

# Organometallic Complexes for Nonlinear Optics. 28.<sup>1</sup> Dimensional Evolution of Quadratic and Cubic Optical Nonlinearities in Stilbenylethynylruthenium Complexes

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**Summary:** Quadratic nonlinearities for octopolar stilbenylruthenium complexes are large for compounds without strongly accepting substituents. Cubic nonlinearities  $|\gamma|_{800}$  and two-photon absorption cross-sections  $\sigma_2$  increase on “dimensional evolution” from linear analogues to octopolar complexes, the latter possessing some of the largest  $|\gamma|_{800}$  and  $\sigma_2$  values for organometallics thus far, while cubic nonlinearities  $\text{Im}(\chi^{(3)})/N$  from the first application of electroabsorption spectroscopy to organometallics are also large, scaling with the number of metal atoms.

An important theme in contemporary chemistry research is the progression from one-dimensional (linear) to multidimensional compounds and the effect that this “dimensional evolution” has on specific physical properties. The dimensional evolution of nonlinear optical (NLO) properties is of particular interest. Replacing the classical one-dimensional dipolar composition with a two-dimensional or three-dimensional octopolar arrangement has been suggested as a possible means of overcoming the NLO efficiency/optical transparency tradeoff and of disfavoring centrosymmetric packing in the solid state,<sup>2–15</sup> both of which have hampered ef-

ficient quadratic NLO materials design. Dimensional evolution of third-order NLO properties is also of current interest:<sup>16–18</sup> the two-photon absorption (TPA) efficiencies of octopolar compounds have been probed,<sup>19–23</sup> and a nonlinear increase in proceeding from linear compounds to 3-fold symmetry octopolar compounds has been noted.<sup>21,24</sup>

The NLO properties of organometallics have been studied intensively over the past decade, metallocenyl and alkynyl complexes commanding most attention.<sup>25–28</sup> Although the vast majority of reports have considered one-dimensional dipolar complexes, recent studies have highlighted the potential of octopolar and dendritic alkynylruthenium complexes, examples possessing large

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**Table 1. Experimental Linear Optical Spectroscopic, Quadratic Nonlinear Optical, and Cubic Nonlinear Optical Response Parameters<sup>a</sup>**

compound	$\lambda_{\max}$ (nm) [ $\epsilon$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )]	$\beta_{1064}$ ( $10^{-30}$ esu)	$\beta_{800}$ ( $10^{-30}$ esu)	$\gamma_{\text{real}, 800}$ ( $10^{-36}$ esu)	$\gamma_{\text{imag}, 800}$ ( $10^{-36}$ esu)	$ \gamma _{800}$ ( $10^{-36}$ esu)	$\sigma_2^d$ ( $10^{-50}$ $\text{cm}^4 \text{ s}$ )
<i>trans</i> -[Ru{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CHPh}Cl(dppm) <sub>2</sub> ] ( <b>1</b> )	397 [2.3]	200 ± 40	920 ± 92 <sup>c</sup>	-600 ± 400	700 ± 400	920 ± 600	170 ± 100
<i>trans</i> -[Ru{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CHPh}Cl(dppe) <sub>2</sub> ] ( <b>2</b> )	404 [2.9]			300 ± 400	300 ± 100	420 ± 350	70 ± 30
[1,3,5-( <i>trans</i> -[(dppm) <sub>2</sub> ClRu{(E)-4-C≡CHC <sub>6</sub> H <sub>4</sub> CH=CH}] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub> )] ( <b>3</b> )	396 [2.0]	165 ± 33 (101 ± 62)	483 ± 100 (298 ± 62)	-900 ± 500	700 ± 400	1100 ± 700	170 ± 100
1,3,5-( <i>trans</i> -[(dppm) <sub>2</sub> ClRu{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CH}] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) ( <b>4</b> )	415 [4.9]	244 ± 50 (150 ± 92)	935 ± 31 (577 ± 19)	-640 ± 500	2000 ± 500	2100 ± 600	480 ± 120
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> ClRu{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CH}] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) ( <b>5</b> )	426 [8.7]			-4600 ± 2000	4200 ± 800	6200 ± 2000	1000 ± 200
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> ClRu(4-C≡C-C <sub>6</sub> H <sub>4</sub> C≡C)] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) ( <b>7</b> ) <sup>b</sup>	414 [10.4]	(94 ± 9)		-330 ± 100	2200 ± 500	2200 ± 600	520 ± 120
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> (PhC≡C)Ru{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CH}] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) ( <b>6</b> )	421 [13.0]			-11200 ± 3000	8600 ± 2000	14000 ± 4000	2100 ± 500
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> (PhC≡C)Ru(4-C≡CC <sub>6</sub> H <sub>4</sub> C≡C)] <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) ( <b>8</b> ) <sup>b</sup>	411 [11.6]	(93 ± 9)		-600 ± 200	2900 ± 500	3000 ± 600	690 ± 120

