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LETTER

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Enhanced two-photon absorption cross-sections of zinc(II) tetraphenylporphyrins peripherally substituted with d^6-metal alkynyl complexes†

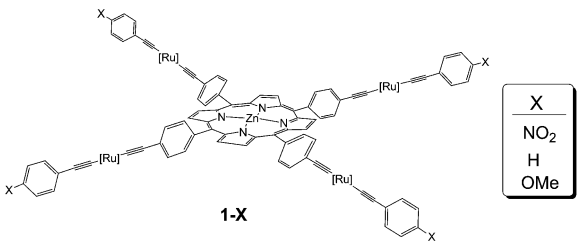
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The syntheses of new Zn(II) tetraphenylporphyrin (ZnTPP) derivatives functionalized with electron-rich d^6-transition metal alkynyl complexes at their periphery are reported. Z-scan measurements reveal remarkably large effective two-photon absorption (TPA) cross-sections in the visible range for these compounds.

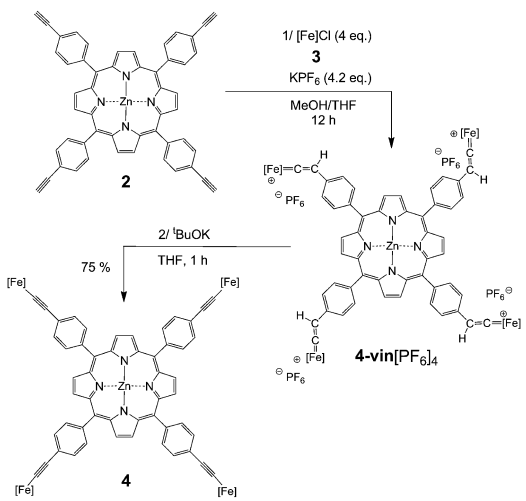
Molecules with significant TPA cross-sections have been attracting increasing attention over recent years because of the huge number of promising applications in emerging biophotonic and nanophotonic technologies that exploit this unusual third-order nonlinear optical (NLO) property.[1,2] The outstanding cubic NLO properties of porphyrins were recognized very early,[3,4] with several families of porphyrins being systematically screened for their TPA capabilities in the visible/near-IR range.[5,6] Among the various Zn(II) derivatives examined so far, some conjugated dimers were shown to possess remarkable TPA capabilities, while the corresponding monomeric Zn(II) porphyrin derivatives are usually much poorer two-photon absorbers.[7–10]

We have recently found that monomeric ZnTPP derivatives such as **1-X** (Scheme 1) exhibit quite large effective TPA cross-sections in the visible range, when peripherally functionalized with Ru(II) alkynyl complexes.[11] We now report the synthesis, characterization and Z-scan studies of two additional related derivatives, and confirm that peripheral organometallic substituents can strongly influence the effective two-photon absorption properties of these novel chromophores at selected wavelengths.



Scheme 1 Functional porphyrins **1-X** ([Ru] = *trans*-Ru(dppe)$_2$).

The synthesis of **4** was effected in two steps, *via* a vinylidene intermediate (**4-vin**[PF_6]$_4$),[12] by reacting the known tetra-alkynyl porphyrin **2**[11,13] with the Fe(II) precursor **3**[14] (Scheme 2). The tetracationic vinylidene intermediate (δ_P = 88.5 ppm in the ^{31}P NMR and $\nu_{Fe=C=C}$ = 1617 cm^{-1} in the IR) was not



Scheme 2 Synthesis of **4** ([Fe] = Fe(η^5-C_5Me_5)(dppe)).

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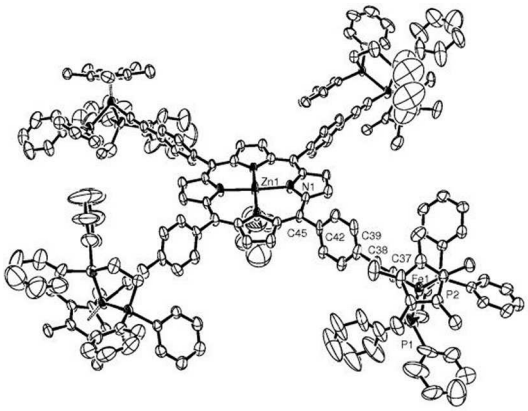


