π -extended diketopyrrolopyrrole-porphyrin arrays: one- and two-photon photophysical investigations and theoretical studies

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A complete one- and two-photon spectroscopic and photophysical characterization of three diketopyrrolopyrrole (DPP)-porphyrin conjugates is reported. The increased conjugation introduced by the incremental addition of one, two and four DPP units on the *meso* porphyrin positions strongly affects the optical properties of the systems. Ground and triplet excited state absorption spectra show a gradual broadening and bathochromic shift and a trend to lower energies is also observed for both fluorescence and phosphorescence emission. Interestingly, the fluorescence quantum yield increases along the series, leading to remarkable NIR emission properties for the larger derivatives. Unlike the model porphyrin, all derivatives exhibit high two-photon absorption activity. An increase in two-photon absorption cross-section in the regions 800–840 nm and 910–930 nm is observed moving from one DPP to two DPP appended units, with a value of the order of 4000 GM at 910 nm for the latter system. The four compounds show high efficiency in generating singlet oxygen, with yields ranging from 0.7 to 0.5, envisaging favourable applications in both one- and two-photon photodynamic therapy. A detailed theoretical exploration of both linear (absorption and emission) and non-linear (two-photon absorption) properties proposes an analysis of the experimental spectra and a comprehensive interpretation of the two-photon activity within the series of compounds.

Introduction

Porphyrins are aromatic compounds displaying unique optical, electronic, redox and catalytic properties, thanks to their eighteen delocalised π -electrons. They are among the most widespread molecules in nature and the most versatile compounds for several applications, from materials science to medicinal chemistry. Natural photosynthetic systems rely on selected pigments related to porphyrins, chlorophylls and bacteriochlorophylls, as components of antenna systems and reaction centres.^{1–8} Because of their superior photo- and electrochemical properties, porphyrins have been used as photoactive units in energy conversion structures^{9–11} and thanks to their attractive optical and electronic properties, they have been widely explored as linear and non-linear materials for optoelectronics^{12, 13} and biomedical research.^{14–17}

Of particular interest is the dependence of these properties on the perturbation of the porphyrin electronic system *via* an enhanced conjugation. Extending the porphyrin π -system by the design of expanded porphyrins, conjugated-porphyrin oligomers or conjugated porphyrin-aromatic systems, is an interesting tool to control electronic coupling, to fine tune the HOMO-LUMO gap, to change absorption and emission features as well as triplet excited states properties and to modulate the redox characteristics. Such extended molecules are promising to develop biomimetic light-harvesting antennas and reaction centres, photosensitizers for dye-sensitized solar cells and molecular wires.^{10, 18–37} In addition, the near-infrared (NIR) absorption and emission features of π -extended porphyrins render them particularly appealing for biomedical (imaging, sensing), optoelectronic and energy conversion applications.^{16, 38–43}

Conjugated porphyrin systems, moreover, have highly polarisable structures leading to strong non-linear optical properties such as two-photon absorption (TPA).^{44–54} The main advantages of TPA with respect to one-photon absorption (OPA), namely the use of lower excitation energies in conjunction with increased 3D spatial resolution, give to two-photon excitation a great potential for application in material sciences, as three-dimensional micro-fabrication, data-storage and optical power limiting.^{18, 55–59} Two-photon excitation performed in the near-infrared (NIR) is also appealing for medical applications due to the transparency of body tissues above 700 nm and the decrease of the photodamage, inherent

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in the use of a low energy light source. Molecules presenting high TPA have been thus developed for fluorescence imaging, spatial control of photoreleased drugs and photodynamic therapy.⁶⁰⁻⁷⁵

Understanding the structural-photophysical properties relationships of π -extended porphyrins on the basis of both experimental and theoretical analysis is of considerable interest to optimize the design of efficient molecules characterized by NIR absorption and fluorescence, high triplet yield and high TPA cross-sections, as good candidates for both linear and non-linear biomedical applications.⁷⁶⁻⁸¹ Theoretical analysis based on OPA and TPA simulated spectra and on calculated emission will enable us to extract the electronic properties at the origin of photophysical processes not directly accessible experimentally.

Diketopyrrolopyrrole (DPP) is a red pigment, which was advantageously associated with porphyrins for dye-sensitized solar cells and material sciences applications.⁸²⁻⁸⁵ Some of us have recently developed new hydrophilic diketopyrrolopyrrole-porphyrin conjugates, **DPP-ZnP** and **(DPP)₂-ZnP**, as photosensitizers for two-photon photodynamic therapy (TP-PDT) (Fig. 1).⁸⁶ These chromophores have shown high TPA properties in the near infrared and strong oxygen generation ability. In order to explore in details how the introduction of incremental DPP units into the porphyrinic π -system affects the photophysical properties, we have performed a comprehensive one-photon and two-photon characterization of the **DPP-ZnP** and **(DPP)₂-ZnP** compounds, as well as of a novel porphyrinic system with four appended DPP units, **(DPP)₄-ZnP**. Detailed spectroscopic and photophysical studies have been integrated with extended theoretical studies that focus on the electronic charge transfer directionality at the origin of OPA and TPA activities. The non-routine computational approach used in the present work is validated by recent preliminary results⁹³ reported for model systems of the DPP-Zn-porphyrin conjugates investigated here.

Fig. 1 Chemical structure of the three diketopyrrolopyrrole-porphyrin conjugates and of the reference compound **ZnP**.

The results support the relevance of the design of DPP-ZnP conjugates to afford promising materials as efficient NIR emitters and one- and two-photon photosensitizers for PDT.

Results and discussion

The chemical structures of the compounds are represented in Fig. 1. The zinc(II) porphyrin **ZnP** has a moderate π -extended system given by the two *meso trans* ethynyl groups whereas the diketopyrrolopyrrole-Zn(II)porphyrin conjugates **DPP-ZnP**, **(DPP)₂-ZnP** and **(DPP)₄-ZnP** present a higher π -conjugation due to, respectively, one, two and four DPP units *meso* linked to the porphyrin core through an ethynyl bridge. Extended conjugation of the porphyrin π -system to the two *trans meso* phenyl groups decorated with triethyleneglycol chains is limited due to the twisting of the phenyl rings which aims at avoiding steric interactions with the *meso* porphyrinic protons. The synthesis of **DPP-ZnP**, **(DPP)₂-ZnP** and **ZnP** was already reported.⁸⁶ The crystal structure of the model compound **ZnP** was obtained by X-ray diffraction analysis (see Fig. S16 and Table S9). Compound **(DPP)₄-ZnP** was prepared in 46% yield with a fourfold Sonogashira coupling reaction performed on the *meso* 5,10,15,20-tetraethynylporphyrin and characterized by NMR and mass spectrometry (Fig. S2-S4).

