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LETTER

Enhanced two-photon absorption cross-sections of zinc(II) tetraphenylporphyrins peripherally substituted with d⁶-metal alkynyl complexes†

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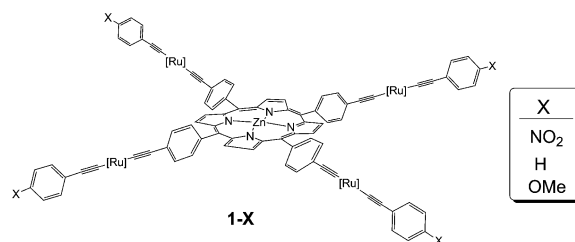
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The syntheses of new Zn(II) tetraphenylporphyrin (ZnTPP) derivatives functionalized with electron-rich d⁶-transition metal alkynyl complexes at their periphery are reported. Z-scan measurements reveal remarkably large effective two-photon absorption (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}

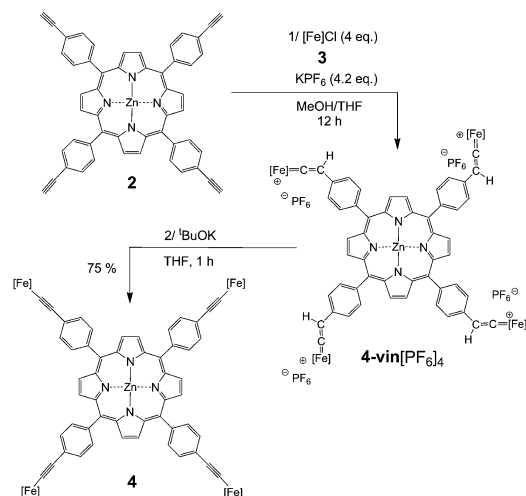
We have recently found that monomeric ZnTPP derivatives such as **1-X** (Scheme 1) exhibit quite large effective TPA cross-sections in the visible range, when peripherally functionalized



Scheme 1 Functional porphyrins **1-X** ([Ru] = *trans*-Ru(dppe)₂).

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.

The synthesis of **4** was effected in two steps, *via* a vinylidene intermediate (**4-vin**[PF₆]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 ($\delta_{\text{P}} = 88.5$ ppm in the ³¹P NMR and $\nu_{\text{Fe}=\text{C}=\text{C}} = 1617$ cm⁻¹ in the IR) was not



Scheme 2 Synthesis of **4** ([Fe] = Fe(η^5 -C₅Me₅)(dppe)).

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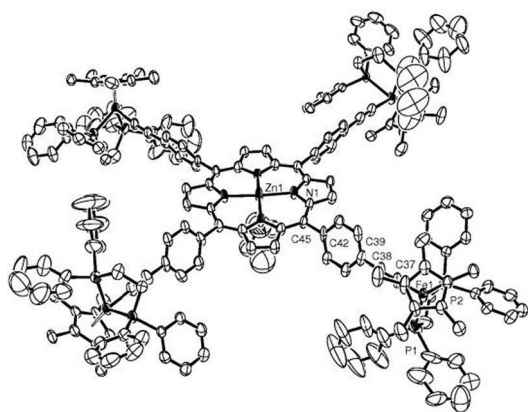


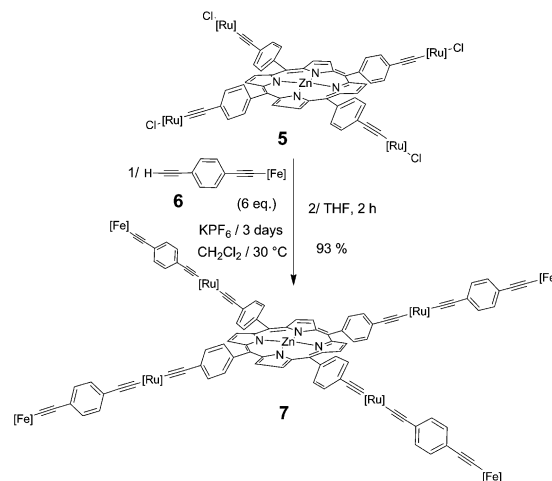
Fig. 1 ORTEP of **4** (50 % probability level). Hydrogen atoms have been omitted for clarity. A disordered Et₂O molecule coordinated to Zn is shown below the porphyrin plane.

