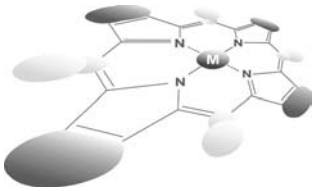
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2010; **14**: 877–884
DOI: 10.1142/S1088424610002720

Published at http://www.worldscinet.com/jpp/



Bisporphyrin connected by pyrimidine: synthesis and photophysical properties

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Received 13 July 2010
Accepted 14 October 2010

ABSTRACT: We report the synthesis of a series of zinc porphyrins conjugated with pyrimidine derivatives. V shaped porphyrin dimer with a pyrimidine central core exhibits a planar geometry according to DFT computational studies, presents an internal charge transfer upon excitation proved by typical solvatochromic behavior and moderate two-photon absorption properties. Such porphyrin conjugates can afford valuable advantages in applications of TPA materials such as in photodynamic therapy and imaging of biological entities.

KEYWORDS: porphyrin, pyrimidine, two photon absorption, cross coupling reactions.

INTRODUCTION

Photodynamic therapy (PDT) is a promising light activated treatment which is used in the clinic to destroy localized diseased tissues such as cancers [1]. When exposed to light, a photosensitive molecule called photosensitizer (Ps) transfers energy from its first triplet excited state to ground-state triplet oxygen molecule generating highly reactive oxygen species (ROS) as singlet oxygen, inducing oxidative damages to the cell and causing localized cell death. Major advantage of PDT in comparison with other treatments such as chemotherapy is that, in the absence of light, the Ps is benign. The majority of photosensitizers are cyclic tetrapyrroles or porphyrinoids because of their long triplet lifetime [2]. These Ps have one-photon absorption peaks in the visible wavelength range (400–700 nm) but one concern is the low penetration depth of visible light which is strongly absorbed by biological tissues. However, absorption is much lower in the optical window of biological tissues in the near-infrared region between 700–1300 nm [3]. Thus, greater treatment depths may be achieved by exciting the photosensitizers *via* simultaneous two-photon absorption (TPA) with near infrared light. Porphyrin compounds have strong one-photon absorption between 400 and 500 nm (Soret Band) corresponding to the combined energy of two photons in the wavelength range from 800 to 1000 nm, that matches to the optical window. Monomeric porphyrins without donor/acceptor groups have only small TPA cross section of less than a few tens of GM where 1 GM = 10^{-50} cm^4.s.$molecule^{-1}$ [4]. However conjugative extensions *via meso-meso* conjugated bridges have led to dramatic improvements in the TPA cross section values for this class of molecules [5]. In order to obtain conjugated porphyrin oligomers, monomers should be linked with bridges that do not twist out the plane with the porphyrin due to steric hindrance. Alkynyl bridges are then one of the most effective way of making connections to the *meso*-position of a porphyrin. Butadiyne [6], diethynylbenzene [7],

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diethynylthiophene [8], diethynylanthracene [9], diethynyltetrathiafulvalene [10], diethynylsquaraine [11] and triethynylphenylamine [12] π-conjugated cores have been described in the literature.

During the past decade, pyrimidine and its derivatives have been extensively studied as electron acceptor in conjugated structures. When combined with electron donor parts, interesting D-A molecules are obtained and fluorescence with internal charge transfer excited state is observed [13]. Oligomers that contain pyrimidine rings have been used as n-type semi-conductor [14], components of electroluminescent diodes [15], pH and polarity sensors [16] and two photon absorption chromophores [17]. Recently dendrimers [18] and supramolecular [19] receptors combining porphyrin and pyrimidine units have been described by Dehaen.

The one-electron reduction of pyrimidine gives its anion radical with a reduction potential of *ca*. 2.63 V *vs*. Ag/AgCl [20] whereas the one-electron oxidation and reduction potentials of tetraphenylporphyrins are around 0.8 and 1 V and -1.11 to -1.33 V respectively [21]. This suggests that porphyrin could become a donor unit when conjugated with pyrimidine to afford interesting D-A molecules with potential TPA properties.

The aim of this paper is to describe synthesis and photophysical properties including non linear absorption properties of bisporphyrin connected by pyrimidine (Fig. 1).