Linear absorption and emission properties

One-photon spectroscopic and photophysical characterization of the four compounds has been performed in dichloromethane (DCM), dimethyl sulfoxide (DMSO) and H₂O added with 1% DMSO.

The absorption spectra of **ZnP**, **DPP-ZnP**, **(DPP)₂-ZnP** and **(DPP)₄-ZnP** in DCM are compared in Fig. 2, whereas those in DMSO are reported in Fig. S5, together with arbitrarily scaled absorption spectra of the four compounds in H₂O + 1% DMSO. A remarkable bathochromic shift of the absorption spectrum is observed, moving from the porphyrin precursor **ZnP** to the conjugates with one, two and four appended DPP units, due to the decrease of the HOMO-LUMO gap of the transitions, as confirmed by theoretical investigations (see below). The Soret region broadens by increasing the number of DPP

Fig. 2 Absorption spectra of the four compounds in DCM.

substituents, becoming an extended envelop of bands ranging from 400 to 600 nm in **(DPP)₄-ZnP** (Fig. 2 and S5). The calculated transitions (see below) give evidence of various π - π transitions involving localised porphyrin states or delocalised DPP-ZnP states in this region. The solvent polarity has a limited influence on the energy of the transitions but in some cases affects their relative intensity.

We can also observe that the intensity of the lowest-energy Q-band increases while it shifts to the red for the three “linear” compounds, in agreement with earlier reports on conjugated porphyrins.^{18, 59, 87, 88}

Normalized emission spectra of the four conjugates in DCM at room temperature are shown in Fig. 3 (see Fig. S6 for the same comparison in DMSO and H₂O + 1% DMSO). Emission parameters (emission maxima, quantum yields, lifetimes, radiative and non-radiative rate constants) are collected in Table 1.

In DCM and DMSO the conjugates show the typical features of porphyrin fluorescence with a bathochromic shift along the series that leads to emission in the NIR region for **(DPP)₄-ZnP** (Fig. 3 and S6). In H₂O, the spectrum of **ZnP**, **DPP-ZnP**, and **(DPP)₂-ZnP** keeps the typical porphyrin fluorescence features, whereas **(DPP)₄-ZnP** shows a broad and structureless emission (Fig. S6b) indicative of important aggregation phenomena.

Measurements in DCM with 1% pyridine were performed for the larger derivative **(DPP)₄-ZnP**, in order to ascertain the occurrence of aggregation in pure DCM. Whereas the absorption spectrum is slightly perturbed by the addition of pyridine, an emission red-shift of ca. 20 nm is observed with respect to pure DCM, together with a fourfold increase of the fluorescence quantum yield (Table 1, Fig. S7). The spectral shift can be ascribed to the axial coordination of pyridine to the central Zn(II) ion of the porphyrin, and the increased emission efficiency is ascribed to aggregate disruption by axial coordination.[‡] The emission spectrum of each compound progressively shifts to lower energy when the polarity of the solvent increases (DCM < DMSO < H₂O), and the extent of the

shift increases along the series. This behaviour can be assigned to the increasing contribution of low-lying charge-transfer (CT) excited states in the emission with the increment of DPP units in the structure. Theoretical modelling supports this description, as discussed below.

Fig. 3 Normalized corrected room temperature emission spectra of the four compounds in DCM.

Interestingly, the fluorescence quantum yield of the compounds in DCM and DMSO increases along the series (Table 1). This is almost unexpected considering the progressive decrease of the emission energy. The apparent contradiction with the “energy gap law”, predicting lower emission yield with the decrease of the emission energy, can be explained by considering that the oscillator strength increases along the series, due to the strong coupling between the central porphyrin and the appended DPP units.⁸⁹ It can be noticed that the emission lifetime decreases and both radiative and non-radiative rate constants increase, moving from **ZnP** to **(DPP)₂-ZnP** (Table 1). While the observed trend for lifetimes and radiative constants can be ascribed to the increased oscillator strength, the behaviour of the non-radiative constant

Table 1 Photophysical parameters and singlet oxygen production quantum yields at room temperature in several solvents

		$\lambda_{\text{max}}^{\text{f}} / \text{nm}^{\text{a}}$	$\phi_{\text{f}}^{\text{b}}$	$\tau / \text{ns}^{\text{c}}$	$k_{\text{r}} / \text{s}^{-1}$	$k_{\text{nr}} / \text{s}^{-1}$	ϕ_{Δ}^{d}
ZnP	DCM	636, 688	0.11	1.68	6.5×10^7	5.3×10^8	0.74
	DMSO	648, 706	0.14	1.70	8.2×10^7	5.1×10^8	0.71
	H ₂ O ^e	642, 704	6.2×10^{-3}	< 0.05			
DPP-ZnP	DCM	658, 724	0.15	1.06	1.4×10^8	8.0×10^8	0.58
	DMSO	672, 734	0.15	1.00	1.5×10^8	8.5×10^8	0.54
	H ₂ O ^e	684, 750 sh	4.2×10^{-3}	< 0.05			
(DPP)₂-ZnP	DCM	684, 752 sh	0.16	0.78	2.1×10^8	1.1×10^9	0.50
	DMSO	698, 768 sh	0.19	0.85	2.2×10^8	9.6×10^8	0.51
	H ₂ O ^e	780, 864 sh	6.0×10^{-3}	0.58 ^f			
(DPP)₄-ZnP	DCM	702, 776 (724, 798)	0.052 (0.20)	1.78 (2.14)	9.3×10^7 ^g	3.7×10^8 ^g	0.47 (0.36) ^h
	DMSO	722, 796	0.20	2.26	8.8×10^7	3.5×10^8	0.45
	H ₂ O ^e	848	1.8×10^{-3}	0.55 ^f			

In brackets values obtained with 1% pyridine. ^a From corrected emission spectra. ^b Fluorescence quantum yields, see Experimental Section for details. ^c Fluorescence lifetimes, excitation at 465 and 560 nm. ^d Singlet oxygen production quantum yields, see Experimental Section for details. ^e With 1% DMSO. ^f Main component of a multi-exponential decay. ^g Calculated by using the fluorescence quantum yield and the lifetime obtained with 1% pyridine. ^h Mean values from four measurements obtained at different concentrations.

is in accordance with the “energy gap law”.

