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 Ruκ2-dppe2 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.

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 applications1–5 such as photonic devices,6 optical data storage,7 microfabrication,8,9 fluorescence imaging and photodynamic therapy.10 Among the various compounds studied so far, dendrimers featuring an extended π-manifold connecting peripheral chromophores to an unsaturated central core emerged recently as an interesting class of molecules.11 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 π-electron systems. In this respect, dendrimers containing organometallic units such as trans-Ruκ2-dppe2 (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.11 As shown with the RuBA model complex (Scheme 1),12 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.5,11,13

Independently from these investigations, large metallated π-architectures such as porphyrins and phthalocyanines were...
also identified as efficient and robust cubic NLO-phores for various applications. An attractive feature of these macrocycles is that peripheral (meso) electron-releasing substituents on the macrocyclic core improve the cubic NLO response. Thus, using zinc(II) tetraphenylporphyrin (ZnTPP) as a central (prototypical) core, we have recently shown that tetra-RuCl(κ^2-dppe)_2 derivatives, such as 1-X (Scheme 1), 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, we have now synthesized the new compound 2, possessing four Ru(κ^3-dppe)_2-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(κ^2-dppe)_2-functionalized porphyrin derivative previously used in similar reactions, we have now used the corresponding tetravinylidene derivative Ru_4ZnTEP-v[PF_6]_4. The latter was generated in situ from the known ZnTEP and a slight excess of cis-[RuCl_2(κ^2-dppe)_2] (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 ^31P 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 ^31P{1H} NMR spectrum during reaction monitoring are diagnostic of the phosphorus atoms of trans-bis(alkynyl) “Ru(κ^3-dppe)_2” units. They correspond, respectively, to the chemically distinct inner (4) and peripheral (8) Ru(κ^3-dppe)_2 groups present in 2. The ^1H and ^13C{1H} NMR spectra exhibit the characteristic signals of the central ZnTPP core and confirm the presence of twelve “Ru(κ^3-dppe)_2” units. Finally, IR spectroscopy confirmed the presence of Ru(n)-alkynyl linkages, which are revealed by the presence of a broad absorption at ca. 2050 cm^{-1} corresponding to the various overlapping ν(C=C) modes. In addition, a second and less intense absorption at 2200 cm^{-1} was also detected for 2, which corresponds to the various overlapped ν(C=C) modes of the tolane spacer.

Cyclic voltammetric studies of 2 in CH_2Cl_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(n)/Ru(n) oxidations of the peripheral and inner trans-Ru(κ^3-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, but scanning to these potentials leads to chemical irreversibility and decomposition of 2. The oxidation of the eight peripheral bis(alkynyl) Ru(κ^3-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(κ^3-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.

The UV-Vis absorption spectrum of 2 in CH_2Cl_2 resembles that of compound 1-H (Fig. 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 π* orbitals of the phenylacetylide ligand. This absorption is diagnostic of the presence of trans-Ru(κ^3-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. Relative to the Soret band, this band in 2 is now more intense than it was in 1-H, in line with the increased

![Scheme 2 Synthesis of compound 2.](image-url)
number of Ru(C^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 π manifold when progressing from 1-H to 2.11

The third-order nonlinearity of 2 was measured by Z-scan at
780 nm to compare the performance at this wavelength with the
|γ| value previously found for the model complex RuBA
(15 × 10^{-34} \text{ esu} \text{ at 800 nm}).12 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 290 nm, resp.).
For instance, the presence of the π^*C=CR ← d 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 × 10^{-34} \text{ esu}), in line with a significantly larger third-
order NLO activity for this molecule. Finally, the molecular
third-order nonlinearities (γ_{THG}) of 1-X (X = NO_2, 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 signif-
icantly resonance-enhanced due to the third harmonic
(635 nm) coinciding with the lowest energy Q-band,3 as is the
case for all the porphyrin derivatives in the present study
(Table). However, as λ_{max} and ε values for compounds 1-H,
1-NO_2 and 2 are similar, these resonance effects may be com-
parable for these molecules and, while remaining mindful of
these considerations, a comparison of their γ_{THG} values at
1907 nm can be made. Among these compounds, the γ_{THG}
value for 2 is much larger than those found for ZnTEP or for the
smaller pentametallic derivatives 1-X (X = H, NO_2).
Comparison between γ_{THG} values of 1-H and 1-NO_2 clearly
shows the effect of a strong electron-acceptor group such as
nitro on the molecular cubic NLO response, leading to a sig-
nificant decrease in the γ_{THG} value, as expected from the
decrease in electronic polarizability towards the porphyrin
core. The γ_{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 mol-
ecular weight, the γ_{THG} values of 2 and 1-H are comparable,
suggesting that γ_{THG} coefficients at 1907 nm relate directly to
the spatial extension of the conjugated π-manifold.

In conclusion, we have reported here the synthesis and
characterization of a new dodecaruthenium(n) porphyrin-ored
dendrimer (2) with remarkably high THG activity at 1907 nm.
Evidence is also provided for the beneficial role played by the
peripheral Ru(C^2-dppe)-containing dendrons and for the
synergy operative between the dendrons and the central por-
phyrin 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 dendrins in 2 will probably
not lead to a dramatic improvement of the magnitude of
macroscopic cubic susceptibilities γ^{(3)} at 1907 nm, further
investigations are underway to assess this conclusion at fre-
frequencies for which little or no resonance enhancement is
operative, and to examine the nonlinear absorption properties
related to the imaginary part of γ.

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