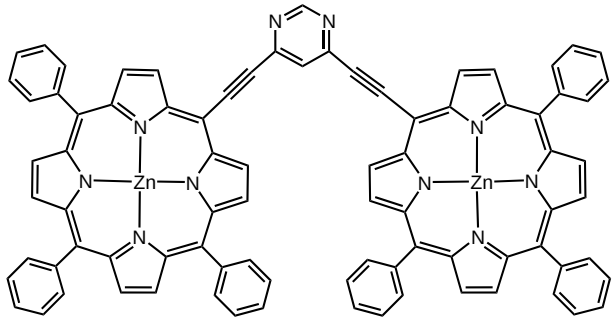

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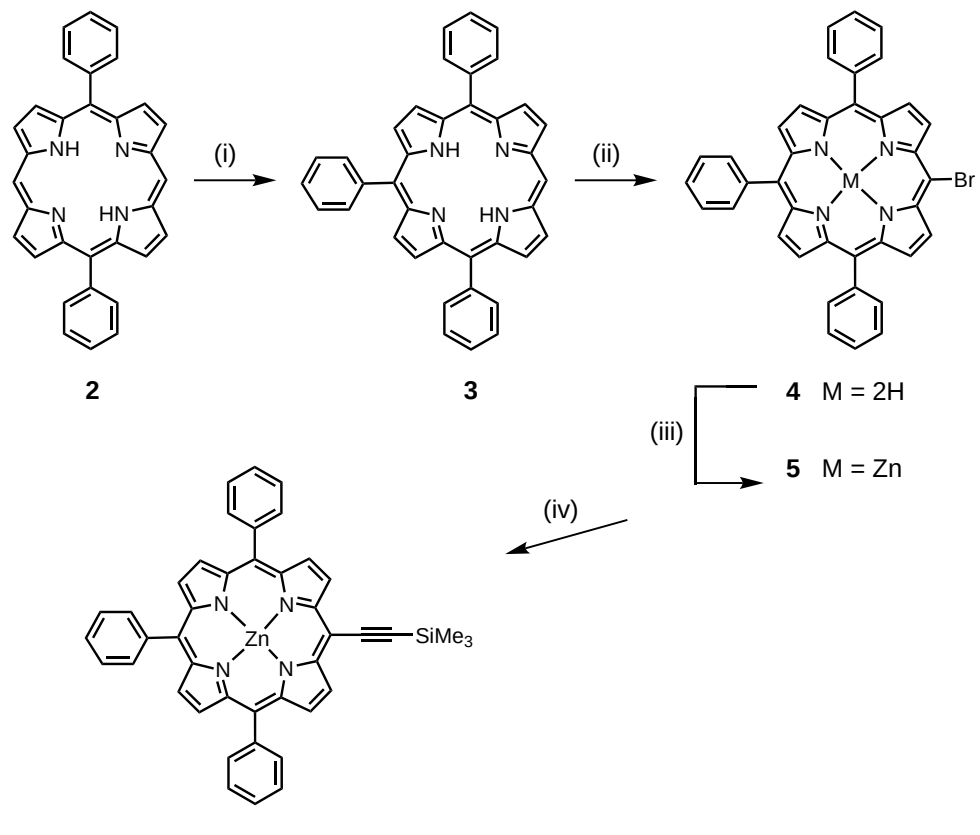
Fig. 1. Chemical structure of bisporphyrin conjugate **1**

RESULTS AND DISCUSSION

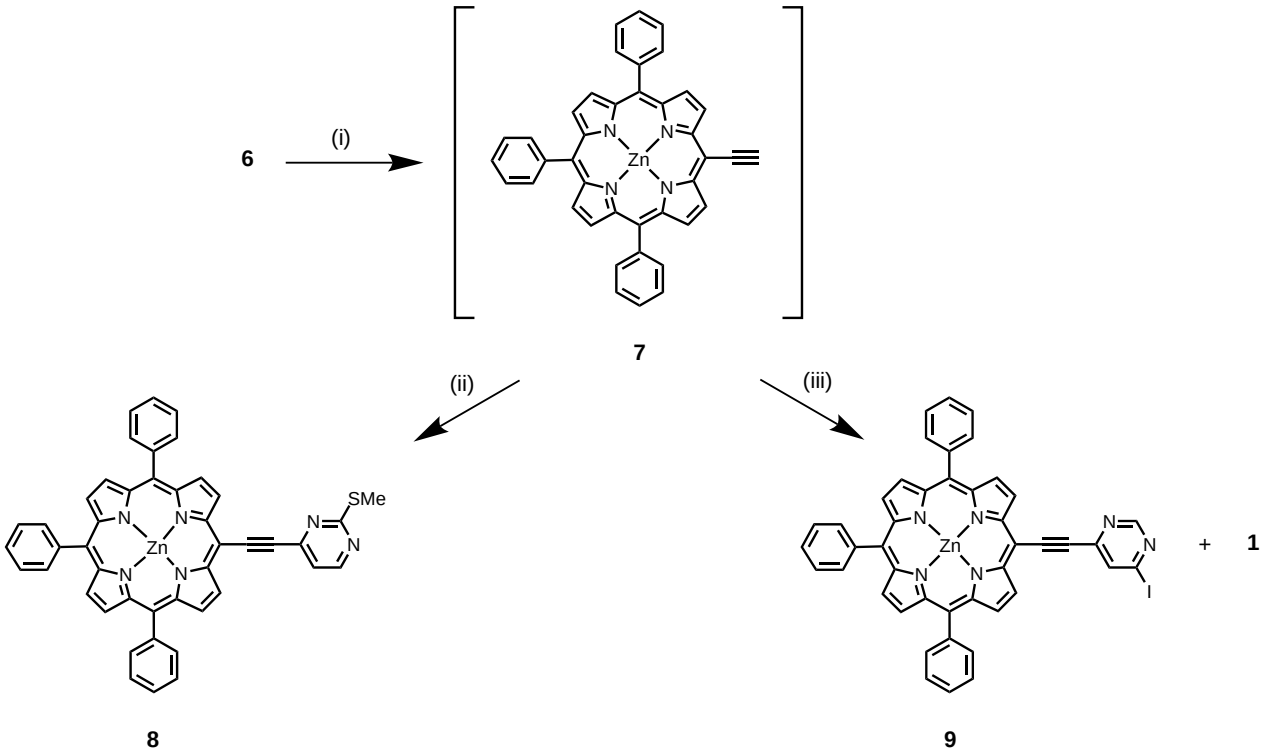
Synthesis

Compound **1** could be obtained by cross coupling reaction of 5-ethynyl-10,15,20-triarylporphyrin derived from protected trimethylsilylethynyl porphyrin **6** with 4,6-dihalogenopyrimidine under Heck or Sonogashira conditions.

Porphyrin monomer **6** was prepared, in four steps, from porphyrin **2** [22] (Scheme 1). The first step consists in the addition of phenyllithium in THF [23]. Monobromination with NBS and metalation with zinc acetate



Scheme 1. (i) C_6H_5Li, THF, rt, 2 h, then O_2, 65%; (ii) NBS, pyridine, $CHCl_3$, 0 °C, 15 min, 97%; (iii) $Zn(OAc)_2$, $CHCl_3$/MeOH, Δ, 5 min, 99%; (iv) TMSA, CuI, $Pd(PPh_3)_2Cl_2$, THF/Et_3N, -196 °C → rt, 15 h, 89%



Scheme 2. (i) TBAF, THF/CH_2Cl_2, rt, 30 min, non-isolated; (ii) 4-iodo-2-thiomethylpyrimidine, CuI, $Pd(PPh_3)_2Cl_2$, THF/Et_3N, rt, 15 h, 46%; (iii) 4,6-diiodopyrimidine, CuI, $Pd(PPh_3)_2Cl_2$, THF/Et_3N, rt, 15 h, **9**: 33%, **1**: 40%

led quantitatively to zinc porphyrin **5**. Sonogashira cross coupling reaction with ethynyltrimethylsilane in the presence of CuI and $Pd(PPh_3)_2Cl_2$, leads to porphyrin monomer **6** in good yield.