<sup>a</sup> All measurements as thf solutions (all complexes are optically transparent at 1064 and 800 nm). Reported  $\beta$  values are  $\beta_{333}$ ; numbers in brackets are  $\sqrt{\langle \beta^2 \rangle}$ . <sup>b</sup> Ref 12. <sup>c</sup> Upper bound only. No complete demodulation of the fluorescence contribution could be achieved. <sup>d</sup> Calculated using the equation  $\sigma_2 = h\beta/2\pi N$ , where  $\beta$  is the two-photon absorption coefficient.<sup>37</sup>

quadratic and cubic optical nonlinearities,<sup>12</sup> the first reported TPA cross-sections  $\sigma_2$  for two-dimensional compounds of 3-fold symmetry,<sup>24</sup> and the first electrochemical switching of third-order nonlinearity  $\gamma$  and switching of nonlinear absorption.<sup>18</sup> These examples were constructed using phenylethynyl “spacer” units. However, the *E*-configured alkene linker has been shown to afford more efficient organic NLO materials than those linked by alkyne groups.<sup>29</sup> We report herein the syntheses of novel two-dimensionally  $\pi$ -delocalized octopolar alkynylruthenium complexes containing *E*-phenylethenyl spacers, their molecular quadratic nonlinearities at both 1064 and 800 nm employing nano- and femtosecond hyper-Rayleigh scattering (HRS), respectively, molecular cubic nonlinearities  $|\gamma|$  (including real ( $\gamma_{\text{real}}$ ) and imaginary ( $\gamma_{\text{imag}}$ ) components) and TPA cross-sections at 800 nm evaluated by femtosecond Z-scan, and third-order nonlinear optical susceptibilities  $\chi^{(3)}$  at ca. 450 nm determined by electroabsorption (EA) spectroscopy.

The synthetic methodologies employed for the preparation of the new complexes are adaptations of those successfully utilized for the preparation of the corresponding phenylalkynyl<sup>30</sup> complexes, but employing linear and octopolar stilbenylalkynes: see the Supporting Information for complete synthetic and spectroscopic details. UV-vis spectra contain absorption maxima in the range 396–426 nm, with the extinction coefficient of the octopolar complexes being significantly higher than those of their corresponding linear analogues (Table 1). The alkynyl complexes **1**, **2**, and **4–6** exhibit  $\nu(\text{C}\equiv\text{C})$  bands in the range 2057–2073  $\text{cm}^{-1}$ . <sup>31</sup>P NMR spectra of complexes **1–6** contain one singlet resonance, consistent with *trans* geometry at the ruthenium center.<sup>31</sup>