Emission quantum yields of all compounds in H₂O + 1% DMSO are of the order of $2 - 6 \times 10^{-3}$ and lower than in the other two solvents, likely due to solubility and aggregation issues, confirmed by short or multi-exponential decays (Table 1).

The emission features of the four compounds at 77 K have been investigated in a DCM:MeOH (1:1) glassy mixture and in the same mixture containing 50% of ethyl iodide (Etl). Fluorescence spectra, recorded in the former matrix, show higher spectral resolution compared to room temperature and for the larger conjugates they extend far in the NIR region (Fig. S8). Singlet excited state energies, determined from the fluorescence maxima in the solid matrix at 77 K, decrease from 1.96 eV for **ZnP** to 1.76 eV for **(DPP)₄-ZnP** (Table S1). In order to explore the phosphorescence features of the compounds and gain information on their triplet excited state energies we took advantage of an external heavy atom effect by adding Etl in the solvent mixture. Luminescence spectra collected at 77 K in DCM:MeOH:Etl (1:1:2) reveal a clear phosphorescence for precursor **ZnP**, with maxima at 872 and 996 nm, and weak bands emerging from the tail of fluorescence for the three derivatives (see Fig. S9). Since these bands are not present in the luminescence spectra measured in absence of Etl, we can safely ascribe them to phosphorescence emission. The triplet emission maxima are observed at 914, 1062 and 1220 nm for **DPP-ZnP**, **(DPP)₂-ZnP**, and **(DPP)₄-ZnP**, respectively (Table S1), revealing a decrease in the energy of the emitting triplet that follows the trend observed for fluorescence emission. It can be noticed that the singlet-triplet energy gap increases along the series, from 0.54 eV to 0.74 eV (Table S1). The data indicate that all the examined compounds can sensitize singlet oxygen through a T-T energy transfer, given the energy level of singlet oxygen at 0.98 eV.

In view of the important role of the triplet excited state for singlet oxygen generation, this state has been characterized also by laser flash photolysis experiments in air-free DMSO. The end of pulse transient absorption spectra are shown in Fig. 4 and triplet lifetimes are collected in Table S2. Ground state bleaching features in the region 400–800 nm and a pronounced absorption at 470 and 730 nm for **ZnP** and in the 800–1100 nm range for the DPP-containing molecules are observed. The triplet absorption spectra, representing T₁–T_n transitions, follow the same trend to lower energies observed for ground state absorption spectra, due to the increased delocalization introduced by the conjugated DPP units which decreases the gaps in the excited triplet manifold. The calculated T₁ → T_n transitions and the low-lying triplet states properties are reported and discussed in the section dedicated to the theoretical analysis.

Fig. 4 End of pulse transient absorption spectra of air-free DMSO solutions of the four compounds upon excitation at 532 nm ($E = 3$ mJ/pulse). $A_{532} = 0.2$. The spectrum of **(DPP)₄-ZnP** is multiplied by 5.

Singlet oxygen production

Singlet oxygen quantum yield determinations for the four compounds have been performed by direct measurement of singlet oxygen phosphorescence in DCM and by an indirect method in DMSO.⁹⁰ Determinations in H₂O (or D₂O) were precluded by the low solubility of the compounds in this solvent.

Singlet oxygen luminescence spectra recorded from optically matched DCM solutions of **ZnP**, **DPP-ZnP**, **(DPP)₂-ZnP**⁸⁶ and **(DPP)₄-ZnP** and the chosen standard are reported in Fig. S10. The measured ϕ_{Δ} are collected in Table 1, and show a decrease from 0.74 to 0.47 along the series.

The singlet oxygen quantum yields measured in DMSO (see Fig. S11 and Experimental Section for details) are reported in Table 1 and are almost identical to the values obtained in DCM, showing the same trend along the series.

The decrease of ϕ_{Δ} with the incremental addition of DPP units is consistent with a similar trend in the triplet formation yield, expected on the basis of the increase of the fluorescence quantum yield along the series. In addition, in the case of **(DPP)₄-ZnP**, the weak driving force (ca. 0.04 eV) in the sensitization of singlet oxygen, can also play a role. Overall, the values measured for the four compounds are significantly high, suggesting that the samples can be promising photosensitizers for PDT.

Theoretical analysis of linear optical properties

Structural and electronic properties. The structures of the four ZnP compounds investigated experimentally were simplified as follows: all di- and triethylene glycol chains were cut and replaced either by methoxy groups on the phenylene units or by methyl groups on the DPP units. The main characteristics of the optimized geometries of the four model compounds, so-called m-ZnP, m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP in the electronic ground state, are reported in Table S3 and the corresponding coordinates are given in Table S4. The

optimized structure of m-ZnP is compared to the X-ray structure of ZnP in Fig. S12 and the optimized structures of m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP are depicted in Fig. S13.

The geometrical parameters reported in Tables S3-S4 and the comparison between ZnP and m-ZnP validate the model structures. In addition, insignificant bond lengths variations are observed when going from the reference molecule to the extended systems for which no X-ray structures are available. Geometry optimization of the lowest singlet excited state S₁ (¹A_u) of m-ZnP, main contributor to the intense Q-band, leads to a very small deformation of the structure and a stabilization of ~ 0.06 eV. This corresponds to a calculated emission wavelength of 613 nm to be compared to the experimental value of the emissive intense band observed at 636 nm in DCM. The emissive properties are discussed in more details in the dedicated section (see below).

The frontier Kohn-Sham (KS) orbitals of the four model systems are depicted in Fig. S14a-d.