Synthesis of ethynylporphyrin pyrimidines starts with the deprotection of trimethylsilyl group of compound **6** with TBAF to lead quantitatively to compound **7** which was not isolated due to its instability and was immediately engaged in the following reaction. Sonogashira cross coupling was revealed to be more efficient than Heck cross coupling reaction, generally used to link ethynylporphyrins to halogenoaryl [24]: compounds **1**, **8** and **9** have been obtained in moderate rate starting from 4-iodo-2-thiomethylpyrimidine and 4,6-diiodopyrimidine (Scheme 2). It should be noted that even when using 4 equivalents of ethynylporphyrin with 4,6-diiodopyrimidine, a mixture of monocoupled product **9** (33%) and dicoupled product **1** (40%) as well as the butadiyne core porphyrin dimer was obtained. Yield of product **1** was not upgraded by increasing the temperature. Compound **9** can be recycled by reaction with **7** to give product **1**. All porphyrin compounds were fully characterized. Assignments of the NMR resonance to individual protons are based on integration and selective homonuclear correlation (COSY). Heteronuclear multiple coherence (HMQC, HMBC) spectra were also obtained for all compounds and allow assignments of the NMR resonance to carbon atoms. Data of MALDI-TOF and elemental analyses for all compounds are consistent with their molecular formula.

Calculated geometric properties

To explore geometrical features of bisporphyrin connected by pyrimidine, DFT calculation at the B3LYP/321++G* level of theory was performed [25]. Phenyl groups and zinc atoms were omitted for simplification. The optimized geometry reveals that the two porphyrin macrocycles in dimer **1** adopts a completely planar structure as shown on Fig. 2, indicating a good conjugation between the porphyrin rings and the pyrimidine central core.

Absorption and fluorescence properties

Figure 3 shows the UV-vis absorption spectra of compounds **1**, **6**, **8** and **9** in dichloromethane. The Soret bands of ethynylpyrimidine porphyrins **1**, **8** and **9** (444–445 nm) are red shifted of about 15 nm in comparison with porphyrin building block **6** (430 nm). The less energetic Q-band denoted Q(0,0) is also red shifted (from 606 nm for compound **6** to 619–625 nm for compounds **1, 8**

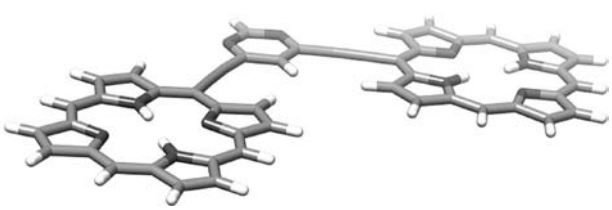


Fig. 2. The optimized geometry of compound **1** (phenyl rings and zinc atoms have been omitted for simplification) by DFT calculation

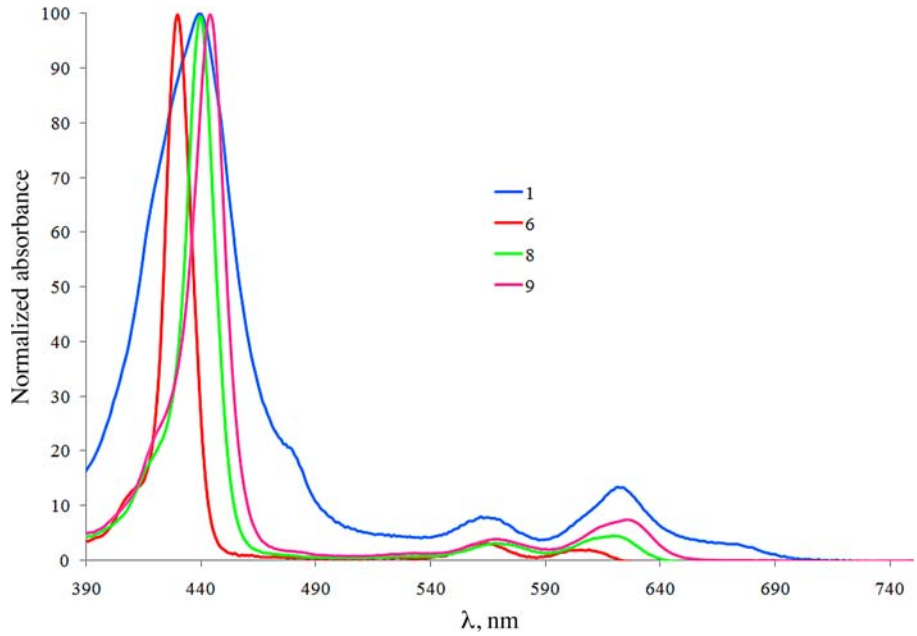


Fig. 3. Normalized absorption spectra of compounds **1**, **6**, **8** and **9** in dichloromethane, c = 5 × 10^{-6}–10^{-5} M

and **9**). On the contrary, the first Q-band [Q(1,0)] between 564–568 nm was not significantly modified by coupling with pyrimidine. When the spectrum of bisporphyrin **1** is compared to these of porphyrins **8** and **9**, no important differences concerning the absorption band position are observed, however their relative intensity is modified: the Soret band of dimer **1** is remarkably broadened and lower relative to that of monomer **8** and **9** whereas the Q-bands are two times more intense in case of dimer. This is in agreement with the literature concerning conjugated porphyrin oligomers [26]. As shown on absorption spectra, the ground state absorption of dimer **1** remarkably differs from that of monomers **8** and **9**, this indicating an electronic coupling between the porphyrin chromophores which is consistent with calculated geometrical features of **1**.