The results of linear optical and molecular quadratic and cubic NLO measurements are shown in Table 1. Replacing dpmm by dppe in proceeding from **1** to **2** or **4**

to **5** results in a red-shift in  $\lambda_{\max}$  and increase in  $\epsilon$ ; similar trends in  $\lambda_{\max}$  and  $\epsilon$  are noted in proceeding from vinylidene complex **3** to alkynyl complex **4** and from linear complexes **1** and **2** to octopolar analogues **4** and **5**, respectively. Extending the  $\pi$ -system through the metal center (in proceeding from **5** to **6**) and replacing ene- with yne-linkage [in proceeding from **5** to **7** and **6** to **8** both result in blue-shifts in  $\lambda_{\max}$ . For these structural modifications, differences in optical absorption maxima are slight, whereas progression from linear to octopolar geometry results in a 2- to 3-fold increase in oscillator strength.

HRS measurements of **1**, **3**, and **4** at 1064 nm employing nanosecond pulses are listed in Table 1. All three complexes are transparent at the second-harmonic wavelength of 532 nm, permitting assessment of the impact of structural variation on quadratic NLO merit. Nonlinearities for **3** and **4** are large for octopolar complexes without polarizing acceptor substituents, but data for **1**, **3**, and **4** are experimentally indistinguishable within the error margins; the ene-linked alkynyl complexes have  $\beta_{1064}$  values larger than those for the related yne-linked complexes **7** and **8** we reported previously.<sup>12</sup> HRS measurements of **1**, **3**, and **4** at 800 nm with femtosecond pulses are listed in Table 1; fluorescence contributions could not be completely eliminated from the data for **1**, but are absent from our reported nonlinearities of **3** and **4** (there is no demodulation of the signals for **3** and **4** as modulation frequency is varied). Proceeding from vinylidene complex **3** to alkynyl complex **4** results in a 2-fold increase in  $\beta_{800}$ , the latter consistent with the significant increase in  $\epsilon$  on this structural modification and suggestive of a similar increase in  $\beta_{1064}$  obscured by error margins. Complexes **3** and **4** are rare examples of organometallics for which quadratic optical nonlinearities have been determined at more than one wavelength. The  $\beta_{800}$  values for **3** and **4** are significantly larger than their  $\beta_{1064}$  value, consistent with significant resonance enhancement for the former resulting from close proximity of the optical absorption maxima to the second-harmonic wavelength (400 nm).

Molecular third-order nonlinearities for **1–6** determined by Z-scan at 800 nm are collected in Table 1. The  $\gamma_{\text{real}}$  values for many complexes are negative, and the

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**Table 2. Experimental Cubic Nonlinear Optical Response Parameters in Solid Solution in PMMA Measured by Electroabsorption**

compound	$\lambda_{\max}$ (nm)	$\text{Im}(\chi^{(3)})/N$ (negative peak) <sup>a</sup> ( $10^{-36}$ esu) @ $\lambda$ (nm) <sup>b</sup>	$\text{Im}(\chi^{(3)})/N$ (positive peak) <sup>a</sup> ( $10^{-36}$ esu) @ $\lambda$ (nm) <sup>a</sup>
<i>trans</i> -[Ru{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CHPh}Cl(dppe) <sub>2</sub> ] ( <b>2</b> )	400	-31000 @ 420	36000 @ 452
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> ClRu{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CH}]) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ( <b>5</b> )	420	-120000 @ 438	100000 @ 472
1,3,5-( <i>trans</i> -[(dppe) <sub>2</sub> (PhC≡C)Ru{(E)-4-C≡CC <sub>6</sub> H <sub>4</sub> CH=CH}]) <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> ( <b>6</b> )	418	-95000 @ 436	77000 @ 472

<sup>a</sup> To cancel the influence of concentration,  $\chi^{(3)}$  was normalized by the number density of the molecule  $N$  (cm<sup>-3</sup>) in PMMA matrix.

<sup>b</sup> Peak value at the wavelength written after @.

