

Organometallic Complexes for Nonlinear Optics. 16.¹ Second and Third Order Optical Nonlinearities of Octopolar Alkynylruthenium Complexes

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There has been considerable interest recently in the quadratic nonlinear optical (NLO) properties of molecules that possess octopolar symmetry.² The traditional approach to the design of materials with enhanced molecular second-order NLO coefficients has been to use molecules with extended π -systems and significant molecular dipoles. There exist several drawbacks to this methodology, though, such as the NLO efficiency/transparency tradeoff and the proclivity of dipolar molecules to adopt centrosymmetric packing in the solid state.³ Nondipolar molecules may be effective in overcoming these problems: the presence of a 3-fold symmetry axis in octopolar 1,3,5-substituted aromatic ring systems may lead to better transparency characteristics,⁴ and the lack of a molecular dipole enhances the prospects of noncentrosymmetric crystal packing. Recent studies have highlighted the potential of both metal-containing⁵ and particularly organic compounds⁶ as octopolar quadratic NLO materials. We present herein quadratic NLO data for octopolar alkynylruthenium complexes, together with the first reported data exploring the third-order NLO potential of an organometallic octopolar compound.

The octopolar complexes and a linear analogue (Figure 1) were prepared using established methodologies. Compounds **1** (a, b)

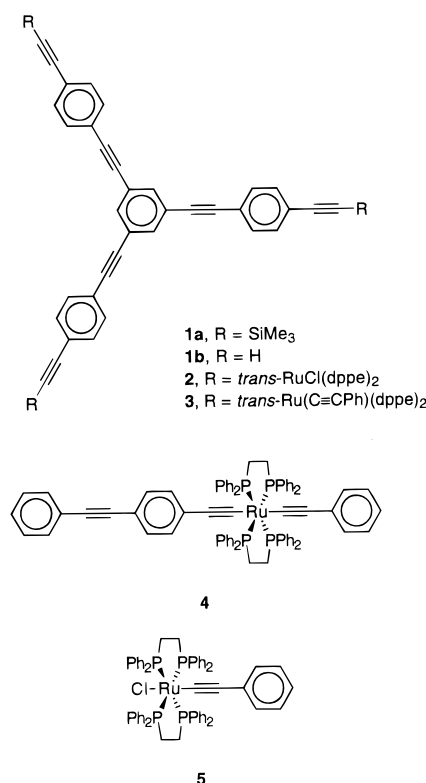


Figure 1.

were prepared by the reaction of 1,3,5-triethynylbenzene⁷ with 4-(trimethylsilylethynyl)iodobenzene⁸ using the palladium(II)-catalyzed coupling method of Sonogashira *et al.*⁷ Syntheses of **2** and **3** proceed via [PF₆]⁻-stabilized vinylidene intermediates, using adaptations of the method of Dixneuf and co-workers.⁹ The syntheses of **1** and **2** were reported¹⁰ while the current paper was in preparation. The linear complex *trans*-[Ru(4-C≡CC₆H₄C≡CPh)(C≡CPh)(dppe)₂] (**4**) was prepared similarly, and the related *trans*-[Ru(C≡CPh)Cl(dppe)₂] (**5**) was prepared as previously reported.⁹

HRS measurements were performed at 1064 nm using a Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR130-10, 8 ns

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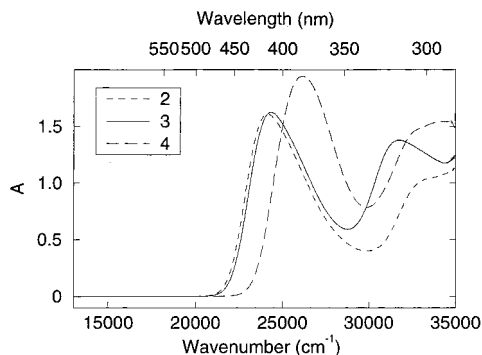
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Table 1. Experimental Linear Optical Spectroscopic, Quadratic Nonlinear Optical and Cubic Nonlinear Optical Response Parameters for **1a**, **2–5**^a

compd	λ (nm) [ϵ (10^4 $M^{-1} cm^{-1}$)]	$\sqrt{\langle \beta^2 \rangle^b}$ (10^{-30} esu)	γ_{real}^c (10^{-36} esu)	γ_{imag}^c (10^{-36} esu)	$ \gamma $ (10^{-36} esu)
1a	342 [0.5]	8	95 ± 20	0	95 ± 20
2	414 [10.4]	94	-330 ± 100	2200 ± 500	2200 ± 600
3	411 [11.6]	93	-600 ± 200	2900 ± 500	3000 ± 600
4	383 [3.8]	34	-670 ± 300^d	1300 ± 300^d	1500 ± 500
5	319 [1.8]	6	-170 ± 40^d	71 ± 20^d	200 ± 50