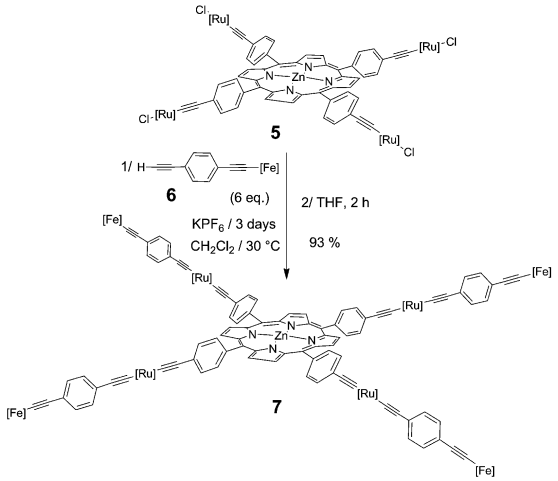
Fig. 1 ORTEP of **4** (50 % probability level). Hydrogen atoms have been omitted for clarity. A disordered Et_2O molecule coordinated to Zn is shown below the porphyrin plane.

purified, but rather was deprotonated directly after isolation to give the desired porphyrin **4** in 75% overall yield. The structure of **4** was confirmed by X-ray diffraction (Fig. 1).[15] Possibly due to slow desolvation of the pentane solvates or of the Et_2O molecule coordinated to the Zn(II) atom of the porphyrin, no accurate elemental analysis of this compound was obtained, but the molecular ion peak was detected by ESI-HRMS as the di-, tri- and tetra-protonated species (ESI†).

In the cyclic voltammogram, the oxidation of all Fe(II) endgroups was observed as a single and chemically reversible event at −0.15 V *vs.* SCE (ESI†).[16] The corresponding Fe(III) tetracation **4**$[PF_6]_4$ was isolated as a green solid after oxidation of **4** with four equivalents of [FcH][PF_6]. A characteristic shift to lower wavenumbers of the $\nu_{C\equiv C}$ is observed for **4**$[PF_6]_4$ (1989 cm^{-1}) compared to the corresponding band for **4**.[17] The ^1H NMR spectrum of **4**$[PF_6]_4$ in CD_2Cl_2 reveals the expected Fe(III) alkynyl polyradical, with the *ortho* and *meta* protons of the *meso* phenyl groups resonating at −40.8 and 30.1 ppm, respectively, and the pyrrolic protons as a singlet near 10.5 ppm (see ESI†).[18] The weak interaction between the unpaired electrons in this Fe-centered tetra-radical is indicated by ESR at 70 K; a rhombic spectrum was detected for **4**$[PF_6]_4$ (g_1 = 2.024, g_2 = 2.105 and g_3 = 2.253),[19] while a broad and featureless signal would have been observed in the case of strong spin–spin exchange coupling.[20]

Starting from **5**,[11] and from the known complex **6**,[21] the nonametallic porphyrin **7** featuring two alkynyl complexes in each branch was also synthesized (Scheme 3).[22] This compound (**7**) was isolated in good yield (93%) but, as seen with related compounds,[13] it could not be characterized by ESI- or MALDI-MS spectroscopy. However, a consistent set of spectral signatures was obtained from IR, ^{31}P and ^1H NMR, as well as diagnostic cyclic voltammograms, in which the Fe(II)- and Ru(II)-centered oxidations occur at −0.22 V and 0.44 V *vs.* SCE in a chemically reversible way and with equal intensities (ESI†).

The UV-Vis absorption spectra of **4** and **7** were recorded in dichloromethane (Fig. 2). The strong Soret band near 420 nm is the source of the green color of these compounds. This band is slightly red-shifted in **4** compared to **7** and also to **5**, the latter compounds possessing spectra closer to those of **1-X** derivatives.[11]



Scheme 3 Synthesis of **7** ([Fe] = Fe(η^5-C_5Me_5)(dppe) and [Ru] = *trans*-Ru(dppe)$_2$).

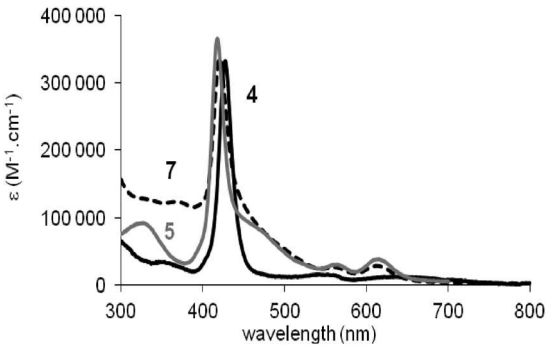


Fig. 2 UV-vis spectra of **4**, **5** and **7** (dotted line) in CH_2Cl_2.