Emission spectra of compounds **1, 6, 8** and **9** in dichloromethane are presented in Fig. 4 and photophysical parameters are summarized in Table 1. As expected in view of the literature [27], porphyrins derivatives exhibit two emission bands Q(0,0) and Q(0,1) respectively at 645–648 and 692–698 nm by excitation at 440 nm for the porphyrins conjugated to pyrimidine, these band are shifted to lower energy than those of building block **6** (630 nm and 679 nm). As described in the literature for porphyrins derivatives the relative intensity of these two bands strongly depend on the excitation wavelength [27b]. A fluorosolvatochromic study has been carried

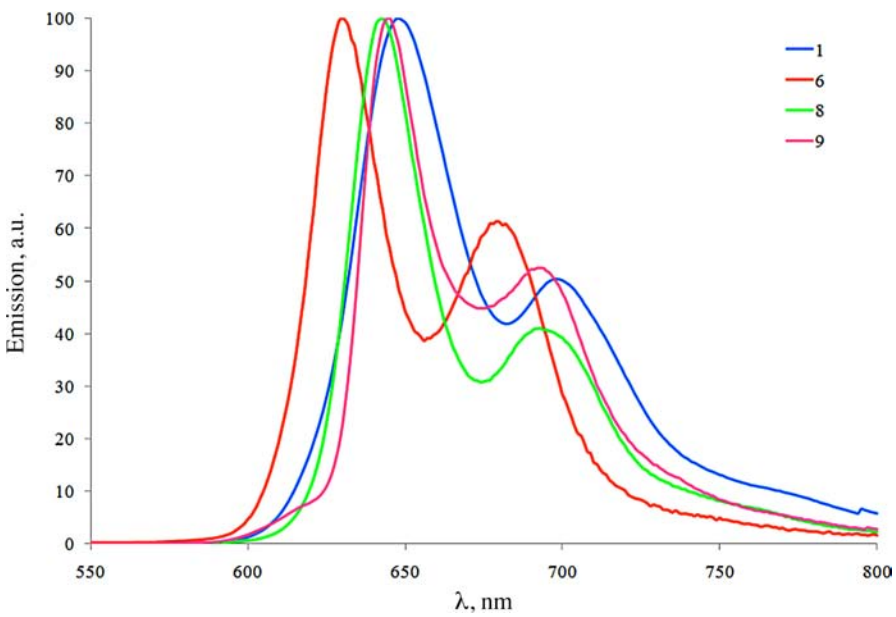


Fig. 4. Normalized emission of compounds **1**, **6**, **8** and **9** in dichloromethane, c = 5 × 10^{-7}–10^{-6} M

Table 1. Photophysical parameters of porphyrins **1**, **6**, **8** and **9** in dichloromethane. λ_{max}(abs) is the absorption peaks wavelength in nm, ε is extinction coefficient in L.mmol^{-1}.cm^{-1}, λ_{max}(em) the absorption peaks wavelength in nm (excitation at absorption maximum), Φ_F is the fluorescence quantum yield in ethanol *vs*. Rhodamine 101 (1.00) [32]

Compound	**1**	**6**	**8**	**9**
λ_{max}(abs)	444, 565, 622	430, 564, 606	440, 568, 619	444, 568, 625
ε	549, 45, 76	543, 17, 12	610, 19.7, 28.2	660, 24, 43
λ_{max}(em)	648, 702	630, 679	643, 693	645, 692
Φ_F	0.11	0.14	0.18	0.12

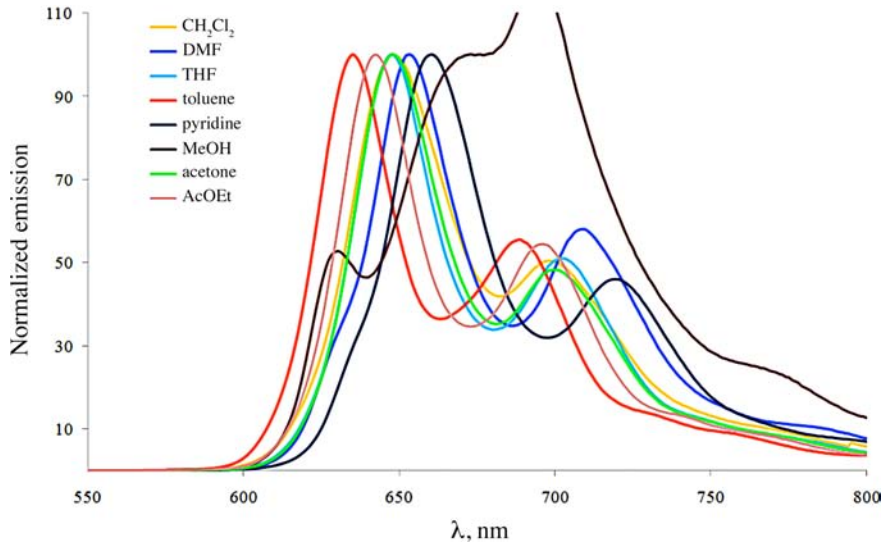


Fig. 5. Normalized emission of compound **1** in various solvent. c = 10^{-6} M

out on compounds **1** and **6**. For compound **1**, a bathochromic shift of highest energy emission band can be observed with increasing solvent polarity estimated by solvent orientation polarizability [28] (Fig. 5). In contrast the absorption is not significantly shifted. The emission spectrum shape in methanol is modified relative to other solvents probably due to aggregation of compound **1** in this solvent at working concentration. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds presenting an internal charge transfer upon excitation and has been fully documented with donor-acceptor fluorophores [29]. On the contrary, no significant fluorosolvatochromy is observed with compound **5** except with solvents such as pyridine that are able to complex zinc cations in porphyrin rings and lead to a bathochromic shift (λ_{emDCM} = 630 nm, $\lambda_{emPyridine}$ = 637 nm).

