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Tuning photochemical properties of phosphorus(v) porphyrin photosensitizers†

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Photosensitizing and emission properties of P(v) porphyrins were studied. The nature of the axial ligands, occupying the apical position on the P centre adopting an octahedral coordination geometry, strongly influences singlet oxygen generation and charge transfer and allows switching between the two processes.

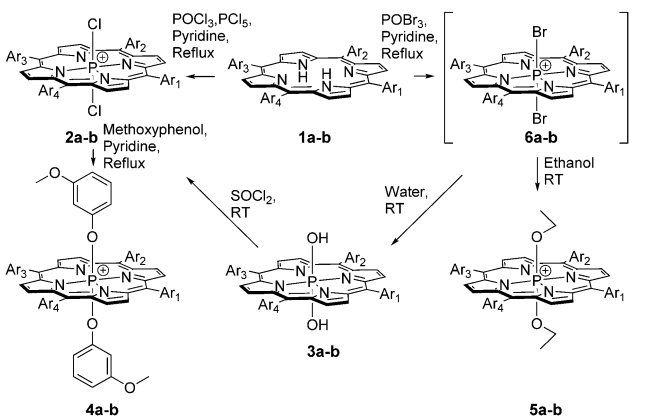
The very rich photochemical as well as photophysical properties of porphyrin derivatives have triggered extensive investigations including their role as photosensitizers in catalysis and medicines.[1–5] In photosensitization, water-soluble derivatives, in particular cationic ones, are of interest, in particular in medicine. Indeed, owing to their charge nature, porphyrin based dyes by crossing the cell membrane bind to DNA molecules by intercalation.[6–9] This process is of prime importance for antimicrobial photodynamic therapy owing to increasing resistance of bacteria to antibiotics. Usually, the generation of cationic species of porphyrin derivatives is achieved by the implementation of positive charges at their periphery.[7,8,10] Alternatively, one may take advantage of the propensity of the porphyrin tetraaza core to bind metal centres to generate charged species by using metal cations with the oxidation state greater than 2. This approach has been explored using P(v)*meso*-tetraphenylporphyrins.[9,11–15] For these species, the phosphorous atom, located at the centre of the porphyrin backbone, is hexacoordinated adopting a distorted octahedral coordination geometry surrounded by four N atoms and two axial ligands occupying the two apical positions. For some P(v)TPP derivatives, rather high quantum yields (up to 0.7) in water for singlet oxygen generation (SO) were reported.[9,11,12] In a careful survey of the literature, it appeared that the nature of axial ligands plays a major role in their photophysical features. For example, for P(v) porphyrins bearing aryloxy moieties, the photoinduced electron transfer (PET) processes from the aromatic axial ligands to the porphyrin core may be modulated.[13]

However, to the best of our knowledge, relationships between singlet oxygen generation and the nature of axial ligands or peripheral substituents of the porphyrin core have not been explored to date.

Herein we report on the design and synthesis of two series of P(v) porphyrin (TPP and MPyP (*meso*-(5-pyridyl)-(10,15,20-triphenyl)porphyrin)) derivatives bearing four different types of axial ligands (Scheme 1) and their propensity to generate singlet oxygen in water and in chloroform and DMSO.

The parent porphyrins **1a** and **1b**, as well as P(v) porphyrins **2a**, **2b**, **3a**, **3b**, **4a**, and **4b**[15] and ethoxy derivatives **5a** and **5b**, were synthesized (for synthetic procedures and full characterization, see the ESI,† Fig. S2–S23).

For all described compounds, steady-state luminescence properties were measured in the same solvents (Table 1). Emission spectra and Stokes shifts are presented in Fig. 1 and in the ESI†



Scheme 1 Syntheses of P(v) porphyrins in this communication; **1a–6a**: Ar_1, Ar_2, Ar_3, Ar_4 = phenyl, **1b–6b**: Ar_1 = pyridyl, Ar_2, Ar_3, Ar_4 = phenyl.

