	σ_2 [GM]	Output
ov(II)	0	0	0	1
oa(II)	1	0	200	0
cv(II)	0	1	400	0
ca(II)	1	1	500	0

Table 2: INH gate from Ru^{II}/Ru^{III} and open (**o**)/closed (**c**) switching of two-photon absorption at 1550 nm.

Complex	Ru^{II} = 0, Ru^{III} = 1	o = 0, **c** = 1	σ_2 [GM]	Output
oa(II)	0	0	0	0
oa(III)	1	0	0	0
ca(II)	0	1	50	1
ca(III)	1	1	0	0

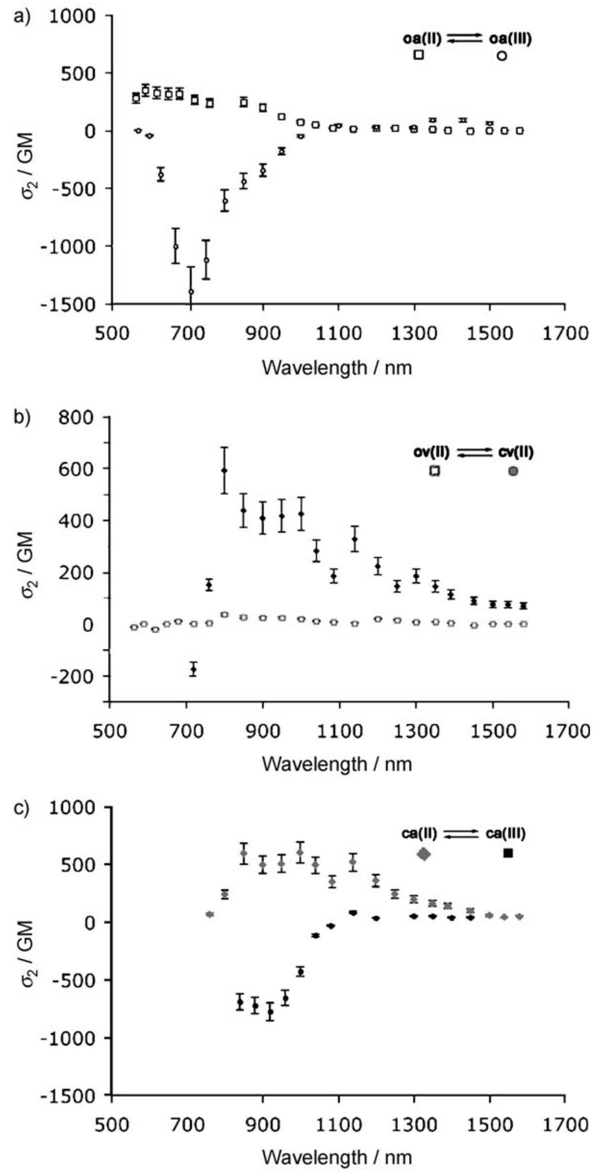

Figure 1. Nonlinear absorption spectra for a) **oa(II)** (squares) and **oa(III)** (circles), b) **ov(II)** (squares) and **cv(II)** (circles), and (c) **ca(II)** (diamonds) and **ca(III)** (squares). For ease of comparison, the **oa(III)** and **ca(III)** values are plotted as 1/10 of their true value. The effective two-photon cross-sections are presented in GM (Göppert–Mayer) units, where 1 GM $= 10^{-50}$ cm^4 s.

orthogonal electrochromism and halochromism (acidochromism, protochromism);[5b] the present nonlinear photochromism is understood as the change of nonlinear absorptivity of a substance under the action of light. These nonlinear "chromisms" are potentially of wider use, providing distinctly modified properties of a chromophore that can be detected by laser techniques, for example, for sensing or for the modification of the propagation characteristics of laser beams in optical devices. These results also highlight the utility of organometallics in such applications. While organics currently dominate the field of molecular nonlinear optics, the facile redox switching at metal centers in organometallics adds a new dimension to this field.

Experimental Section

The identity and purity of **oa(II)**, **ca(II)**, **ov(II)**, and **cv(II)** were confirmed by ^{1}H, ^{31}P, and ^{13}C NMR and UV/Vis spectroscopy, ESI mass spectrometry, and elemental analyses, while the oxidized species **oa(III)** and **ca(III)** were characterized by UV/Vis and IR spectroscopy. Full details of the syntheses and characterization of all new compounds are given in the Supporting Information. The protonation/deprotonation sequences to interconvert **oa(II)** and **ov(II)** as well as **ca(II)** and **cv(II)** were carried out ex situ by sequential use of HBF_4 and NEt_3. The oxidation/reduction sequences to interconvert **oa(II)** and **oa(III)** as well as **ca(II)** and **ca(III)** were carried out in an OTTLE cell while monitoring changes in the optical nonlinearity, as described in the Supporting Information. The photoisomerization sequences to interconvert the pairs **ov(II)** and **cv(II)**, **oa(II)** and **ca(II)**, and **oa(III)** and **ca(III)** were carried out in situ in the spectroscopy cell employed for the NLO studies, as described in the Supporting Information.

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