Two photon properties

TPA spectrum of compound **1** has been determined by detecting the upconverted fluorescence following excitation between 790–950 nm. As shown in Fig. 6, for fluorescence emission collected at 648 nm [Q(0,0) band], the highest recorded cross section is observed around 790 nm

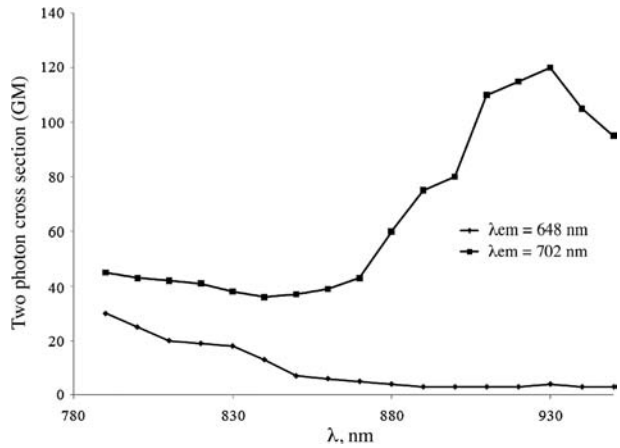


Fig. 6. TPA spectra of compound **1** in DCM. c = 10^{-6} M

(δ_{max} = 45 GM) corresponding to two photon excitation of Q(0,0) absorption band whereas for fluorescence emission collected at 702 nm [Q(0,1) band], the highest recorded cross section is observed at 930 nm (δ_{max} = 120 GM) corresponding to two photon excitation of Q(1,0) absorption band. Similar TPA bands have been previously obtained for porphyrin dimers [30]. These results indicates that compound **1** exhibits better two photon cross section than the corresponding monomer (about 20 GM)

[26] and validate the oligomeric design [5]. However these values remain lower than other porphyrin dimers linked with a butadiyne and an ethynyl bridge (more than 5000 GM) [26]. This may be explained by a lower conjugation between the porphyrin rings *via meta*-pyrimidine moiety leading to a lower resonance of excitation light with the Q-bands.

EXPERIMENTAL

Materials

All solvents (reagent grade) and the starting materials were acquired from Sigma-Aldrich and were used without purification. Methylene chloride (DCM) was distilled from calcium hydride and kept over 4 Å sieves. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Et_3N was dried and kept over potassium hydroxide. Column chromatography was performed with the indicated solvents using E. Merck silica gel 60 (particle size 0.035–0.070 mm). Macherey-Nagel precoated plates (SIL G-200, 2 mm) were used for preparative thin-layer chromatography. Yields refer to chromatographically and spectroscopically pure compounds. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer at ambient temperature using an internal deuterium lock. Chemical shift values are given in ppm relative to tetramethyl silane (TMS). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. Quantitative UV-vis spectra were recorded with a UVIKON xm SECOMAM spectrometer (molar extinction coefficient values are given in $L.mmol^{-1}.cm^{-1}$). Fluorescence spectra were recorded using Spex FluoroMax-3 Jobin-Yvon Horiba apparatus. Microanalysis were obtained from ICSN-CNRS Elemental Analysis Center at Gif-sur-Yvette, France. The MALDI-TOF mass spectra were performed with MALDI-TOF Voyager Spec equipped with a N_2 Laser emitting at 337 nm. The TPA cross-section in the range 750–950 nm were obtained by up-conversion fluorescence using a mode locked Ti:sapphire femtosecond laser (Tsunami Spectra-Physics) with pulse duration 100 fs and at a repetition rate of 82 MHz. The measurements were done at room temperature in DCM and at concentration of 5×10^{-6} M–10^{-5} M. The excitation beam (5 mm diameter) is focalized with a lens (focal length 10 cm) at the middle of the fluorescence cell (10 mm). The fluorescence, collected at 90° to the excitation beam, was focused into an optical fiber (diameter 600 µm) connected to an Ocean Optics S2000 spectrometer. The incident beam intensity was adjusted to 50 mW in order to ensure an intensity-squared dependence of the fluorescence over the whole range. The detector integration time was fixed to 1 s. Comparison of the spectra was performed with the published Fluorescein and Rhodamine B two-photon absorption spectra [31].

Synthesis

5,10,15-triphenyl-20-trimethylsilanylethynyl porphyrinato Zn(II) (6) [32]**.** A flask containing 5-bromoporphyrin **5** (800 mg, 1.17 mmol), CuI (22 mg, 0.12 mmol) and $Pd(PPh_3)_2Cl_2$ (82 mg, 0.12 mmol) was purged with N_2, and then charged with anhydrous THF (40 mL) and dry Et_3N (7.2 mL). After this solution was frozen with liquid nitrogen, trimethylsilylacetylene (2.34 mL, 16.4 mmol) was added and the mixture was then degassed. The mixture was stirred for 12 h at room temperature, quenched with water and evaporated to remove organic solvents. Organic compounds were extracted with DCM, the organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The residue was separated over a silica gel column with heptane/DCM (1/1, v/v) to give **6** (730 mg, 89%) as a purple solid. UV-vis (CH_2Cl_2): λ_{max}, nm (ε, $L.mmol^{-1}.cm^{-1}$) 430 (543), 564 (17), 606 (12). ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H, ppm 9.76 (d, 2H, J = 4.8 Hz, H-2, 18), 8.98 (d, 2H, J = 4.8 Hz, H-3, 17), 8.87 (s, 4H, H-7, 13/8, 12), 8.20–8.16 (m, 12H, H-Ph), 7.78–7.73 (m, 18H, H-Ph), 0.61 [s, 9H, $Si(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ_C, ppm 152.6–149.9 (C-1, 19/4, 16/6, 14/9, 11), 142.6 (C-1Ph), 142.5 (C-1Ph), 134.4 (C-Ph), 134.3 (C-Ph), 132.9–131.0 (C-2, 3, 7, 8, 12, 13, 17, 18), 127.6 (C-Ph), 126.6 (C-Ph), 126.5 (C-Ph), 122.9 (C10), 121.9 (C-5/15), 107.6 (C-20), 101.3 (C-alkyne), 99.7 (C-alkyne). Anal. calcd. for $C_{43}H_{32}N_4SiZn + H_2O$ (716.23): C 72.11, H 4.78, N 7.82. Found C 72.21, H 4.93, N 7.56.

