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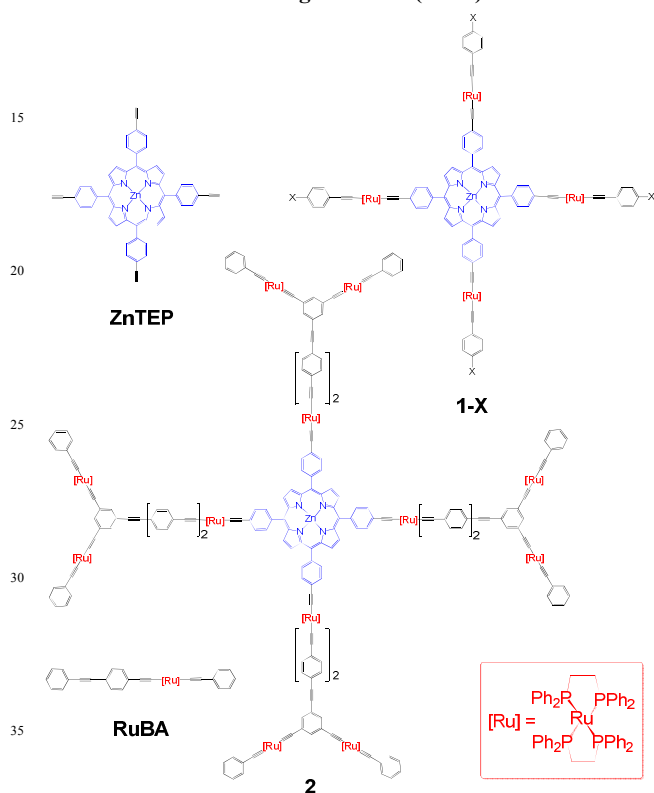
# A Hybrid Ruthenium Alkynyl/Zinc Porphyrin “Cross Fourchée” with Large Cubic Nonlinear Optical Properties

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A new Zn(II) porphyrin-cored ruthenium alkynyl dendrimer (**2**) containing twelve Ru( $\kappa^2$ -dppe)<sub>2</sub> bis-alkynyl fragments has been prepared in two steps from 5,10,15,20-tetra(4-ethynylphenyl)porphyrinatozinc(II) and shown to be highly active for third-harmonic generation (THG) at 1907 nm.



Scheme 1: Selected TPP-based molecules and the model complex RuBA.

Since the mid-1980s, there has been increasing interest in third-order nonlinear optical (NLO)-active organometallic materials because of their promising potential for various technological applications<sup>1-5</sup> such as photonic devices,<sup>6</sup> optical data storage,<sup>7</sup> microfabrication,<sup>8,9</sup> fluorescence imaging and photodynamic therapy.<sup>10</sup> Among the various compounds studied so far, dendrimers featuring an extended  $\pi$ -manifold connecting peripheral chromophores to an unsaturated central core emerged recently as an interesting class of molecules.<sup>11</sup> Indeed, because of the inherent cooperativity between the outer chromophores and the central core, comparatively high third-order optical nonlinearities were often observed with these three-dimensional structures.

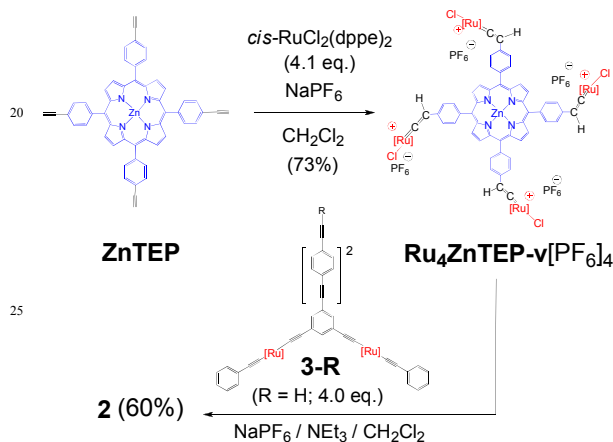
NLO effects generally require large and polarizable  $\pi$ -electron systems. In this respect, dendrimers containing organometallic units such as *trans*-Ru( $\kappa^2$ -dppe)<sub>2</sub> (dppe = 1,2-bis(diphenylphosphino)ethane) constitute remarkable chromophores, since it was recently established that these compounds are more NLO-active than fully organic alternatives of similar size.<sup>11</sup> As shown with the RuBA model complex (Scheme 1),<sup>12</sup> this is due to the existence of strongly allowed metal-to-ligand charge-transfer (MLCT) transitions in the 300-500 nm range, which improve optical nonlinearities with respect to those of the corresponding fully organic analogues. Furthermore, modifying the environment around the ruthenium affords the possibility of tuning their NLO performances.<sup>5,11,13</sup>

