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Cubic nonlinear optical properties of new zinc tetraphenyl porphyrins peripherally functionalized with electron-rich Ru(II) alkynyl substituents

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We report the synthesis and characterization of new organometallic assemblies consisting of a central Zn(II) tetraphenylporphyrin (ZnTPP) core surrounded by four Ru(II) alkynyl complexes (*trans*-Ru(dppe)$_2$R) appended at the *para* phenyl positions and acting as peripheral donor groups. The synthesis of the tetra-chlorido derivative **2** (R=Cl) is reported first, followed by that of three extended homologues (**3**–X) obtained from this building block by substitution of the chlorido ligands by functionalized arylacetylenes (R=C≡C(4-C_6H_4X); X=NO_2, H, OMe). Measurement of the nonlinear absorption properties of the pentametallic derivatives **3**–X reveals that these extended π-networks incorporating polarizable organometallic units behave as good two-photon absorbers in the visible and near-IR range.

1. Introduction

Materials with cubic nonlinear optical (NLO) properties are required in emerging photonics-based technologies for various applications, including optical data storage, nanophotonics, and biophotonics.[1,2] The processing of optical signals such as ultrafast switching or modulation of optical beams using materials with sizeable third-order NLO responses is of significant interest.[3] Amongst the wide range of molecular chromophores investigated in the last 30 years, organometallic and coordination compounds have emerged as very promising building blocks to access new NLO-active materials.[4,5] In particular, several examples of formally alkynyl-d^6 complexes featuring an equatorial 'Ru(dppe)$_2$' core [dppe=1,2-bis(diphenylphosphino)ethane] have been explored.[5,6] When such polarizable units are incorporated into extended π networks, a tremendous enhancement of the nonlinear optical response was often observed.[6,7] In the pursuit of optimized systems, these organometallic units permit great structural control, as the diphosphines coordinating the metal centre, the oxidation state of the metal, and the ligand trans to the alkynyl ligand can all be varied at will. Moreover, due to the existence of kinetically stable oxidized state(s) with distinct NLO properties at selected wavelengths, redox-switching of the NLO behaviour has been demonstrated in several instances with these particular building blocks.[8,9]

On another front, large metallated π-compounds such as porphyrins or phthalocyanines were also identified very early as efficient and robust cubic NLO-phores.[10–12] For instance, Rao et al. showed in 2000 that various metallated tetra-*p*-tolylporphyrins (TTP) could exhibit quite high cubic optical nonlinearities at 532 or 600 nm.[13] These properties were measured using nanosecond (and to a lesser degree picosecond) pulses, the results being consistent with contributions from mechanisms involving real excited states rather than virtual states only, as is the case with nonresonant cubic nonlinear responses, but rendering these molecules quite promising for optical limiting or all-optical switching purposes.[2] More recently, multi-porphyrin assemblies exhibiting enhanced cubic nonlinear absorption properties were also developed by various groups for related applications.[14,15] Thus, depending on the overall

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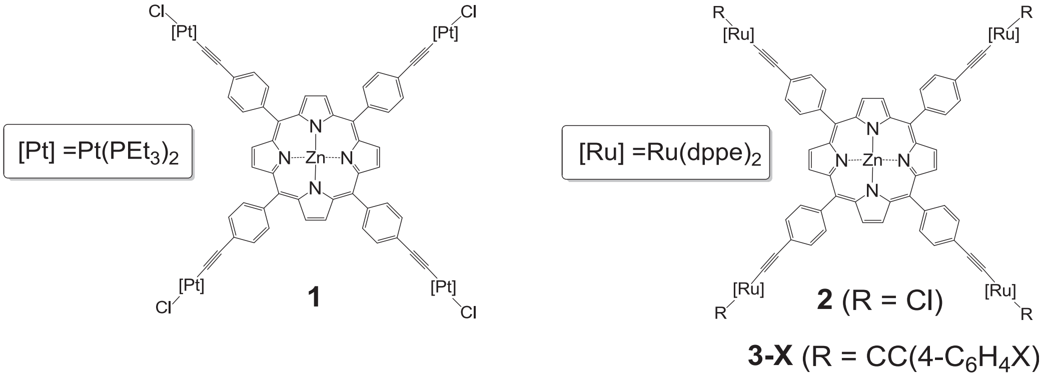
symmetry of a given porphyrin, on the nature of the central metal ion, and on the peripheral substituents of the macrocyclic core, widely different nonlinearities can result. The presence of a metallic centre inside the porphyrin cavity usually proves to be crucial, since it planarizes the π-manifold, which is essential to achieve high hyperpolarizabilities.[11,12] Depending on its nature, the metal ion can also provide an additional electronic contribution to the NLO response. Accordingly, varying its nature is often a powerful way to optimize the cubic NLO response of a porphyrin-based chromophore tailored for a given application. In that respect, metal centres with low-lying charge-transfer states[16] or open-shell structures have often been usefully used.[11] In comparison, far fewer investigations have focused on the role of the peripheral substituents. However, among the scant experimental data available on metallated TPP derivatives, some investigations have suggested that electron-releasing substituents at the *para*-positions of the *meso*-aryl groups might afford higher cubic NLO activities.[11,17]