When going from the reference m-ZnP molecule to the fourfold DPP substituted system m-(DPP)₄-ZnP the calculations evidence an important decrease of the HOMO-LUMO energy gap explained by a destabilization of the HOMO and a significant stabilization of the LUMO as soon as one branch is added (m-DPP-ZnP) due to an electronic delocalization over the new π -conjugated DPP component (Scheme 1). The substitution by DPP units generates also low-lying vacant orbitals localized on the DPP component in our model systems (see Fig. S14) and induces delocalization of the LUMO over the branches as illustrated in Scheme 1, explaining its stabilization. The consequence will be the occurrence of an increasing number of low-lying excited states below 2.6 eV (~ 480 nm) when adding extended ligands with generation of a high density of DPP centered transitions and porphyrin-to-DPP charge-transfer states.

Scheme 1 HOMO and LUMO of m-ZnP, m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP. The KS orbitals energies (in eV) are given for information.

One-photon absorption spectroscopy. The computed OPA spectra of the compounds in DCM are represented in Fig. 5.

The corresponding absorption wavelengths, associated transitions and oscillator strengths are reported in the ESI (Table S5). The most intense ¹A_u transitions are reported in Table S6 and Table S7 together with the involved Kohn-Sham orbitals for m-ZnP/m-DPP-ZnP and m-(DPP)₂-ZnP/m-(DPP)₄-ZnP, respectively.

Fig. 5 TD-DFT one-photon absorption spectra of m-ZnP (top, with experimental spectra of the series in inset), m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP (bottom) in DCM. (The electronic transitions have been obtained with the Dgrid package).⁹¹

The computed spectra of all systems are characterized by a low-energy band with a maximum at 596 nm ($f = 0.536$) in m-ZnP, 670 nm ($f = 1.71$) in m-DPP-ZnP, 720 nm ($f = 2.45$) in m-(DPP)₂-ZnP and 758 nm ($f = 1.633$) for m-(DPP)₄-ZnP. This observed red-shift within the series by substitution of extended ligands, also observed experimentally, is due to an expected destabilization of the HOMO together with a stabilization of the LUMO as discussed before. Whereas the lowest energy calculated band attributed to the Q-band ($S_0 \rightarrow S_1$ transition) in m-ZnP is shifted to the blue with respect to the experimental one by about 33 nm ($\lambda_{\text{max exp}} = 629$ nm), the same band is shifted to the red in the DPP-substituted complexes. The red-shift as compared to the experimental values increases from DPP-ZnP (~ 22 nm, $\lambda_{\text{max exp}} = 648$ nm) to (DPP)₂-ZnP and (DPP)₄-ZnP (~ 55 nm, $\lambda_{\text{max exp}} = 663$ nm and 703 nm respectively). This illustrates the difficulty at computing excited states properties in these large systems. Nevertheless the agreement is still semi-quantitative. The different behaviour of the reference m-ZnP molecule could be explained by the

contribution of another transition to the Q-band corresponding mainly to the HOMO-1 $\rightarrow$ LUMO excitation. This $S_0 \rightarrow S_2$ transition is calculated at 580 nm with a modest oscillator strength $f = 0.062$ (Table S5). This contribution disappears in the 2- and 4-DPP substituted compounds since the HOMO-1 is significantly stabilized with respect to the HOMO by becoming localized on the extended ligands (Fig. S14).

Six transitions calculated at 415 nm ($f = 0.525$), 431 nm ($f = 0.05$), 446 nm ($f = 0.526$), 467 nm ($f = 0.12$), 472 nm ($f = 1.433$) and 481 nm ($f = 1.06$), contribute to the intense Soret band observed in the model complex m-ZnP between 400 and 500 nm. These transitions lead to either $\pi-\pi^*$ states localized on the porphyrin ring or to less intense transitions corresponding to charge separated (CS) from the phenylene to the porphyrin π system. The agreement between the theoretical spectrum of m-ZnP (Fig. 5, in red) and the experimental spectrum of the reference molecule **ZnP** (Fig. 2, in red) is excellent both in energies and relative intensities. In contrast, while the theoretical spectra of m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP reproduce qualitatively the shape and energies of the experimental spectra of the title molecules, the relative theoretical intensities of the Q and Soret bands are reversed as compared to the experimental one's. This may be due to the limited number of eigenvalues requested in the TD-DFT calculations (40 roots) that is reasonable for the small molecule but less valid for the extended systems. Indeed, upper states are important for the computation of the lowest part of the spectra because they interact with the lowest states giving them more intensity. This bias is even more dramatic for the two-DPP and four-DPP substituted model systems m-(DPP)₂-ZnP and m-(DPP)₄-ZnP. Improving the calculations by increasing the number of requested eigenvalues to 80 roots is impossible in these large molecules and is beyond the current computer facilities. Furthermore we have neglected the flexibility of the molecule. Rotations in the DPP arms by breaking the delocalization between the porphyrin ring and the DPP would shift the spectra towards the blue. Nevertheless, the experimental band that characterizes **DPP-ZnP** between 400 and 520 nm (Fig. 2, in blue) is well reproduced by theory with a shoulder composed of three states calculated at 482 nm ($f = 0.67$), 514 nm ($f = 0.67$) and 532 nm ($f = 0.181$) and one intense peak attributed to four transitions at 460 nm ($f = 0.387$), 448 nm ($f = 0.547$), 442 nm ($f = 0.275$) and 426 nm ($f = 0.732$) as compared to an experimental maximum at 450 nm. The small absorption observed at 585 nm on the experimental spectrum is also reproduced at 600 nm with very modest oscillator strength of 0.057. This transition and the next one calculated at 560 nm ($f = 0.136$), both of low intensity, describe a major charge transfer from the DPP ligand to the porphyrin ring (Scheme 1 and Table S5). In the three DPP-substituted model molecules the theoretical spectra exhibit an intense Q-band remaining localized, similarly to the experimental spectra of the title systems. The theory points to a significant broadening of the Soret band in m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP due to increasing charge transfer contributions and large mixing

between excited states in this domain of energy, especially for the four-DPP substituted system.