The lowest-energy absorptions (near 550 and 620 nm) correspond to the porphyrin Q-bands; these are less intense, and blue- and red-shifted, respectively, for **4** relative to **7** and to **5**. The $d_M \rightarrow \pi_{C\equiv C}^*$ MLCT bands (M = Fe, Ru) expected in the 400–300 nm range are obscured by the other absorptions.[16] The nonlinear absorption behavior of **4** and **7** were next measured in the spectral range of 600 to 1600 nm using Z-scan (ESI†), and were compared to those of the **1-X** derivatives (Table 1). The effective TPA cross-sections were then deduced from the imaginary part of the cubic hyperpolarizability γ. The latter exhibit a complicated wavelength-dependence, with three maxima and one minimum (Table 1), reminiscent of that previously observed for **1-X** derivatives.[11]

Due to the centrosymmetric nature of these porphyrins, the one-photon-allowed states cannot be involved in any TPA process because of the differing selection rules.[11] Nevertheless, the first maximum near 1100 nm for **4** and **1-X** compounds corresponds to excited TPA states in the porphyrin core Q-bands region while the minimum near 600 nm, which occurs at the wavelength of the one-photon band at lowest energy, certainly corresponds to a saturable absorption (SA) process involving this absorption band. The second TPA maximum occurs near 710 nm, with effective cross-sections up to 10 200 GM (for **4**); in contrast to the TPA process centered at 1100 nm, the σ_{2eff} values of the 710 nm TPA bands appear strongly influenced by the nature of the organometallic endgroups. Because the

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Table 1 Extremal values of the effective two-photon absorption cross-sections (σ_{2eff}) for given wavelengths[a]

	1st max		2nd max		3rd max		1st min	
Cpnd	λ_{max}[b]	σ_{2eff}[c]/GM	λ_{max}[b]	σ_{2eff}[c]/GM	λ_{max}[b]	σ_{2eff}[c]/GM	λ_{max}[b]	σ_{2eff}[c]/GM
1-NO$_2$	530	6000 ± 500	770	6000 ± 3000	1000	1500 ± 500	620	−4500 ± 200
1-H	–	–	710	4800 ± 500	1300	1400 ± 500	595	−2800 ± 600
1-OMe	< 530	3400 ± 500	710	4200 ± 500	1000	1300 ± 100	620	−1400 ± 400
4	570	6600 ± 1000	740	10 200 ± 1000	1000	600 ± 200	650	−6100 ± 1000
7	550	8900 ± 1500	740	8000 ± 500	–[d]	–[d]	620	−1500 ± 1000

[a] Measurements performed in dichloromethane. [b] In nm. [c] In Göppert-Mayer units (1 GM = 1×10^{-50} cm^4 s^{-1}). [d] Not determined due to sample photodegradation.

largest cross-sections are found for **4** and **7**, which possess the more electron-rich metal center (M = Fe) connected to the porphyrin core, it is tempting to ascribe the excited state at the origin of the TPA process to a centrosymmetric $d_M \rightarrow \pi_{C\equiv C}^*$ MLCT state (M = Fe, Ru),[4,23] located at *ca.* 350 nm.[16] Finally, the TPA maxima occurring at wavelengths below 600 nm, *i.e.* in an energy range where many excited states coexist, again exhibit the highest intensities for **4** and **7**. The excited states at the origin of these two-photon absorptions are more difficult to assign and necessitate calculations.

In conclusion, we report here the synthesis of two new ZnTPP derivatives functionalized at their periphery by "Fe(η^5-C_5Me_5)-(dppe)C≡C" fragments. Moreover, we show that these new π-conjugated polynuclear assemblies incorporating electron-rich metal alkynyl fragments (**4** and **7**) exhibit TPA maxima at *ca.* 550 and 740 nm, with significantly larger effective cross-sections than analogous compounds featuring less electron-rich endgroups, such as bis-alkynyl "*trans*-Ru(dppe)$_2$(C≡CAr)C≡C" fragments (**1-X**). Indeed, when compared to most of the monomeric Zn(II) porphyrin derivatives investigated to date,[7,8] much larger TPA cross-sections are found at technologically-significant wavelengths for these new organometallic derivatives, with effective cross-sections up to 10 200 GM for **4** at 740 nm. From the perspective of the practical use of TPA absorbers, the existence of a strong SA peak near 620 nm for **4** (−6100 GM) further widens the interest of this particular compound. Finally, preliminary investigations indicate that the tetracationic Fe(III) tetraradical **4**[PF_6]$_4$ possesses significant kinetic stability; work is now aimed at assessing the potential of **4** and **7** for electro-switching their remarkable cubic NLO properties.[22,24]

Experimental

The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were freshly distilled under argon using standard procedures.