^a All measurements in THF solvent except where indicated. All complexes are optically transparent at 1064, 800, and 532 nm. ^b HRS at 1064 nm; values $\pm 10\%$, using *p*-nitroaniline ($\beta = 21.4 \times 10^{-30}$ esu) as a reference. ^c All results are referenced to the nonlinear refractive index of silica $n_2 = 3 \times 10^{-16}$ cm²/W. ^d CH₂Cl₂ solvent.

**Figure 2.** UV-vis spectra for **2–4**.

pulses, 10 Hz) which was focused into a cylindrical cell (14 mL) containing the sample. The intensity of the incident beam was varied by rotation of a half-wave plate placed between crossed polarizers. The harmonic scattering and linear scattering were distinguished by appropriate filters; gated integrators were used to obtain intensities of the incident and harmonic scattered light. Z-scan measurements were performed at 800 nm using 100 fs pulses from a system consisting of a Coherent Mira Ar-pumped Ti-sapphire laser and a Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz. The closed-aperture and open-aperture Z-scans were recorded at a few concentrations of each compound in THF and the real and imaginary part of the nonlinear phase shift determined by numerical fitting using equations given in reference 11. The real and imaginary part of the hyperpolarizability of the solute was then calculated by linear regression from the concentration dependencies. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm² W⁻¹ was assumed.

The results of quadratic and cubic nonlinear optical and UV-vis measurements are shown in Table 1. Importantly, these complexes have absorption bands far from the second harmonic wavelength of 532 nm (Figure 2), permitting assessment of the impact of structural variation on quadratic NLO merit. Incorporation of the ligated metal fragment in proceeding from the organic acetylene **1a** to the organometallic complex **2** leads to a significant

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increase in β_{HRS} . Extending the delocalized π -system through the metal in progressing from **2** to **3**, though, is ineffective in increasing β , indicating that the *trans*-phenylalkynyl ligand is acting largely as a π -donor ligand (we have previously noted that phenylalkynyl ligands are pseudo-halides in complexes of this type);¹² a similar lack of β enhancement on extending the π -system through a metal has been reported recently in a dipolar system.¹³ Complex **4** is the linear fragment of the octopolar complex **3**. Progressing from **4** to **3** results in a 3-fold increase in oscillator strength for λ_{max} and in its quadratic NLO merit, with little loss of optical transparency accompanying the large increase in β_{HRS} . Complex **3** formally results from coupling **1a** with *trans*-[Ru(C≡CPh)Cl(dppe)₂] (**5**); importantly, β_{HRS} for **3** is significantly larger than the β_{HRS} values for **1a** or **5**. The absolute values of β_{HRS} for **2** and **3** are among the largest thus far for octopolar compounds optically transparent at the second-harmonic, for which resonance enhancement is much less important. They are also among the largest thus far for octopolar compounds lacking a formal acceptor moiety (results with organic compounds suggest that a further increase in β_{HRS} is likely upon replacing the arene ring with an electron acceptor such as 2,4,6-trinitroaryl or 2,4,6-triazine groups).¹⁴

Table 1 contains the first third-order NLO data for organometallic octopolar molecules.¹⁵ The significant γ_{imag} for **2–5** are indicative of two-photon absorption, which becomes important as λ_{max} approaches 2ω . The negative γ_{real} for **2–5** are therefore likely to result from two-photon dispersion effects, rather than being indicative of zero-frequency negative cubic hyperpolarizabilities. Structure–NLO property correlations must be cautious, particularly given the significant errors involved, but the data thus far (**2** cf. **3**; **4** cf. **5**) are suggestive of an increase in γ on chain-lengthening through the metal center, in contrast to the above-mentioned results with β_{HRS} . Inspection of $|\gamma|$ for **3** and **4** reveals a significant increase in this parameter upon progressing from the linear to the octopolar complex.

Complex **2** is a thermally stable ($T_{dec} > 220$ °C) building block for arylalkynylruthenium dendrimers, which, in the absence of steric effects, should maintain idealized D_{3h} symmetry and purely octopolar NLO responses. We are proceeding to explore the NLO potential of these π -delocalized organometallic dendrimers; the results of these investigations will be reported shortly.

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Supporting Information Available: Experimental procedures for synthesis and nonlinear optical measurements, and characterization data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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