Emissive properties and low-lying triplet states. The $S_0 \rightarrow T_n$ transitions calculated at the electronic ground state and lowest triplet T_1 excited state optimized structures of m-ZnP, m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP are reported in Table S8, as well as the $T_1 \rightarrow T_n$ transition energies directly contributing to the experimental transient absorption spectra depicted in Fig. 4. Five low-lying $T_1 \rightarrow T_n$ transitions with significant oscillator strengths may contribute to the transient absorption spectra of **ZnP** and **DPP-ZnP** depicted in Fig. 4. These transitions are calculated between 1019 nm and 697 nm (m-ZnP) with intense absorptions at 765 nm and 705 nm in agreement with the experimental data (Table S2). The series of $T_1 \rightarrow T_n$ transitions in m-DPP-ZnP is calculated between 991 nm and 664 nm with oscillator strengths that never exceed 0.099 but within the experimental spectral range. Only a few lowest $T_1 \rightarrow T_n$ transitions of m-(DPP)₂-ZnP and m-(DPP)₄-ZnP have been accessible by the calculation due to the size of the molecules (see Table S8).

The model systems are characterized by a lowest triplet T_1 (3A_u) excited state calculated at 1000 nm for m-ZnP, 1170 nm and 1177 nm for m-(DPP)₂-ZnP and m-(DPP)₄-ZnP, respectively (Table 2) slightly above the triplet-singlet O_2 energy level of 1270 nm. These values corroborate the good quantum yield of singlet oxygen production determined for the three molecules and compare rather well with the experimental values provided in Table 2 for comparison.

In contrast the T_1 state (3A) of m-DPP-ZnP is calculated at 1509 nm with the standard method and 1231 nm when corrected by the Tamm Dancoff Approximation (TDA) that takes into account the defect of TD-DFT at describing low-lying triplet excited states in some specific situations. These theoretical values do not correlate with the significant singlet oxygen quantum yield of **DPP-ZnP** determined experimentally. The underestimation of the energy of the lowest T_1 state of m-DPP-ZnP as compared to the experimental value of 914 nm and to the other molecules, owning a centre of inversion, can be

Table 2 Theoretical emissive properties of m-ZnP, m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP described by the low-lying singlet and triplet S_1 , T_1 and T_2 states (transition energies in eV and the corresponding wavelengths).

	m-ZnP	m-DPP-ZnP	m-(DPP) ₂ -ZnP	m-(DPP) ₄ -ZnP
Exp. Max. at 77K	872 nm 996 nm	914 nm	1062 nm	1220 nm
T_1	1.249 a^3A_u 1000 nm 908 nm ^a	0.828 1509 nm 1231 nm ^a	1.068 a^3A_u 1170 nm -	1.062 a^3A_u 1177 nm -
T_2	1.822 c^3A_u 686 nm	-	1.584 c^3A_u 789 nm	-
S_1	2.038 $f=0.63$ a^1A_u 613 nm	-	1.571 $f=2.90$ a^1A_u 796 nm	-

^a With the Tamm Dancoff Approximation.

explained by an overestimation of the nuclear relaxation due to lack of symmetry constraints. This is illustrated by a stronger HOMO-LUMO electronic delocalisation in the corresponding transition (Scheme 1), a situation of large overlap leading to well known triplet instabilities within the TD-DFT framework, corrected in principle by TDA.⁹²

Tentative assignment of the experimental emissive properties of the title molecules is based on the energies of the lowest singlet and triplet states reported in Table 2. The intense peaks observed in DCM at 636 nm (**ZnP**), 658 nm (**DPP-ZnP**), 684 nm (**(DPP)₂-ZnP**) and 702 nm (**(DPP)₄-ZnP**) (Fig. 3 and Table 1) are assigned to the lowest S_1 states. This is confirmed in the case of m-ZnP with the presence of the S_1 (b^1A_u) state calculated at 613 nm and corresponding to the HOMO-LUMO excitation.

The shoulders of decreasing intensities when going from **ZnP** to the DPP substituted molecules and observed at lower wavelengths (Fig. 3) are more difficult to attribute. Indeed the calculations do not put in evidence other singlet states around 688 nm, emission wavelength of the shoulder observed for the reference molecule ZnP (Table 1). There is no experimental evidence at room temperature of a possible contribution to this shoulder of the T_2 state (c^3A_u) calculated at 686 nm in the model system m-ZnP (Table 2). Consequently the origin of this shoulder can be associated either to vibrational features in S_1 or to the contribution of other conformers.

The emissive S_1 wavelength of 796 nm (Table 2) calculated for m-(**DPP**)₂-ZnP does not coincide with the experimental value of the most intense emission observed at 684 nm in DCM for this molecule (Table 1) but is close to the lowest shoulder at 752 nm. It is difficult to confirm the emission spectra assignment for the DPP substituted molecules because of the limits of the calculations due to the size of the systems and the number of TD-DFT roots to be requested in the optimization procedure which is especially challenging in the case of the singlet excited states.

Two-photon absorption spectroscopy

The TPA properties were investigated by the two-photon induced fluorescence method, as already reported.⁸⁶ The experimental two-photon excitation spectra of **ZnP**, **DPP-ZnP** and **(DPP)₂-ZnP** in DCM (already reported)⁸⁶ and the one of **(DPP)₄-ZnP** in pyridine are represented in Fig. 6. In DCM, at the concentration (10^{-4} M) used for this experiment, aggregation of **(DPP)₄-ZnP** was noticed even upon addition of 1-5% pyridine whereas in pure pyridine, **(DPP)₄-ZnP** was soluble allowing two-photon excitation spectra to be recorded. For this last compound, σ_2 has been determined beyond 890 nm to ensure a quadratic dependency of the fluorescence intensity toward the excitation power, indicating a two-photon process. Compared to **ZnP**, showing a low two-photon absorption cross section σ_2 of less than 20 GM over the whole spectra, **DPP-ZnP** and **(DPP)₂-ZnP** display significant two-photon absorption in two spectral regions, from 800 to 840 nm and from 910 to 930 nm (Fig. 6). A high increase in σ_2 values is noticed on going from the one DPP to the two DPP conjugated systems, from 640 to

Fig. 6 Two-photon excitation spectra of (a) **ZnP** (red), **DPP-ZnP** (blue) and **(DPP)₂-ZnP** (green) in DCM and (b) **(DPP)₄-ZnP** in pyridine (purple).