Independently from these investigations, large metallated  $\pi$ -architectures such as porphyrins and phthalocyanines were also identified as efficient and robust cubic NLO-phores for various applications.<sup>14-16</sup> An attractive feature of these macrocycles is that peripheral (*meso*) electron-releasing substituents on the macrocyclic core improve the cubic NLO response.<sup>17</sup> Thus, using zinc(II) tetraphenylporphyrin (ZnTPP) as a central (prototypical) core, we have recently shown that tetra-Ru(II) derivatives, such as **1-X** (Scheme 1),<sup>18,19</sup> possess quite remarkable cubic NLO responses in the near-IR range relative to those of related unsubstituted porphyrins. In a continuation of these investigations, and inspired by the synthesis of related Pt(II) alkynyl-containing dendrimers,<sup>20</sup> we have now synthesized the new compound **2**, possessing four Ru( $\kappa^2$ -dppe)<sub>2</sub>-based dendrons at the *meso* positions, and have assessed its efficiency for third-harmonic generation (THG) at 1907 nm.

This porphyrin-based dendrimer was obtained by reacting four equivalents of dendron **3-R** (R = H) with a suitable porphyrin-containing precursor formed *in situ* (Scheme 2). However, instead of using the tetra-RuCl( $\kappa^2$ -dppe)<sub>2</sub>-functionalized porphyrin derivative previously used in similar reactions,<sup>18,19</sup> we have now used the corresponding tetra-vinylidene derivative **Ru<sub>4</sub>ZnTEP-v[PF<sub>6</sub>]**.<sup>21</sup> The latter was generated *in situ* from the known ZnTEP and a slight excess of *cis*-[RuCl<sub>2</sub>( $\kappa^2$ -dppe)] (4.1 eq.), precipitated from the reaction medium and then directly engaged with four equivalents of the dinuclear wedge **3-H**. The reaction was monitored by <sup>31</sup>P NMR; a singlet at 54.3 ppm and a singlet at 54.6 ppm appeared with concomitant disappearance of the signal of the starting material, indicating its total consumption after 48 h. Compound **2** was then precipitated from hexane and isolated in 60% yield as a green solid (ESI).

In spite of its low solubility, this new organometallic

dendrimer (**2**) could be characterized by means of NMR and IR spectroscopy, and by elemental analysis. Thus, the two singlets that were observed at *ca.* 54.3 and 54.6 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum during reaction monitoring are diagnostic of the phosphorus atoms of *trans*-bis(alkynyl) “Ru( $\kappa^2$ -dppe) $_2$ ” units.<sup>22,23</sup> They correspond, respectively, to the chemically distinct inner (4) and peripheral (8) Ru( $\kappa^2$ -dppe) $_2$  groups present in **2**.<sup>24,25</sup> The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra exhibit the characteristic signals of the central ZnTPP core and confirm the presence of twelve “Ru( $\kappa^2$ -dppe) $_2$ ” units. Finally, IR spectroscopy confirmed the presence of Ru(II)-alkynyl linkages, which are revealed by the presence of a broad absorption at *ca.* 2050  $\text{cm}^{-1}$  corresponding to the various overlapping  $\nu_{\text{Ru}=\text{C}}$  modes.<sup>19</sup> In addition, a second and less intense absorption at 2200  $\text{cm}^{-1}$  was also detected for **2**, which corresponds to the various overlapped  $\nu_{\text{C}=\text{C}}$  modes of the tolane spacer.<sup>26</sup>