5,10,15-triphenyl-20-ethynyl porphyrinato Zn(II) (7). Tetrabutylammonium fluoride (TBAF) in solution in THF (1 M, 0.744 mL) was added to a solution of **6** (200 mg, 0.286 mmol) dissolved in DCM (12 mL). The reaction was stirred at room temperature for 15 min, followed by addition of anhydrous calcium chloride (2 g). The mixture was stirred for 10 min, filtered into a flask and the solvent evaporated.

General procedure for Sonogashira cross-coupling reaction. Porphyrin **7** (0.286 mmol) was combined with iodopyrimidine (0.125 mmol), CuI (0.029 mmol) and $Pd(PPh_3)_2Cl_2$ (0.029 mmol) in anhydrous THF (10 mL) and Et_3N (10 mL) under argon. The reaction mixture was stirred at room temperature overnight then poured from the reaction vessel into a separatory funnel containing 50 mL of H_2O and 50 mL of DCM. The layers were separated, the aqueous layer was extracted with DCM (3 × 25 mL) and the combined organic layers were washed with water and dried over sodium sulfate, filtered and evaporated under reduced pressure. Crude product was purified by chromatography over preparative TLC (silica, AcOEt/n-heptane (3/7, v/v)).

Bis[5-ethynyl-(10,15,20-triphenyl)porphyrinato Zn(II)]-4′,6′-pyrimidine 1. Dark green solid (66 mg, 40%). UV-vis (CH_2Cl_2): λ_{max}, nm (ε, $L.mmol^{-1}.cm^{-1}$) 444 (549), 565 (45), 622 (76). ^1H NMR (300 MHz, $Pyrd_5$,

Me_4Si): δ_H, ppm 10.33 (d, 4H, *J* = 4.5 Hz, H-2, 18), 9.88 (s, 1H, H-2_{pyrim}), 9.23 (d, 4H, *J* = 4.5 Hz, H-3, 17), 9.05 (d, 4H, *J* = 4.5 Hz, H-7, 13/8, 12), 9.02 (d, 4H, *J* = 4.5 Hz, H-7, 13/8, 12), 8.98 (s, 1H, H-5_{pyrim}), 8.36–8.34 (m, 12H, H-Ph), 7.81–7.76 (m, 18H, H-Ph). MS (MALDI-TOF): *m/z* 1325.25 ($C_{84}H_{49}N_{10}Zn_2$, $[M + H]^+$, requires 1325.27). Anal. calcd. for $C_{84}H_{48}N_{10}Zn_2$ + 11 H_2O: C 66.10, H 4.62, N 9.18. Found C, 66.06 H, 4.53 N, 8.95.

[5-ethynyl-(10,15,20-triphenyl)porphyrinato Zn(II)]-2′-(methylthio)pyrimidine 8. Dark green solid (43 mg, 46%). UV-vis (CH_2Cl_2): λ_{max}, nm (ε, L.mmol^{-1}.cm^{-1}) 440 (610), 568 (19.7), 619 (28.2). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H, ppm 9.76 (d, 2H, *J* = 4.8 Hz, H-2, 18), 9.00 (d, 2H, *J* = 4.8 Hz, H-3, 17), 8.86 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.83 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.46 (d, 1H, *J* = 5 Hz, H-6_{pyrim}), 8.20–8.15 (m, 6H, H-Ph), 7.78–7.73 (m, 9H, H-Ph), 7.47 (d, 1H, *J* = 5 Hz, H-5_{pyrim}), 2.67 (s, 3H, SMe). MS (MALDI-TOF): *m/z* 748.14 (calcd. for $[M]^+$ 748.14). Anal. calcd. for $C_{45}H_{28}N_6SZn$ + 8 H_2O: C 60.43, H 4.96, N 9.40, S 3.59. Found C, 60.81 H, 5.25 N, 9.51, S 3.43.

[5-ethynyl-(10,15,20-triphenyl)porphyrinato Zn(II)]-6′-(iodo)pyrimidine 9. Dark green solid (34 mg, 33%). UV-vis (CH_2Cl_2): λ_{max}, nm (ε, L.mmol^{-1}.cm^{-1}) 444 (660), 568 (24), 625 (43). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H, ppm 9.32 (d, 2H, *J* = 4.8 Hz, H-2, 18), 8.94 (d, 2H, *J* = 4.8 Hz, H-3, 17), 8.85 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.81 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.20–8.18 (m, 7H, H-Ph + H-2_{pyrim}), 7.90 (s, 1H, H-5_{pyrim}), 7.80–7.76 (m, 9H, H-Ph). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ_C, ppm 170.0 (C-2_{pyrim}), 154.0 (C-4_{pyrim}), 153.0–149.6 (C-1, 19/4, 16/6, 14/9, 11), 142.73 (C-1Ph), 142.67 (C-1Ph), 134.4 (C-Ph), 134.3 (C-Ph), 131.6–131.1, (C-2, 3, 7, 8, 12, 13, 17, 18), 128.2 (C-Ph), 128.1 (C-Ph), 127.5 (C-5_{pyrim}), 126.5 (C-Ph), 126.4 (C-Ph), 122.6 (C-5/15) 121.9 (C-10), 106.4 (C-20), 103.4 (C-alkyne), 97.1 (C-alkyne). MS (MALDI-TOF): *m/z* 828.05 (calcd. for $[M]^+$ 828.06).