Some of us recently reported multistable alkynyl-d^6complexes exhibiting large and redox-switchable third-order (cubic) nonlinearities.[18] Others have reported the synthesis and properties of tetrafluorenyl porphyrin derivatives[19] and evidenced the determining role of the *meso*-substituents on the photophysical properties of these porphyrins.[20] However, to the best of our knowledge, only a few porphyrins featuring alkynyl metal complexes as peripheral substituents have been reported thus far,[21] with very few constructed around a TPP-core, such as in **1** (Scheme 1).[22] Moreover, none were studied from the perspective of their cubic NLO properties. We have consequently pursued the synthesis and third-order NLO responses of a series of new ZnTPP derivatives functionalized with electron-releasing alkynyl-d^6 Ru(II) complexes at the *para*-location of their *meso*-aryl groups.[23] By using the controlled stepwise reactivity of the *cis*-[RuCl$_2$(dppe)$_2$] and *trans*-Ru(C$\equiv$CAr)Cl(dppe)$_2$] complexes,[24,25] derivatives with organoruthenium termini possessing differently functionalized terminal arylalkynyl ligands were targeted, in order to evidence the effect of electron-releasing or electron-attracting *para* substituents on their cubic NLO response. In this contribution, we report the stepwise synthesis and characterization of three new derivatives **3**–X (NO$_2$, H, OMe) via the corresponding tetra-chlorido precursor (**2**), followed by *Z*-scan measurements of their cubic nonlinear absorption properties.



Scheme 1. Selected TPP-based porphyrins substituted with alkynyl complexes.

2. Results and discussion

2.1. Synthesis and characterization of the tetra(ruthenium-chloride) ZnTPP

Reacting the known *cis* ruthenium(II) organometallic precursor complex **4**[26] with the known tetra-alkyne zinc(II) porphyrin **5**,[22] itself obtained after metallation[27] of the corresponding tetra-alkyne free base, affords access to the pentametallic complex **2** (Scheme 2) in an overall yield of 32%. Although the tetra-alkyne Zn porphyrin **5** had been previously synthesized in fair yields (29%),[22] the present work (see Supplementary data) resulted in an improved yield (34% over 3 steps) by using the BF$_3$(OEt$_2$) complex as a Lewis-acid promoter to assist the synthesis of the free base **1**.[28] The tetra-vinylidene complex that forms upon reaction of the Ru(II) precursor **4** with **5** by a 1,2-hydrogen shift was not characterized,[29] but was precipitated before being deprotonated in situ by excess triethylamine to give **2**. Completion of the reaction forming **2** can be monitored by following the disappearance of the ^{1}H NMR alkynyl proton (C$\equiv$CH) of **5** at 3.37 ppm in CDCl$_3$. This new complex was characterized by the usual spectroscopies (NMR, UV–vis and IR), microanalysis and electrospray mass spectrometry (ESI-MS).

In its ^{1}H NMR spectrum, **2** exhibits both the spectral signatures of the porphyrin core (a characteristic singlet at ca. 9 ppm, corresponding to the 8 equivalent β-pyrrolic protons) and signals typical of the σ-alkynyl Ru(II) endgroups, such as the broad singlet at ca. 3 ppm corresponding to the 32 equivalent CH$_2$ protons of the ruthenium-coordinated dppe. Between 6.5 and 9 ppm are the signals of the various aromatic protons of the porphyrin and of the dppe. The ^{31}P NMR spectrum of **2** reveals a sharp singlet corresponding to the 16 equivalent phosphorus atoms from the 8 dppe ligands coordinated to the ruthenium endgroups (Table 1); the chemical shift of this signal (ca. 50 ppm) is characteristic of monosubstituted σ-alkynyl ruthenium complexes of this kind.[30] Further evidence for the structure of this compound comes from the ^{13}C NMR spectrum, in which all carbon atoms of **2** can be observed and assigned by polarization transfer studies, except for the weak quintuplet corresponding to the C$_\alpha$-alkyne carbon atoms, which escaped from detection. The presence of the four alkynyl bonds in **2** is nevertheless revealed by a broad singlet near 115 ppm, corresponding to the equivalent C$_\beta$ carbon atoms.[25,31] The presence of these alkynyl bonds is more clearly revealed by infrared, since **2** displays an intense absorption band at ca. 2050 cm^{-1} (Table 1), characteristic of the $\nu_{C\equiv C}$ mode of these Ru(II) σ-alkynyl complexes.[25,30]

2.2. Synthesis and characterization of the tetra{ruthenium-bis(alkynyl)} Zn(II) porphyrins

Using the pentametallic porphyrin **2** as starting material, we have isolated three new derivatives **3**–X (X=NO$_2$, H, OMe) by ligand metathesis. This reaction was performed in the presence of sodium hexafluorophosphate and with an excess of the