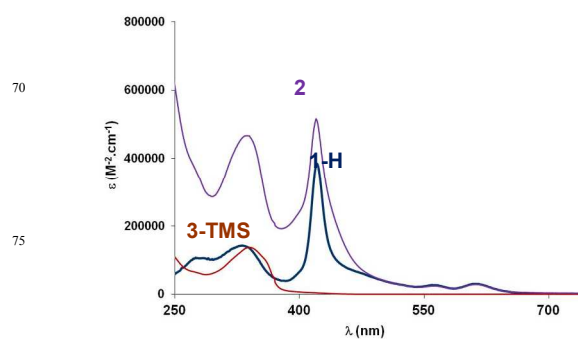


**Scheme 2:** Synthesis of compound **2**.

Cyclic voltammetric studies of **2** in  $\text{CH}_2\text{Cl}_2$  revealed two overlapped oxidation waves in a 2:1 ratio. Viewed anodically, the first two waves, at 0.45 and 0.53 V vs. SCE, are easily attributed to the Ru(II)/Ru(III) oxidations of the peripheral and inner *trans*-Ru( $\kappa^2$ -dppe) $_2$  fragments, based on their relative intensities. Weaker waves at higher potentials which are expected as the first and second oxidation processes of the porphyrin ring could not be clearly detected by CV,<sup>19</sup> but scanning to these potentials leads to chemical irreversibility and decomposition of **2**. The oxidation of the eight peripheral bis(alkynyl) Ru( $\kappa^2$ -dppe) $_2$  units in **2** occur first, presumably due to the more electron-rich environment at the periphery of the complex, and their oxidation is followed by those of the inner groups at a potential *ca.* 70 mV higher than that for **1-H** (0.46 V), a difference due to the prior oxidation of the outer Ru( $\kappa^2$ -dppe) $_2$  groups. The first and second Ru-centered oxidation waves in **2** appear to be chemically reversible, which opens the possibility of using these electron-transfer processes for switching of the NLO properties of this compound.<sup>27-30</sup>

The UV-Vis absorption spectrum of **2** in  $\text{CH}_2\text{Cl}_2$  resembles that of compound **1-H** (Figure 1 and Table 1) with a Soret band at 420 nm and two Q bands at 565 and 613 nm. In addition, the UV-

Vis spectrum of **2** possesses an absorption band centered around 338 nm, which can be attributed to a MLCT transition from the metal d orbitals to the  $\pi^*$  orbitals of the phenylacetylide ligand. This absorption is diagnostic of the presence of *trans*-Ru( $\kappa^2$ -dppe) $_2$  units. Such a band was previously observed at 330 nm in **1-H** and was detected at 340 nm for the silyl-protected precursor of the dendron (**3-TMS**) in dichloromethane.<sup>22,25,31</sup> Relative to the Soret band, this band in **2** is now more intense than it was in **1-H**, in line with the increased number of Ru( $\kappa^2$ -dppe) $_2$  fragments (12 vs. 4). The slight red shift of 8 nm experienced by this band in **2** (relative to **1-H**) contrasts with the relative constancy of the other characteristic transitions. This shift can be rationalized by considering the extension of the  $\pi$  manifold when progressing from **1-H** to **2**.<sup>11</sup>



**Figure 1:** UV-Vis absorption spectra of the zinc porphyrins **1-H**, **2** and of the wedge model **3-TMS** in  $\text{CH}_2\text{Cl}_2$  at 25 °C.

**Table 1.** Linear and Cubic Nonlinear Optical Data for Selected Molecules.<sup>a</sup>

Cpnd	$\lambda_{\text{abs}}^{\text{max}}$ (nm) [ $\epsilon$ ] <sup>b</sup>	$\epsilon^b$ at 635 nm	$\gamma_{\text{THG}}$ ( $10^{-34}$ esu)	$\gamma_{\text{THG}}/M^c$ ( $10^{-34}$ esu)
<b>ZnTEP</b>	302 [2.4], 424 [55.6], 552 [2.3], 594 [0.6]	0.03	-13	-0.016
<b>1-H</b> <sup>d</sup>	330 [14.2], 421 [38.5], 460 [sh, 7.4], 563 [2.7], 612 [3.0]	1.5	-550	-0.115
<b>1-NO<sub>2</sub></b>	322 [7.7], 420 [24.8], 466 [sh, 10.4], 556 [4.2], 607 [3.0]	0.9	-170	-0.034
<b>2</b>	338 [46.4], 420 [51.4], 460 [11.4], 562 [2.1], 612 [2.6]	1.1	-1840	-0.134
<b>3-TMS</b>	340 [13.7], 360 [sh, 12.0]	0.0	-24	-0.010

<sup>a</sup> Cubic hyperpolarizabilities ( $\pm 10\%$ ) obtained from a THG experiment at 1907 nm in  $\text{CHCl}_3$ . <sup>b</sup> Extinction coefficients in  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . <sup>c</sup> Molecular cubic hyperpolarizabilities corrected for the molecular mass (M) in  $\text{g} \cdot \text{mol}^{-1}$ . <sup>d</sup> UV-vis data remeasured for **1-H**.