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Table 1 Photosensitizing and fluorescence properties of P(v) porphyrins **2a,b**, **3a,b**, **4a,b** and **5a,b**. For SO quantum yield determination, TPP and 5,10,15,20-tetra(4-sulfonatophenyl)-porphyrin in organic media and water respectively were used

	Chloroform		DMSO		Water	
Complex	Φ_Δ	Φ_f	Φ_Δ	Φ_f	Φ_Δ	Φ_f
2a	0.93	0.014	0.36	0.016	Hydrolysis	
3a	0.73	0.027	0.24	0.126	0.11	0.119
4a	0.18	0.009	0.00	0.005	0.00	0.008
5a	0.77	0.036	0.34	0.125	0.12	0.073
2b	1.00	0.012	0.41	0.029	Hydrolysis	
3b	0.99	0.029	0.31	0.119	0.29	0.113
4b	0.16	0.005	0.00	0.006	0.00	0.007
5b	0.99	0.060	0.37	0.104	0.46	0.083

(Table S1 and Fig. S24–S29). SO generation quantum yields were determined *via* chemical methods using SO sensitive traps (Fig. 2 and Fig. S30, S31) such as 1,3-diphenylisobenzofuran (DPBF) for non-aqueous media (chloroform and DMSO)[1] and Singlet Oxygen Sensor Green (SOSG)[16] for water (for experimental procedures and calculations, see the ESI†).

For all compounds investigated, quantum yields of SO generation are in the 0–100% range; however, up to 12% variation for the fluorescence quantum yield is observed (Table 1). Complexes **2a** and **2b**, bearing axial chloro ligands, undergo partial hydrolysis in water and thus were not investigated.

Analysis of the data gathered in Table 1 reveals three main dependences of both quantum yield of SO generation and steady-state fluorescence resulting from the nature of solvent, *meso*-substituents and axial ligands.

The photosensitizing efficiency and solvent nature are correlated through the SO lifetime: $\sim 2.5 \times 10^{-4}$ s in chloroform,[17] $\sim 5.5 \times 10^{-6}$ s in DMSO[18] and $\sim 4 \times 10^{-6}$ s in water,[19] indicating that, for example, for the same compound **5a**, the quantum yield is decreased by *ca.* 6 times when replacing $CHCl_3$ by H_2O. At the same time, the fluorescence quantum yields for **5a** and for **3a** are increased by a factor of two and four, respectively.

The nature of substituents located at the *meso* positions of the porphyrin also plays a pertinent role in both the quantum yields of SO generation and steady-state fluorescence. Indeed, TPP derivatives (series **a**) are less efficient than MPyP complexes (series **b**). Although a difference of *ca.* 1.3 times in the quantum yield of SO generation between **5a** and **5b** is observed in chloroform, in water a factor of *ca.* 4 is obtained. Such an increase in water could result from a higher solubility of P(v)MPyP owing to the presence of the pyridyl unit. Although one would also expect a difference in the fluorescence quantum yield, almost the same values are observed in water and in organic media.

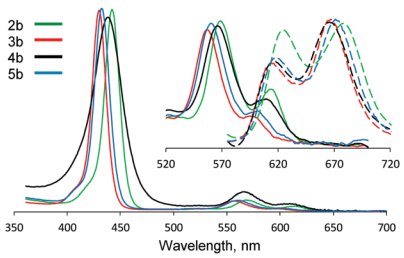


Fig. 1 Normalized absorption (solid line) and fluorescence (dashed line, λ_{ex} = 550 nm) spectra of **2b–5b** in DMSO at room temperature.