$\gamma_{\text{imag}}$  values for most are significant, consistent with two-photon effects contributing to the observed molecular nonlinearities  $|\gamma|_{800}$ ; comment on the effect of structural variation on the magnitude of  $|\gamma|_{800}$  is therefore cautious, particularly in light of the error margins. Nevertheless, several trends may be noted. Replacing dpmm by dppe in proceeding from **4** to **5** leads to an increase in  $|\gamma|_{800}$ . Extending the  $\pi$ -system through the metal center, in proceeding from **5** to **6**, and replacing yne- with ene-linkage, in proceeding from **7** to **5** and **8** to **6**, result in significant increases in  $|\gamma|_{800}$ . To the best of our knowledge, the  $\gamma_{\text{real}}$  value for **6** is the largest thus far for an organometallic complex. Table 1 also includes TPA cross-sections  $\sigma_2$  calculated from  $\gamma_{\text{imag}}$ . TPA is a third-order NLO property which is of interest for applications in multiphoton microscopy, optical limiting, and optical data storage, and for which structure–activity trends therefore are identical with those for  $\gamma_{\text{imag}}$ . It is worth noting that the datum for **6** is of the same order of magnitude as that of the best organics<sup>19,32</sup> and one of the largest thus far for an organometallic complex.<sup>24,33</sup> Also noteworthy is that dimensional evolution from the linear complex **2** to the octopolar complex **5** results in a nonlinear increase in  $|\gamma|_{800}$  and  $\sigma_2$ .

Third-order nonlinear susceptibilities  $\chi^{(3)}$  were also determined for **2**, **5**, and **6** by EA spectral measurements at 350–550 nm, the first application of EA spectroscopy to evaluate cubic nonlinearities of organometallics.<sup>34</sup> In contrast to Z-scan, which measures  $\chi^{(3)}(-\omega:\omega, -\omega, \omega)$  for interacting light waves of frequency  $\omega$ , the quadratic EA effect measures  $\chi^{(3)}(-\omega:\omega, 0, 0)$ , for which the zero frequencies correspond to the dc electric field; the techniques are therefore complementary, in that they sample different NLO interactions. The linear optical absorption maxima and  $\text{Im}(\chi^{(3)})/N$  values, the imaginary parts of the EA-derived nonlinear susceptibility normalized by the number density of molecules in poly(methyl methacrylate) (PMMA) matrix, are summarized in Table 2. The optical absorption maxima for **2**, **5**, and **6**

undergo blue-shifts of 3–6 nm on proceeding from thf solution to solid solution in PMMA. The  $\text{Im}(\chi^{(3)})/N$  values for the complexes in PMMA reach a negative peak at wavelengths ca. 20 nm longer than  $\lambda_{\max}$  and a positive peak at wavelengths ca. 50 nm longer than  $\lambda_{\max}$ .  $\text{Im}(\chi^{(3)})/N$  values for **5** and **6** are not greatly different from each other, but are 3-fold that for **2**, reflecting the number of ligated ruthenium centers in these molecules. These  $\text{Im}(\chi^{(3)})/N$  values are 1 to 2 orders of magnitude larger than the molecular cubic nonlinearities  $\gamma$  obtained by Z-scan. This difference arises partly from the fact that division by a local field factor  $L_{\omega}^2 L_0^2$  is needed to convert  $\chi^{(3)}/N$  to  $\gamma$ . Assuming  $L_{\omega} = (\epsilon_{\omega} + 2)/3$ , one can estimate this as a factor of approximately 4 for these solid solution samples. Additionally, the wavelength dispersion effects are expected to work in different ways for the two processes, although both are resonantly enhanced. Few third-order NLO data for organometallics doped into organic polymer hosts exist, the limited previous examples including ruthenium nitrile complexes in PMMA<sup>35</sup> and a biferrocenyl complex in polystyrene.<sup>36</sup> A detailed analysis of spectral profiles and anisotropy for the present series of complexes will be presented elsewhere.

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**Supporting Information Available:** Experimental procedures for synthesis and characterization of **1–6** and nonlinear optical measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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