The third-order nonlinearity of **2** was measured by Z-scan at 780 nm to compare the performance at this wavelength with the  $|\gamma|$  value previously found for the model complex **RuBA** ( $15 \times 10^{-34}$  esu at 800 nm).<sup>12</sup> Both measurements were likely subject to resonance enhancement due to significant extinction coefficients in the proximity of the second harmonic of the measurement wavelengths (400 nm and 390 nm, resp.). For instance, the presence of the  $\pi^*_{\text{C}=\text{CR}} \leftarrow d_{\text{Ru}}$  MLCT band near 400 nm (383 nm and 338 nm, resp.) is noticeable for each compound. A much larger (absolute) value was found for **2** ( $8400 \times 10^{-34}$  esu), in line with a significantly larger third-order NLO activity for this molecule. Finally, the molecular third-order nonlinearities ( $\gamma_{\text{THG}}$ )

of **1-X** (X = NO<sub>2</sub>, H), **2**, **3-TMS** and **ZnTEP** were determined by third-harmonic generation (THG) studies at 1907 nm (Table 1). The THG data obtained at a fundamental wavelength of 1907 nm are also likely to be significantly resonance-enhanced due to the third harmonic (635 nm) coinciding with the lowest energy Q-band,<sup>3</sup> as is the case for all the porphyrin derivatives in the present study (Table). However, as  $\lambda_{\max}$  and  $\epsilon$  values for compounds **1-H**, **1-NO<sub>2</sub>** and **2** are similar, these resonance effects may be comparable for these molecules and, while remaining mindful of these considerations, a comparison of their  $\gamma_{\text{THG}}$  values at 1907 nm can be made. Among these compounds, the  $\gamma_{\text{THG}}$  value for **2** is much larger than those found for **ZnTEP** or for the smaller pentametallic derivatives **1-X** (X = H, NO<sub>2</sub>). Comparison between  $\gamma_{\text{THG}}$  values of **1-H** and **1-NO<sub>2</sub>** clearly shows the effect of a strong electron-acceptor group such as nitro on the molecular cubic NLO response, leading to a significant decrease in the  $\gamma_{\text{THG}}$  value, as expected from the decrease in electronic polarizability towards the porphyrin core. The  $\gamma_{\text{THG}}$  value of **2** is also much larger than four times the value for the wedge model (**3-TMS**) added to that of the metallated core model (**ZnTEP**), suggesting considerable synergy between these fragments. However, scaled by the molecular weight, the  $\gamma_{\text{THG}}$  values of **2** and **1-H** are comparable, suggesting that  $\gamma_{\text{THG}}$  coefficients at 1907 nm relate directly to the spatial extension of the conjugated  $\pi$ -manifold.

In conclusion, we have reported here the synthesis and characterization of a new dodecaruthenium(II) porphyrin-cored dendrimer (**2**) with remarkably high THG activity at 1907 nm. Evidence is also provided for the beneficial role played by the peripheral Ru( $\kappa^2$ -dppe)<sub>2</sub>-containing dendrons and for the synergy operative between the dendrons and the central porphyrin core. Comparison of appropriate figures of merit for **2** and for the related metallated porphyrin **1-H** reveals that the increase in third-order NLO activity for **2** over **1-H** essentially scales with the increase in molecular size (as determined by the molecular mass). While this observation suggests that further extension of the peripheral dendrons in **2** will probably not lead to a dramatic improvement of the magnitude of macroscopic cubic susceptibilities  $\chi^{(3)}$  at 1907 nm, further investigations are underway to assess this conclusion at frequencies for which little or no resonance enhancement is operative, and to examine the nonlinear absorption properties related to the imaginary part of  $\gamma$ .

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## Notes and references

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## Graphic Content Entry

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An impressive cubic nonlinear optical coefficient ( $\gamma_{\text{THG}}$ ) was determined by third-harmonic generation at 1907 nm for a new star-shaped Zn(II) porphyrin-based metallo-dendrimer containing twelve Ru(II) centers.