CONCLUSION

In this contribution, we have successfully synthesized a V-shaped bisporphyrin conjugate using a *meta*-difunctionalized pyrimidine core and two *meso*-ethynylporphyrin arms. Computational and photophysical studies show that this structure is a promising D-π-A-π-D fluorophore. Such porphyrin conjugates can afford valuable advantages in applications of TPA materials such as in photodynamic therapy and imaging of biological entities.

Acknowledgements

We thank Mr. Jean Bernard for TPA measurements, Mr Vincent Guérineau for MALDI-TOF analysis and the center of computing services of the Paris-Sud IT department. This work has been supported by INCa (2009–1-RT-08-IC-1) and the French association "Rétinostop" (http://www.retinostop.org). Sylvain Achelle also thanks the fondation Pierre-Gilles de Gennes for a postdoctoral fellowship.

REFERENCES

1. a) Dougherty TJ, Gomer CJ, Henderson BW, Jori G, Kessel D, Korbelik M, Moan J and Peng Q. *J. Nat. Canc. Inst.* 1998; **90**: 889–905. b) *Chemical Aspects of Photodynamic Therapy*, Bonnet R. (Ed.) Gordon and Breach Science Publishers: Amsterdam, 2000. c) MacDonald IJ and Dougherty TJ. *J. Porphyrins Phthalocyanines* 2001; **5**: 105–129. d) Dolmans DEJGJ, Fukumura D and Jain RK. *Nat. Rev.* 2003; **3**: 380–386. e) Robertson CA, Hawkins Evans D and Abrahamse H. *J. Photochem. Photobiol., B* 2009; **96**: 1–8.
2. Bonnett R. *Chem. Soc. Rev.* 1995; **24**: 19–33.
3. a) *Electrooptics Handbook*, Waynant RW and Ediger MN. (Eds.) McGraw-Hill: New York, 1993; Chapter 24. b) Tromberg BJ, Shah N, Lanning R, Cerussi A, Espinoza J, Pham T, Svaasand L and Butler J. *Neoplasia* 2000; **2**: 26.
4. a) Goyan RL and Cramb DT. *Photochem. Photobiol.* 2000; **72**: 821–827. b) Dichtel WR, Serin JM, Edder C, Frechet JM, Matuszewski M, Tan LS, Ohulchanskyy TY and Prassad PN. *J. Am. Chem. Soc.* 2004; **126**: 5380–5381.
5. a) Karotki A, Drobizhev M, Dzenis Y, Taylor PN, Anderson HL and Rebane A. *Phys. Chem. Chem. Phys.* 2004; **6**: 7–10. b) Frampton MJ, Akdas H, Cowley AR, Rogers JE, Slagle JE, Fleitz PA, Drobizhev M, Rebane A and Anderson HL. *Org. Lett.* 2005; **7**: 5365–5368. c) He GS, Tan LS, Zheng Q and Prasad PN. *Chem. Rev.* 2008; **108**: 1245–1330.
6. a) Arnold DP, Johnson AW and Mahendran M. *J. Chem. Soc. Perkin Trans. 1* 1978; 366–370. b) Arnold DP and James DA. *J. Org. Chem.* 1997; **62**: 3460–3469. c) Anderson HL. *Chem. Commun.* 1999; 2323–2330. d) Balaz M, Collins HA, Dahlstedt E and Anderson HL. *Org. Biomol. Chem.* 2009; **7**: 874–888. e) Kuimova MK, Collins HA, Balaz M, Dahlstedt E, Levitt JA, Sergent N, Suhling K, Drobizhev M, Makarov NS, Rebane A, Anderson HL and Phillips D. *Org. Biomol. Chem.* 2009; **7**: 889–904. f) Collins HA, Khurana M, Moriyama EH, Mariampillai A, Dahlstedt E, Balaz M, Kuimova MK, Drobizhev M, Yang VXD, Phillips D, Rebane A, Wilson BC and Anderson HL. *Nat. Photonics* 2008; **2**: 420–424.
7. a) Arnold DP and Nitschinsk LJ. *Tetrahedron Lett.* 1993; **34**: 693–696. b) Arnold DP and James DA. *J. Org. Chem.* 1997; **62**: 3460–3469.
8. Arnold DP, James DA, Kennard CHL and Smith G. *J. Chem. Soc. Chem. Commun.* 1994; 2131–2132.
9. Taylor PN, Wylie AP, Huuskonen J and Anderson HL. *Angew. Chem. Int. Ed.* 1998; **37**: 986–989.