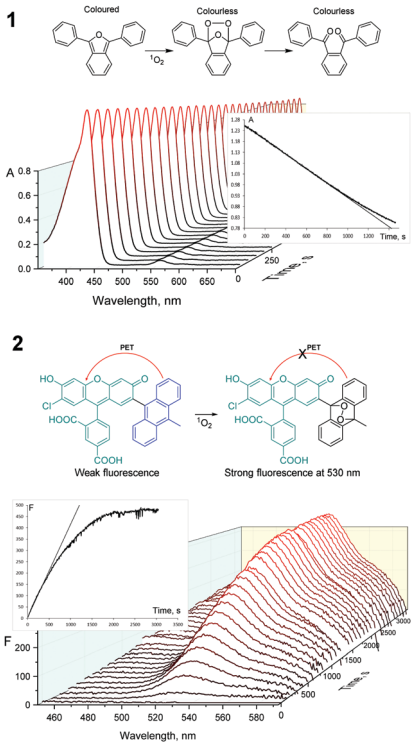


Fig. 2 Oxidation of DPBF by **5b** in chloroform (1) and SOSG in water (2) in the presence of singlet oxygen, monitored by UV-Vis spectroscopy and fluorimetry. Plots of DPBF and **5b** overlapped absorption peaks (428 nm) and SOSG emission peaks (530 nm, λ_{ex} = 405 nm) *vs.* time are presented in the insets.

Depending on the nature of axial ligands, substantial changes in the quantum yields of SO generation and fluorescence are observed. Indeed, the presence of aromatic methylresorcinol at the apical positions (complexes **4a** and **4b**) dramatically decreases both values. These derivatives no longer generate singlet oxygen in water and in DMSO. As previously described, this should result from another competitive relaxation pathway such as charge-transfer (CT) processes.[13] In order to verify this hypothesis, time-resolved transient absorption spectroscopy was used. Transient absorption spectra (TA) revealed the presence of a prominent bleaching band (BL) corresponding to the Soret absorption band close to *ca.* 440 nm. A wide excited absorption band (ESA) at 470–490 nm, partially overlapping with the weak BL Q-bands, is observed.

TA changes show kinetic components that correspond to three time scales (Fig. S32 and S33, ESI†): (1) 100–200 fs for intramolecular vibrational energy redistribution; (2) ~1 ps for vibrational redistribution caused by elastic collision with solvent molecules; and (3) time scale from a dozen to hundreds ps and ns corresponding to the intramolecular transitions between different electronic states. TA experiments revealed the significant

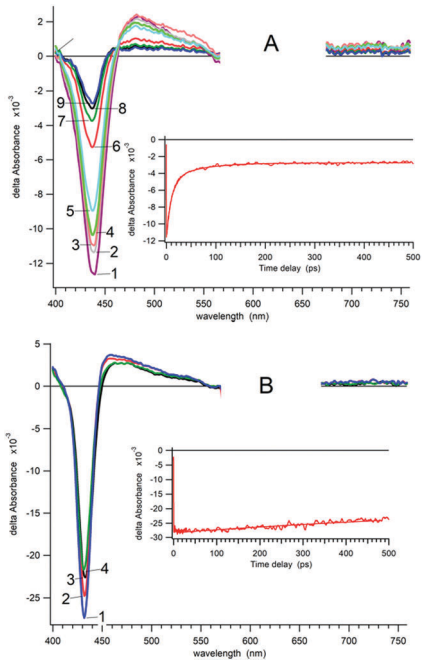


Fig. 3 Transient absorption spectra of **4b** (A) and **5b** (B) in acetonitrile (λ_{exc} = 620 nm). Time delay (**4b**): (1) 100 fs; (2) 500 fs; (3) 900 fs; (4) 2.1 ps; (5) 5 ps; (6) 20 ps; (7) 50 ps; (8) 100 ps; (9) 450 ps; time delay (**5b**): (1) 100 fs; (2) 5 ps; (3) 50 ps; (4) 450 ps. Transient kinetics decay are presented in the insets.