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 Et₂O 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**[PF₆]₄ was isolated as a green solid after oxidation of **4** with four equivalents of [FcH][PF₆]. A characteristic shift to lower wavenumbers of the $\nu_{C\equiv C}$ is observed for **4**[PF₆]₄ (1989 cm⁻¹) compared to the corresponding band for **4**.¹⁷ The ¹H NMR spectrum of **4**[PF₆]₄ in CD₂Cl₂ 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**[PF₆]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 nonmetallic 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, ³¹P 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 -C₅Me₅)(dppe) and [Ru] = *trans*-Ru(dppe)₂).

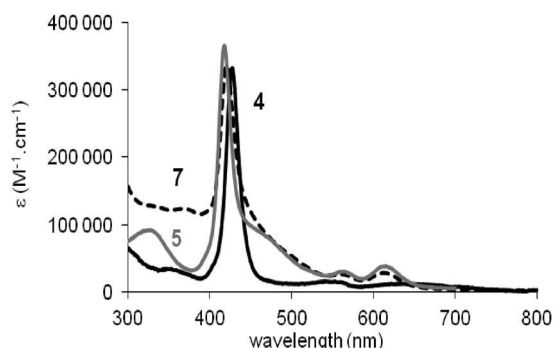


Fig. 2 UV-vis spectra of **4**, **5** and **7** (dotted line) in CH₂Cl₂.

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

Table 1 Extremal values of the effective two-photon absorption cross-sections ($\sigma_{2\text{eff}}$) for given wavelengths^a

Cpnd	1st max		2nd max		3rd max		1st min	
	λ_{max}^b	$\sigma_{2\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{2\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{2\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{2\text{eff}}^c/\text{GM}$
1-NO₂	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} cm⁴ 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 -C₅Me₅)-(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**[PF₆]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 -C₅Me₅)(dppe)FeCl (**3**;¹⁴ 0.225 g, 0.360 mmol), KPF₆ (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 ^tBuOK (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 CH₂Cl₂ solution of **4**. HRMS (ESI, MeOH-CH₂Cl₂, *m/z*): [M + 2H]²⁺ calc. for C₁₉₆H₁₈₂Fe₄N₄P₈Zn 1563.4477, found: 1563.4472 (10%); [M + 4H]⁴⁺ calc. for C₁₉₆H₁₈₄Fe₄N₄P₈Zn 782.2278, found: 782.2274 (100%). IR (ν , KBr-CH₂Cl₂, cm⁻¹): 2043/2052 (*vs.