1360 GM at 810 nm and from 1950 to 4020 GM at 910 nm for **DPP-ZnP** and **(DPP)₂-ZnP**, respectively. The same trend is observed in DMSO; however, the σ_2 values obtained are much lower, as an example, a σ_2 of 535 GM was measured for **(DPP)₂-ZnP** at 910 nm (see Fig. S15). Moving to four conjugated DPPs, the spectrum of **(DPP)₄-ZnP** in pyridine displays also a maximum at 910 nm, with a σ_2 value of 1340 GM. Obviously, the polarity and coordination properties of the solvent have limited effect on the energy of the two-photon induced absorption transitions but affect more strongly their probabilities, as already noticed in the linear absorption properties of these molecules (see above).

Theoretical analysis of two-photon absorption properties

The calculated two-photon absorption spectra of m-(**DPP**)₂-ZnP and m-(**DPP**)₄-ZnP in DCM are represented in Fig. 7. The TPA wavelengths and associated cross-sections are reported in Table 3 and the changes in electronic densities between the electronic ground state and the TPA active intermediate states are depicted in Fig. 8.

In agreement with the experiments we observe a significant activity of m-(**DPP**)₂-ZnP with a maximum at about 1065 nm, red-shifted as compared to the experimental value of 915 nm. This intense band is composed of two peaks calculated at 1064 nm and 1170 nm with large theoretical cross-sections $\delta_{TP} = 4.43 \times 10^6$ a.u. (17 700 GM) and $\delta_{TP} = 3.91 \times 10^6$ a.u. (12 800 GM), respectively (Table 3). The weaker bands at 820 - 960 nm are

Fig. 7 Theoretical two-photon absorption spectra of $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$ in DCM.

composed of several bands at 821 nm, 882 nm, 898 nm, 939 nm and 964 nm of modest cross-sections ($\sim 104\text{--}105$ a.u.). $m\text{-(DPP)}_4\text{-ZnP}$ is characterized by three peaks calculated at 1040 nm, 1140 nm and 1200 nm of very high intensities (Table 3). Only the active states with cross sections greater than 10 000 GM are reported in Table 3. The theoretical TPA values obtained for the ten lowest active intermediate states, as well as those of the less active molecules, namely $m\text{-ZnP}$ and $m\text{DPP-ZnP}$ are reported elsewhere.⁹³

As illustrated by the changes in electronic densities depicted in Fig. 8, both charge transfers, either from the DPP entities to the porphyrin or from the porphyrin core to the DPP branches, give large TPA cross sections (Table 3). Of course, charge transfer from the porphyrin core to the DPP branches is more favourable because it follows the natural trends, namely a donor to acceptor or to a neutral group CT. This is exemplified by the most intense TPA cross sections obtained for the states $|2\rangle$ and $|6\rangle$ of the $(\text{DPP})_2$ and $(\text{DPP})_4$ substituted systems, respectively. Increasing the number of DPP entities does not necessarily improve the δ^{TP} cross section. However, the directionality that will drive the transfer of electronic density along one axis in $m\text{-(DPP)}_2\text{-ZnP}$ or two axis in $m\text{-(DPP)}_4\text{-ZnP}$ is an important factor as this is illustrated in the case of the $(\text{DPP})_4$ substituted molecule (Fig. 8). Indeed, the two active states $|6\rangle$ and $|5\rangle$ are described by very similar electronic density changes. They correspond to excitations from the HOMO (Scheme 1) to low-lying vacant orbitals of symmetry a_u depicted in Scheme 2. In the most intense $|0\rangle \rightarrow |6\rangle$ transition

the directionality of the CT is identical for the four DPP branches generating four additive components along x and four additive components along y by projection of the transition dipole moment vectors on the x and y axis. This results into two large TP tensor terms, namely S_{xx} and S_{yy} evaluated at ~ 3000 a.u., each. In the less intense TP $|0\rangle \rightarrow |5\rangle$ transition the CT directionalities are different along the two axes of the DPP branches because of the change of phase in the vacant accepting orbital (Scheme 2). In turn this results into non-additive contributions of the dipole transition moments and only one significant TP tensor term S_{xy} evaluated to ~ 3000 a.u. As a consequence the δ^{TP} cross section of the $|0\rangle \rightarrow |5\rangle$ transition is roughly half of the δ^{TP} cross section of the $|0\rangle \rightarrow |6\rangle$ transition (Table 3).

A careful analysis of the changes in electronic densities of the active TP transitions in $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$ (Fig. 8) indicates that an initial delocalized electronic density will drive the CT process along the π conjugation channel more efficiently. The relevance of this criteria is confirmed by the very similar nature of CT in the most active state $|2\rangle$ of $m\text{-(DPP)}_2\text{-ZnP}$ and $|6\rangle$ of $m\text{-(DPP)}_4\text{-ZnP}$.

In contrast to the theoretical results the experimental spectra exhibit moderate cross sections for $m\text{-(DPP)}_2\text{-ZnP}$ (< 4000 GM) and $m\text{-(DPP)}_4\text{-ZnP}$ (< 1500 GM) (Fig. 6). Moreover they do not show any TPA activity beyond 1000 nm whereas the theoretical TPA (Fig. 7) exhibit intense peaks between 1000 and 1200 nm with cross sections greater than 10 000 GM (Table 3).

A direct comparison between theoretical and experimental TPA properties is hazardous for several reasons. The solvent effects and the various conformers present in the real experiment are not realistically modelled by the present theoretical approach. Indeed the molecules are surrounded by a polarized continuum cavity taking into account implicitly the static solvent effects within the non-linear response theory. This is a crude approximation but the only one available nowadays. Alternative molecular dynamics simulations coupled to QM/MM approaches are not applicable to large molecular systems.⁹⁴ Other important limitation is the occurrence of resonances that increase artificially the theoretical cross sections by at least one order of magnitude because of the neglect of double excitations that is intrinsic to TD-DFT.⁹⁵ Other effects such as vibronic coupling or the limited number of states requested in the non-linear response framework may overestimate the theoretical TPA cross-sections and underestimate the frequencies.

Table 3 TD-DFT TPA wavelengths (nm) and cross sections δ^{TP} (GM) of the active $|n\rangle$ 1A_g intermediate states of $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$.