10. Ogawa K and Nagatsuka Y. *J. Porphyrins Phthalocyanines* 2009; **13**: 114–121.
11. Odom SA, Webster S, Padilha LA, Peceli D, Hu H, Nootz G, Chung SJ, Ohira S, Matichak JD, Przhonska OV, Kachkovski AD, Barlow S, Brédas JL, Anderson HL, Hagan DJ, Van Stryland EW and Marder SR. *J. Am. Chem. Soc*. 2009; **131**: 7510–7511.
12. Seo JW, Jang SY, Kim D and Kim HJ. *Tetrahedron* 2008; **64**: 2733–2739.
13. a) Pascal L, Vanden Eynde JJ, Van Haverbeke Y, Dubois P, Michel A, Rant U, Zojer E, Leising G, Van Dorn LO, Gruhn NE, Cornil J and Brédas JL. *J. Phys. Chem. B* 2002; **106**: 6442–6450. b) Itami K, Yamazaki D and Yoshida J. *J. Am. Chem. Soc.* 2004; **126**: 15396–15397. c) Achelle S, Ramondenc Y, Dupas G and Plé N. *Tetrahedron* 2008; **64**: 2783–2791. d) Achelle S, Plé N, Kreher D, Attias AJ, Arfaoui I and Charra F. *Tetrahedron Lett.* 2009; **50**: 7055–7058.
14. Kambara T, Kushida T, Saito N, Kuwayiama I, Kubuta K and Yamamoto T. *Chem. Lett.* 1992; 583.
15. a) Wang C, Jung GY, Batsanov AS, Bryce MR and Petty MC. *J. Mater. Chem.* 2002; **12**: 173–180. b) Wong KT, Hung TS, Lin Y, Wu CC, Lee GH, Peng SM, Chou CH and Su YO. *Org. Lett.* 2002; **4**: 513–516.
16. a) Achelle S, Ramondenc Y, Marsais F and Plé N. *Eur. J. Org. Chem.* 2008; 3129–3140. b) Achelle S, Nouira I, Pfaffinger B, Ramondenc Y, Plé N and Rodríguez-López J. *J. Org. Chem*. 2009; **74**: 3711–3717. c) Bagley MC, Lin Z and Pope SJA. *Tetrahedron Lett.* 2009; **50**: 6818–6822.
17. a) Liu Z, Chen T, Liu B, Huang Z-L, Huang T, Li S, Xu Y and Qin J. *J. Mater. Chem.* 2007; **17**: 4685–4689. b) Liu B, Hu XL, Liu J, Zhao YD and Huang ZL. *Tetrahedron Lett.* 2007; **48**: 5958–5962. c) Liu Z, Shao P, Huang Z, Liu B, Chen T and Qin J. *Chem. Commun.* 2008; 2260–2262. d) Li L, Tian YP, Yang JX, Sun PP, Wu JY, Zhou HP, Zhang SY, Jin BK, Xing XJ, Wang CK, Li M, Cheng GH, Tang HH, Huang WH, Tao XT and Jiang MH. *Chem. Asian J.* 2009; **4**: 668. e) Akdas-Kilig H, Roisnel T, Ledoux I and Le Bozec H. *New J. Chem.* 2009; **33**: 1470–1473.
18. a) Maes W, Vanderhaeghen J, Smetts S, Asokan CV, Van Renterghem LM, Du Prez FE, Smet M and Dehaen W. *J. Org. Chem.* 2006; **71**: 2987–2994. b) Maes W, Amabilino DB and Dehaen W. *Tetrahedron* 2003; **59**: 3937–3943. c) Maes W and Dehaen W. *Eur. J. Org. Chem.* 2009; 4719–4752.
19. Van Rossom W, Kundrát O, Ngo TH, Lhotk P, Dehaen W and Maes W. *Tetrahedron Lett.* 2010; **51**: 2423–2426.
20. a) Elving PJ and O'Reilly JE. *J. Am. Chem. Soc.* 1971; **93**: 1871–1979. b) O'Reilly JE and Elving PJ. *J. Electroanal. Chem.* 1977; **75**: 507–522.
21. a) Hodge JA, Hill MG and Gray HB. *Inorg. Chem.* 1995; **34**: 809–812. b) Ravikanth M, Reddy D, Misra A and Chandrashekar TK. *J. Chem. Soc. Dalton Trans.* 1993; 1137–1141.
22. Varamo M, Loock B, Maillard Ph and Grierson DS. *Org. Lett.* 2007; **9**: 4689–4692.
23. a) Kalicsh WW and Senge MO. *Angew. Chem. Int. Ed.* 1998; **37**: 1107–1109. b) Senge MO and Feng X. *Tetrahedron Lett*. 1999; **40**: 4165–4168.
24. Raymond JE, Bhaskar A, Goodson III T, Makiuchi N, Ogawa K and Kobuke Y. *J. Am. Chem. Soc.* 2008; **130**: 17212–17213.
25. Jaguar, version 7.6, Schrodinger, LLC, New York, NY 2009.
26. Drobizhev M, Stepanenko Y, Dzenis Y, Karotki A, Rebane A, Taylor PN and Anderson HL. *J. Phys. Chem. B* 2005; **109**: 7223–7236.
27. a)Pérez-Morales M, de Miguel G, Bolink HJ, Martín-Romero MT and Camacho L. *J. Mater. Chem.* 2009; **19**: 4255–4260. b) Suriyanarayanan P and Krishnan V. *Photochem. Photobiol.* 1983; **38**: 533–536.
28. Myśliwa-Kurdziel B, Solymosi K, Kruk J, Böddi B and Strzalka K. *Eur. Biophys. J.* 2008; **37**: 1185–1193.
29. a) Katan C, Terenziani F, Mongin O, Werts MHV, Porres L, Pons T, Mertz J, Tretiak S and Blanchard-Desce M. *J. Phys. Chem. A* 2005; **109**: 3024–3037. b) Lartia R, Allain C, Bordeau G, Schmidt F, Fiorini-Debuischert C, Charra F and Teulade-Fichou MP. *J. Org. Chem*. 2008; **73**: 1732–1744.
30. Odom SA, Kelley RF, Ohira S, Ensley TR, Huang C, Padilha LA, Webster S, Coropceanu V, Barlow S, Hagan DJ, Van Stryland EW, Brédas JL, Anderson HL, Wasielewski MR and Marder SR. *J. Phys. Chem. A* 2009; **113**: 10826–10832.
31. Makarov NS, Drobizhev M and Rebane A. *Proc. SPIE* 2008; **6891**: 689105.
32. Fathalla M and Jayawickramarajah J. *Eur. J. Org. Chem.* 2009; 6095–6099.