* FeC≡C). ³¹P{¹H} NMR (81 MHz, C₆D₆, δ in ppm): 101.7 (broad s, 8P, (dppe)Fe). ¹H NMR (200 MHz, C₆D₆, δ in ppm): 9.21 (s, 8H, H $_{\beta}$ -pyrrolic), 8.22 (s, 24H, H $_{\text{Ph/dppe}}$ + H $_{\text{Ar}}$), 7.64 (d, 8H, ³J $_{\text{H,H}}$ = 7.6 Hz, H $_{\text{Ar}}$), 7.50–7.00 (m, 64H, H $_{\text{Ar/dppe}}$ + H $_{\text{phenyl}}$), 2.90 (m, 8H, CH₂), 1.88 (m, 8H, CH₂), 1.66 (s, 60H, C₅(CH₃)₅). ¹³C{¹H} NMR (125 MHz, C₆D₆, δ in ppm):¹⁵ 151.3 (s, C $_{\alpha}$ -pyrrolic), 139.9 (t, ³J $_{\text{P,H}}$ = 38 Hz, Fe-C≡C), 139.6 (s, C $_{\text{Ar}}[C_{\text{a}}]$), 140.6 and 138.8 (2 × s, C $_{i/\text{dppe}}$), 136.1 (s, CH $_{\text{Ar}}[C_{\text{b}}]$), 135.4 and 135.1 (2 × broad s, 2CH $_{\text{O/dppe}}$), 132.8 (s, CH $_{\beta}$ -pyrrolic), 131.2 (s, C $_{\text{Ar}}[C_{\text{d}}]$), 130.1 and 129.5 (2 × broad s, CH $_{\text{p/dppe}}$), 129.3 (s, CH $_{\text{Ar}}[C_{\text{c}}]$), 128.3 and 128.1 (2 × broad s, 2CH $_{\text{m/dppe}}$), 122.5 (s, C $_{\text{meso}}$), 121.5 (broad s, Fe-C≡C), 88.6 (s, C₅(CH₃)₅), 31.9 (m, CH₂/dppe), 11.3 (s, C₅(CH₃)₅). UV-vis (CH₂Cl₂, λ_{max} , (ϵ , 10³ M⁻¹ cm⁻¹), nm): 351 (34), 428 (330), 537 (16), 635 (15). CV (CH₂Cl₂, 0.1 M [Bu₄N][PF₆], 20 °C, 0.1 V s⁻¹, E^o 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 -C₅Me₅)-FeC≡C(1,4-C₆H₄)C≡CH (**6**;²¹ 95 mg, 0.13 mmol) and KPF₆ (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 ^tBuOK (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 Et₂O 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). ³¹P{¹H} NMR (81 MHz, C₆D₆, δ in ppm): 101.8 (s, 8P, (dppe)Fe), 55.1 (s, 16P, (dppe)₂Ru). ¹H NMR (500 MHz, C₆D₆, δ in ppm): 9.41 (s, 8H, H $_{\beta}$ -pyrrolic), 8.40 (d, 8H, ³J $_{\text{H,H}}$ = 6.3 Hz, H $_{\text{Ar}}$), 8.12 (m, 16H, H $_{\text{Ar/dppe}}$), 7.87 (m, 48H, H $_{\text{Ar/dppe}}$), 7.57 (d, 8H, ³J $_{\text{H,H}}$ = 6.6 Hz, H $_{\text{Ar}}$), 7.45–6.80 (m, 192H, H $_{\text{Ar/dppe}}$ + H $_{\text{Ar}}$), 2.72 (m, 32H, CH₂/dppe/Ru), 2.59 (m, 8H, CH₂/dppe/Fe), 1.89 (m, 8H, CH₂/dppe/Fe), 1.59 (s, 60H, C₅(CH₃)₅). UV-vis (CH₂Cl₂, λ_{max} nm (ϵ , 10³ M⁻¹ cm⁻¹): 351 (98), 424 (347), 560 (24), 614 (28). CV (CH₂Cl₂, 0.1 M [Bu₄N][PF₆], 20 °C, 0.1 V s⁻¹, E^o in V vs. SCE): -0.22, 0.44.