	Intermediate state $ n\rangle$	TPA wavelength ^a	δ^{TPa}
$m\text{-(DPP)}_2\text{-ZnP}$	$ 1\rangle$	1170	12 800
	$ 2\rangle$	1064	17 700
$m\text{-(DPP)}_4\text{-ZnP}$	$ 3\rangle$	1200	18 500
	$ 5\rangle$	1140	11 100
	$ 6\rangle$	1040	19 100

^a From Ref. 93.

Fig. 8 Changes in electronic densities when going from the electronic ground state to the intermediate TP active 1A_g excited states of $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$ (red: decrease of density; green: increase of density).

Scheme 2 Vacant accepting orbitals of symmetry a_u involved in the $|0\rangle \rightarrow |6\rangle$ (left) and $|0\rangle \rightarrow |5\rangle$ (right) transitions in $m\text{-(DPP)}_4\text{-ZnP}$. Red arrows indicate the directionality of the CT in term of dipole transition moments components.

The theoretical results analysed above reflect an ideal situation of an isolated molecule in a totally transparent medium, which is a particular situation very different from the reality. Nevertheless the low TPA activity detected experimentally for $m\text{-(DPP)}_4\text{-ZnP}$ is difficult to interpret and rationalize according to the clear criteria developed above in term of electron densities and generated dipole transition moments. One hypothesis is that the measured TP induced fluorescence is biased and does not reflect entirely the potential activity determined by theory. Indeed according to a detailed analysis recently published on the present systems⁹³ several singlet states are accessible via TPA. The calculations put in evidence significant TPA activity at 1025, 1064 and 1040 nm for $m\text{-DPP-ZnP}$, $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$, respectively. TPA at these wavelengths will populate singlet A states of $m\text{-DPP-ZnP}$ and A_g states of $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$ situated around 500 nm, nearly degenerate with A and A_u OPA excited states calculated between 480 and 550 nm. We may expect very efficient internal conversion between the TPA and OPA singlet states by vibronic coupling. Consequently TPA will induce efficient fluorescence from the OPA states leading to the TPA signal detected experimentally at about 910 nm for the three systems. In contrast the theoretical TPA activity put in evidence around 1200 nm in $m\text{-(DPP)}_2\text{-ZnP}$ and $m\text{-(DPP)}_4\text{-ZnP}$ will potentially populate singlet excited states situated around 600 nm, in a region where the OPA activity is very weak with a low density of absorbing states not necessarily highly fluorescent. Moreover this low density of singlet excited states is less favourable to vibronic couplings at the origin of efficient internal conversion between TPA and OPA singlet excited states. This could explain the absence of experimental TPA signal beyond 1000 nm.

Further joined experimental/theoretical investigations should be pursued in order to conclude about possible correlation between measured TP induced fluorescence and potential TP activity determined by theory.

Conclusions

An in-depth study of the one- and two-photon photophysical properties and a detailed theoretical analysis of three DPP-substituted porphyrins, as well as a model porphyrin compound, is reported. The increased π -conjugation of the porphyrinic systems with one to four *meso*-attached DPP substituents has a notable impact on the ground and excited states properties and singlet oxygen production. Absorption and emission features are gradually shifted towards the infra-red and despite the decrease in the energy of the emitting singlet, the fluorescence of the systems increases. This unusual behaviour is ascribed to the higher oscillator strength of the HOMO-LUMO transition with extended electron delocalisation, as confirmed by TD-DFT calculations. Phosphorescence of the compounds could be measured at low temperature, showing that the lowest triplet excited state decreases in energy with the increased conjugation. It remains nevertheless above that of singlet oxygen leading to efficient singlet oxygen sensitization. Significant values of two-photon absorption cross-section were observed in the systems with one and two DPP appended units. In accordance with the experiments, calculated TP-absorption spectra evidence that these states can be reached efficiently by two-photon absorption from charge-transfer intermediate states involving the DPP branches. Increasing the number of DPP ligands does not necessarily improve the two-photon activity. More important is the directionality of the charge transfer along the acceptor-donor-acceptor axis, as illustrated in the two- and four-substituted DPP systems. Overall the study reveals a high potential as one- and two-photon photosensitizers and NIR emitters for the DPP-ZnP conjugates.

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Experimental Section

Spectroscopy and photophysics

DCM and DMSO were of spectroscopic grade from Merck and Carlo Erba, respectively. Tri-distilled (Millipore Milli-Q) H₂O was used. 1,3-diphenylisobenzofuran (DPBF), Zn-phthalocyanine (ZnPc) and pyridine were from Aldrich. Ethyl iodide was from Alfa Aesar.

Absorption spectra were recorded with a Perkin-Elmer Lambda 650 UV-Vis and with a Lambda 9 UV-Vis-NIR spectrophotometers. In the mixture H₂O + 1% DMSO, close to a pure aqueous environment, the compounds were found to be reasonably soluble but exact molar absorption coefficient determination was precluded.

Emission spectra were collected with an Edinburgh FLS920 fluorimeter equipped with a Peltier-cooled Hamamatsu R928 PMT (200-850 nm), and with an FLS920 fluorimeter (Edinburgh) equipped with an Hamamatsu R5509-72 InP/InGaAs photomultiplier tube supercooled at 193 K in a liquid nitrogen cooled housing and a TM300 emission monochromator with a NIR grating blazed at 1000 nm (sensitivity range: 300-1700 nm). The spectra have been corrected for the wavelength dependent phototube response. The fluorescence quantum yields have been determined with reference to TPP (tetra-phenyl-porphyrin) in aerated toluene ($\phi_{\text{fl}} = 0.11$)⁹⁶ for **ZnP**, **DPP-ZnP**, and **DPP-ZnP**, and with reference to **(DPP)₂-ZnP** in aerated DCM ($\phi_{\text{fl}} = 0.16$, Table 1) for **(DPP)₄-ZnP**. Fluorescence lifetimes have been measured with an IBH Time Correlated Single Photon Counting apparatus with excitation both at 465 nm and 560 nm. The analysis of the luminescence decay profiles against time was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer. Experiments at 77 K in frozen glasses made use of quartz capillary tubes immersed in liquid nitrogen contained in a home-made quartz dewar. Phosphorescence measurements made use of a Kimmon Koha Co. Ltd. HeCd laser as excitation source ($\lambda_{\text{exc}} = 442$ nm, the power has been reduced to ca. 7 mW to avoid annihilation effects).