Compound 4

In an oven-dried Schlenk tube, (η^5-C_5Me_5)(dppe)FeCl (**3**;[14] 0.225 g, 0.360 mmol), KPF_6 (0.075 g, 0.41 mmol), and the Zn(II) porphyrin **2**[13] (70 mg, 0.09 mmol) were suspended in a mixture of methanol and tetrahydrofuran (30 mL, v/v, 2 : 1) and stirred for 12 h at room temperature. After removal of the solvents, the residue was dissolved in 30 mL of dichloromethane in the presence of an excess of ^{t}BuOK (0.046 g, 0.41 mmol) and stirred for 2 h at room temperature. After removal of the solvent, the dark residue was extracted with toluene and the extract concentrated *in vacuo*. Several washings with diethyl ether removed the excess of **2** and yielded the air-sensitive complex **4** as a green solid (211 mg, 75%). X-Ray-quality crystals were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **4**. HRMS (ESI, MeOH–CH_2Cl_2, *m*/*z*): $[M + 2H]^{2+}$ calc. for $C_{196}H_{182}Fe_4N_4P_8Zn$ 1563.4477, found: 1563.4472 (10%); $[M + 4H]^{4+}$ calc. for $C_{196}H_{184}Fe_4N_4P_8Zn$ 782.2278, found: 782.2274 (100%). IR (ν, KBr–CH_2Cl_2, cm^{-1}): 2043/2052 (*vs.* FeC≡C). $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, δ in ppm): 101.7 (broad s, 8P, (dppe)Fe). ^1H NMR (200 MHz, C_6D_6, δ in ppm): 9.21 (s, 8H, $H_{\beta\text{-pyrrolic}}$), 8.22 (s, 24H, $H_{Ph/dppe} + H_{Ar}$), 7.64 (d, 8H, $^3J_{H,H}$ = 7.6 Hz, H_{Ar}), 7.50–7.00 (m, 64H, $H_{Ar/dppe} + H_{phenyl}$), 2.90 (m, 8H, CH_2), 1.88 (m, 8H, CH_2), 1.66 (s, 60H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, δ in ppm):[15] 151.3 (s, $C_{\alpha\text{-pyrrolic}}$), 139.9 (t, $^3J_{P,H}$ = 38 Hz, Fe–*C*≡C), 139.6 (s, $C_{Ar}[C_a]$), 140.6 and 138.8 (2 × s, $C_{i/dppe}$), 136.1 (s, $CH_{Ar}[C_b]$), 135.4 and 135.1 (2 × broad s, $2CH_{o/dppe}$), 132.8 (s, CH_{β}-pyrrolic), 131.2 (s, $C_{Ar}[C_d]$), 130.1 and 129.5 (2 × broad s, $CH_{p/dppe}$), 129.3 (s, $CH_{Ar}[C_c]$), 128.3 and 128.1 (2 × broad s, $2CH_{m/dppe}$), 122.5 (s, C_{meso}), 121.5 (broad s, Fe–C≡*C*), 88.6 (s, $C_5(CH_3)_5$), 31.9 (m, $CH_{2/dppe}$), 11.3 (s, $C_5(CH_3)_5$). UV-vis (CH_2Cl_2, λ_{max}, (ε, 10^3 M^{-1} cm^{-1}), nm): 351 (34), 428 (330), 537 (16), 635 (15). CV (CH_2Cl_2, 0.1 M [Bu_4N][PF_6], 20 °C, 0.1 V s^{-1}, E° in V *vs.* SCE) : – 0.14, 0.88.