Compound 4[PF₆]₄

In a Schlenk tube, **4** (150 mg, 0.048 mmol, 1.0 eq.) and [Fe(η^5 -C₅H₅)₂][PF₆]₄ (64 mg, 0.193 mmol, 4.0 eq.) were stirred for 1 h at 25 °C in CH₂Cl₂ (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[PF₆]₄ complex as a dark green solid (89 mg, 50%). IR (KBr-CH₂Cl₂, cm⁻¹): $\nu = 1986/1989$ (w, FeC \equiv C), 839/846 (vs. PF₆⁻). ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 30.1$ (m, 1H, CH_{Ar}[C₂]), 10.5 (s, 1H, CH _{β -Pyrrole}), 8.0 (s, 2H, H_{Ph-dppe}), 7.0 (m, 8H, H_{Ph-dppe}), 6.4 (m, 2H, H_{Ph-dppe}), 3.7 (s, 4H, H_{Ph-dppe}), 1.9 (s, 4H, H_{Ph-dppe}), -2.7 (m, 2H, CH_{2-dppe}), -10.2 (s, 15H, C₅(CH₃)₅), -40.8 (broad s, 1H, CH_{Ar}[C₁]).

X-Ray crystallography

Diffraction data frames for **4** were collected on a CCD Sapphire 3 Xcalibur diffractometer at 120(2) K using Mo-K α radiation ($\lambda = 0.71073$ 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 WINGX²⁷ 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: C₂₀₀H₁₉₀Fe₄N₄OP₈Zn₄C₅H₁₂, $M = 3490.67$, tetragonal, space group $I 4_1/a$, $a = 36.9262(5)$ Å, $b = 36.9262(5)$ Å, $c = 14.7933(8)$ Å, $U = 20171.3(12)$ Å³, $Z = 4$, $T = 120(2)$ 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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Notes and references

- G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330.
- S. R. Marder, *Chem. Commun.*, 2006, 131–134.
- M. Pawlicki, H. A. Collins, R. G. Denning and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2009, **48**, 3244–3266.
- M. Ravikanth and K. G. Ravindra, *Curr. Sci.*, 1995, **68**, 1010–1017.
- J. L. Humphrey and D. Kuciauskas, *J. Phys. Chem. C*, 2006, **128**, 3902–3903.
- S. V. Rao, N. K. M. N. Srinivas, D. N. Rao, L. Giribabu, B. G. Mayya, R. Philip and G. R. Kumar, *Opt. Commun.*, 2000, **182**, 255–264.
- S. A. Odom, S. Webster, L. A. Padilha, D. Peceli, H. Hu, G. Nootz, S.-J. Chung, S. Ohira, J. D. Matichak, O. V. Przhonska, A. D. Kachkovski, S. Barlow, J.-L. Brédas, H. L. Anderson, D. J. Hagan, E. W. Van Stryland and S. R. Marder, *J. Am. Chem. Soc.*, 2009, **131**, 7510–7511.
- M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 2004, **126**, 15352–15353.
- M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor and H. L. Anderson, *J. Phys. Chem. B*, 2005, **109**, 7223–7236.
- A. Karotki, M. Drobizhev, Y. Dzenis, P. N. Taylor, H. L. Anderson and A. Rebane, *Phys. Chem. Chem. Phys.*, 2004, **6**, 7–10.
- M. G. Humphrey, M. Samoc, F. Paul, C.O. Paul-Roth *et al.*, to be submitted.
- F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431–509.
- K. Onitsuka, H. Kitajima, M. Fujimoto, A. Iuchi, F. Takei and S. Takahashi, *Chem. Commun.*, 2002, 2576–2577.
- C. Roger, P. Hamon, L. Toupet, H. Rabaâ, J.-Y. Saillard, J.-R. Hamon and C. Lapinte, *Organometallics*, 1991, **10**, 1045–1054.
- See ESI† for additional details.
- K. Costuas, F. Paul, L. Toupet, J.-F. Halet and C. Lapinte, *Organometallics*, 2004, **23**, 2053–2068.
- F. Paul, J.-Y. Mevellec and C. Lapinte, *J. Chem. Soc., Dalton Trans.*, 2002, 1783–1790.
- F. Paul, G. da Costa, A. Bondon, N. Gauthier, S. Sinbandhit, L. Toupet, K. Costuas, J.-F. Halet and C. Lapinte, *Organometallics*, 2007, **26**, 874–896.
- F. Paul, L. Toupet, J.-Y. Thépot, K. Costuas, J.-F. Halet and C. Lapinte, *Organometallics*, 2005, **24**, 5464–5478.
- F. Paul, A. Bondon, G. da Costa, F. Malvoti, S. Sinbandhit, O. Cadot, K. Costuas, L. Toupet and M.-L. Boillot, *Inorg. Chem.*, 2009, **48**, 10608–10624.
- J. Courmarcel, G. Le Gland, L. Toupet, F. Paul and C. Lapinte, *J. Organomet. Chem.*, 2003, **670**, 108–122.
- N. Gauthier, G. Argouarch, F. Paul, L. Toupet, A. Ladjarafi, K. Costuas, J.-F. Halet, M. Samoc, M. P. Cifuentes, T. C. Corkery and M. G. Humphrey, *Chem.–Eur. J.*, 2011, **17**, 5561–5577.
- Exploitation of the MLCT state to enhance TPA cross-sections has precedence in porphyrin chemistry; see, for example: J. L. Humphrey and D. Kuciauskas, *J. Phys. Chem. B*, 2004, **108**, 12016–12023.
- M. P. Cifuentes, M. G. Humphrey, J. P. Morrall, M. Samoc, F. Paul, T. Roisnel and C. Lapinte, *Organometallics*, 2005, **24**, 4280–4288.
- A. Altomare, M. C. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.
- G. M. Sheldrick, *SHELX97-2. Program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.
- L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.