Estimated errors are 10% on exponential lifetimes, 20% on quantum yields, 20% on molar absorption coefficients and 3 nm on emission and absorption peaks.

Nanosecond laser flash photolysis experiments were performed by systems based on Nd:YAG lasers: a JK laser (18 ns pulse duration, 532 nm, 3 mJ/pulse, UV-Vis detection) and a Surelite Continuum laser (6 ns pulse duration, 532 nm, 3 mJ/pulse, UV-Vis-NIR detection), using a right-angle analysis on the excited sample.⁹⁷ The samples were bubbled with argon for ca. 15 min and sealed in homemade 10 mm optical path length cells.

Singlet oxygen production quantum yields in DCM have been measured in air equilibrated solutions with reference to Rose Bengal bis(triethyl-ammonium)salt $\phi_{\Delta} = 0.48$ in DCM),⁹⁸ by comparing the intensity of singlet oxygen phosphorescence spectra measured with the NIR fluorimeter described above. Excitation at 442 nm has been performed with a Kimmon Koha Co., Ltd. HeCd laser (with power reduced to ca. 7 mW). For **(DPP)₄-ZnP** a concentration dependent study has been performed in DCM and DCM + 1% pyridine. The measured yields are almost unaffected by the concentration of the solution, with a mean value of 0.47 in DCM and 0.36 in DCM + 1% pyridine (Table 1).

Singlet oxygen production quantum yields in DMSO have been measured with a comparative method using DPBF as a singlet oxygen trap, which is oxidized by singlet oxygen and its degradation can be monitored by the decrease of its

absorbance.⁹⁹ ZnPc has been used as a standard ($\phi_A = 0.67$).¹⁰⁰ Solutions of the standard or of the compound containing DPBF 2.2×10^{-5} M, prepared in the dark, have been irradiated at 646 nm ($A_{646} \sim 0.3$) by using an irradiation set-up composed by a 150 W Xenon lamp (LOT) and a Omni- λ 150 monochromator (Zolix), under continuous stirring. The light intensity was 6 mW/cm². The singlet oxygen quantum yield of the sample (ϕ_A) has been determined by using equation (1):

$$(1) \quad \Phi_A = \Phi_{\Delta}^{Std} \frac{R_{\Delta}^{Std} I_{abs}^{Std}}{R^{Std} I_{abs}}$$

where R and R^{Std} are the DPBF degradation rates for the sample and the standard, respectively, and I_{abs} is the absorption at the excitation wavelength calculated as described previously.¹⁷ The absorption spectrum of DPBF at each irradiation step has been derived by subtracting the constant absorption contribution of the examined compound from the spectrum of the mixture. The decrease of DPBF absorption has been followed at 400 nm, a wavelength chosen to avoid distortion effects due to the high absorbance of some solutions around 450 nm.

Two-photon excitation spectra

The TPA cross-section spectra were obtained by the up-conversion fluorescence method as described previously¹⁰¹ using an Insight Spectra-Physics (680 nm/1300 nm) femtosecond laser. The excitation beam was collimated over the cell length (10 mm). The fluorescence, collected at 90° to the excitation beam, was focused into an optical fiber connected to a spectrometer. The incident beam intensity was adjusted to ensure an intensity-squared dependence of the fluorescence over the whole spectral range. Calibration of the spectra was performed by comparison with the published 800–950 nm Rhodamine B two-photon absorption spectrum.¹⁰² Below 800 nm, a significant contribution from one-photon absorption was noticed for (DPP)₂-ZnP and (DPP)₄-ZnP by a non-quadratic dependence of the emitted fluorescence vs the laser power and points below this wavelength were discarded.

Computational details

The structures of model compounds for the four title complexes ZnP, DPP-ZnP, (DPP)₂-ZnP and (DPP)₄-ZnP (Fig. 1) have been fully optimized in the electronic ground state at the density functional theory (DFT) level with the B3LYP functional^{22, 103} with triple- ζ basis sets.¹⁰⁴ Owing to the size of the molecules depicted in Fig. 1 models have been built by replacing the N-ethylene-glycol chains by N-methyl-glycol groups and the phenyl-polyethylene-glycol chains by methoxy groups. The model systems, the electronic densities of which should not differ dramatically from the one of the real molecules, are labeled m-ZnP, m-DPP-ZnP, m-(DPP)₂-ZnP and m-(DPP)₄-ZnP. All the calculations have been performed with no symmetry for m-ZnP, m-DPP-ZnP and m-(DPP)₂-ZnP and with a center of inversion (CI) for m-ZnP and m-(DPP)₄-ZnP. Both series of results, with and without symmetry, are very similar for m-ZnP including structural and optical properties. All the results presented here are the one obtained without any symmetry, excepted for the 4-substituted molecule

(DPP)₄-ZnP system for which a CI has been kept due to the size of the molecule. A tentative interpretation of the emissive properties in the series is based on the optimized structures of the lowest singlet and triplet excited states at the same level of theory keeping the CI. The scalar relativistic effects are taken into account within the zero-order regular approximation (ZORA).¹⁰⁵ The solvent effects have been taken into account by means of the conductor-like screening model COSMO model^{106–108} (with $\epsilon = X$ for DCM) as implemented in ADF.^{109, 110} On the basis of the electronic ground states optimized geometries the theoretical one-photon absorption spectra of the four model molecules have been calculated at the time-dependent DFT (TD-DFT) level of theory^{111, 112} with the ADF-2013 quantum chemistry package¹¹³ whereas the two-photon absorption spectra of m-(DPP)₂-ZnP and m-(DPP)₄-ZnP have been computed using the poles and residues of quadratic response functions in the framework of TD-DFT as implemented in the DALTON program package.¹¹⁴ The details of the DALTON calculations for the whole series of Zn porphyrin conjugates are reported elsewhere.⁹³

Notes and references

‡ Determinations in pure pyridine were also performed and revealed emission maxima at 728 and 804 nm, emission quantum yield of 0.26 and lifetime of 2.44 ns, values similar to the ones obtained in DCM + 1% pyridine.

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