Compound 7

In a Schlenk tube, the tetraruthenium porphyrin complex **5**[11] (100 mg, 0.022 mmol), the iron compound (dppe)(η^5-C_5Me_5)-FeC≡C(1,4-C_6H_4)C≡CH (**6**;[21] 95 mg, 0.13 mmol) and KPF_6 (24.5 mg, 0.142 mmol) were dissolved in 30 mL of dichloromethane and stirred for 3 days at 30 °C. After removal of the solvent, the green residue was dissolved in THF in the presence of an excess of ^{t}BuOK (11 mg, 0.01 mmol) and stirred for 3 h at room temperature. After evacuation of the solvent, the product was extracted with toluene; the solution was concentrated and washed with Et_2O to afford the complex **7** (150 mg, 0.020 mmol, 93%) as an air-sensitive green solid. IR (ν, KBr, cm^{-1}): 2047 (*vs.* FeC≡C + RuC≡C). $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, δ in ppm): 101.8 (s, 8P, (dppe)Fe), 55.1 (s, 16P, $(dppe)_2Ru$). ^1H NMR (500 MHz, C_6D_6, δ in ppm): 9.41 (s, 8H, $H_{\beta\text{-pyrrolic}}$), 8.40 (d, 8H, $^3J_{H,H}$ = 6.3 Hz, H_{Ar}), 8.12 (m, 16H, $H_{Ar/dppe}$), 7.87 (m, 48H, $H_{Ar/dppe}$), 7.57 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H_{Ar}), 7.45–6.80 (m, 192H, $H_{Ar/dppe} + H_{Ar}$), 2.72 (m, 32H, $CH_{2/dppe/Ru}$), 2.59 (m, 8H, $CH_{2/dppe/Fe}$), 1.89 (m, 8H, $CH_{2/dppe/Fe}$), 1.59 (s, 60H, $C_5(CH_3)_5$). UV-vis (CH_2Cl_2, λ_{max} nm (ε, 10^3 M^{-1} cm^{-1})): 351 (98), 424 (347), 560 (24), 614 (28). CV (CH_2Cl_2, 0.1 M [Bu_4N][PF_6], 20 °C, 0.1 V s^{-1}, E° in V *vs.* SCE) : – 0.22, 0.44.

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Compound 4[PF_6]$_4$

In a Schlenk tube, **4** (150 mg, 0.048 mmol, 1.0 eq.) and [Fe(η^5-C_5H_5)$_2$][PF_6] (64 mg, 0.193 mg, 4.0 eq.) were stirred for 1 h at 25 °C in CH_2Cl_2 (15 mL). After partial removal of the solvent (*ca.* 5 mL), pentane was added (60 mL), the mixture was filtered, and the solvent was removed. The residue was then washed with thoroughly degassed toluene (2 mL) and pentane (2 mL) at 0 °C to obtain the title tetracation **4**[PF_6]$_4$ complex as a dark green solid (89 mg, 50%). IR (KBr–CH_2Cl_2, cm^{-1}): ν = 1986/1989 (w, FeC≡C), 839/846 (*vs.* PF_6^-). ^{1}H NMR (200 MHz, CD_2Cl_2) :[15] δ = 30.1 (m, 1H, CH_{Ar}[C_2]), 10.5 (s, 1H, C$H_{\beta\text{-Pyrrole}}$), 8.0 (s, 2H, $H_{Ph\text{-}dppe}$), 7.0 (m, 8H, $H_{Ph\text{-}dppe}$), 6.4 (m, 2H, $H_{Ph\text{-}dppe}$), 3.7 (s, 4H, $H_{Ph\text{-}dppe}$), 1.9 (s, 4H, $H_{Ph\text{-}dppe}$), −2.7 (m, 2H, C$H_{2\text{-}dppe}$), −10.2 (s, 15H, $C_5(CH_3)_5$), −40.8 (broad s, 1H, CH_{Ar}[C_1]).

X-Ray crystallography

Diffraction data frames for **4** were collected on a CCD Sapphire 3 Xcalibur diffractometer at 120(2) K using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved with a crystallographically imposed $\bar{4}$ symmetry by direct methods using the SIR97 program,[25] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[26] with the aid of the WINGX[27] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were then included in calculated positions. A final refinement on F^2 with 9916 intensities ($I > 2\sigma(I)$) and 522 parameters converged at $wR(F^2)$ = 0.3241 ($R(F)$ = 0.1684). Crystal data: $C_{200}H_{190}Fe_4N_4OP_8Zn{\cdot}4C_5H_{12}$, M = 3490.67, tetragonal, space group $I\,4_1/a$, a = 36.9262(5) Å, b = 36.9262(5) Å, c = 14.7933(8) Å, U = 20 171.3(12) Å^3, Z = 4, T = 120(2) K, D_c = 1.140 g cm^{-3}, 124 170 reflections measured, 9916 unique (R_{int} = 0.0699) which were used in calculations. R was 0.1169 ($I > 2\sigma(I)$). The final $wR(F^2)$ was 0.3301 (all data). CCDC 884562.

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