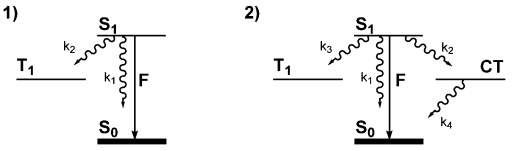
differences between the relaxation kinetics for **4a** and **4b** complexes as well as for compounds **2a**, **2b**, **3a**, **3b**, **5a** and **5b**. For example, Fig. 3 (see also Fig. S32–S35, ESI†) shows the transient absorption spectra of solutions **4b** and **5b** in acetonitrile at different time delays. The transient kinetics (see insets) display a clear double exponential decay for **4b** at the time scale up to 500 ps, whereas for **5b** the decay does not exceed 5% of the initial excitation level during 500 ps. The decay kinetics for **5b** as well as for **2a**, **2b**, **3a**, **3b** and **5a** may be approximately fitted with a monoexponential component:

$$Y_0 + A_1 \exp(-t\tau^{-1})$$

The kinetic behaviour in the spectral region of interest (λ_1, λ_2) corresponding to the BL Soret band was evaluated from the band integral (BI).[20] Bleaching of the Soret band manifests about the depletion of the ground state population that is equal to the total population of the excited stated.

$$\mathrm{BI}(\lambda_1, \lambda_2, t) = \frac{1}{\ln\left(\frac{\lambda_2}{\lambda_1}\right)} \int_{\lambda_1}^{\lambda_2} \frac{\Delta A(\lambda, t) \mathrm{d}\lambda}{\lambda}$$

The time constant of the S_1 decay is close to 1 ns for **2a**, **2b**, **3a**, **3b**, **5a** and **5b** (ESI†). This value is comparable to the time constants for different free-base or light-metal porphyrin complexes.[21] The relaxation rate constant τ^{-1} is the sum of the rate constants of radiative transfer ${\tau_{fl}}^{-1}$, internal conversion in the S_0 state – k_1, and interconversion in the T_1 state – k_2 (Scheme 2). The quantum yield of interconversion into the T_1 state can be estimated from the BI decay in the limit of $t \rightarrow \infty$



Scheme 2 Energy intramolecular transitions in **2**, **3**, **5** (1) and **4** (2).

as $Y_0/(Y_0 + A)$. The double exponential decay observed for **4a** and **4b** suggests the relaxation of S_1 into the S_0 state through an intermediate electronic state, presumably the charge transfer state (CT). Kinetic equations related to Scheme 2 with the CT state have a solution of the BI Soret bleaching decay (see ESI†):

$$Y_0 + A_1 \exp(-t{\tau_1}^{-1}) + A_2(-t{\tau_2}^{-1})$$

The biexponential fit of BI decay for **4b** allows the determination of the triplet quantum yield $Y_0 = 0.20 \pm 0.002$ and rate constants: $k_1 = 0.057 \pm 0.008$ ps^{-1}; $k_2 = 0.086 \pm 0.001$ ps^{-1}; $k_3 = 0.036 \pm 0.003$ ps^{-1}; $k_4 = 0.035 \pm 0.003$ ps^{-1}.

It is worth noting that taking into account the shift of the minima of the BL band at a very early stage requires the use of BI as a measure of a ground state depletion. Probably, conformational changes of a tetrapyrrolic ring may influence the shape of the absorption bleaching band. It has been shown that for P(v) *meso*-substituted derivatives, the porphyrin core is strongly distorted and adopts a ''ruffled'' deformation.[15,22]

The relaxation kinetics and processes for compounds **4a** and **4b** are similar (see ESI†). Kinetics curves for compounds **2** and **3** are similar to the one for **5** (see ESI†). Quantum yields of the T_1 state for all compounds were calculated using the transient absorption data (Table S2, ESI†), which are in the good accordance with the data published by Harriman *et al.*[23]

The results obtained are in agreement with the observed differences in quantum yields of SO generation and fluorescence for P(v) porphyrins bearing aromatic and non-aromatic axial ligands.

In order to further confirm the above given explanations, quantum-chemical calculations have been also performed. Optimizations and calculations were performed *via* DFT (density functional theory) calculations using Spartan'14 software (Wavefunction Inc., CA, USA) with the B3LYP/6-31G* level of theory. Fig. 4 shows the energy minimized structure of the complex **4b** with calculated four frontier molecular orbitals. Both HOMO+1 and HOMO orbitals are located on the electron donor axial aromatic ligands, while after excitation both LUMO and LUMO−1 move to the positively charged porphyrin core.

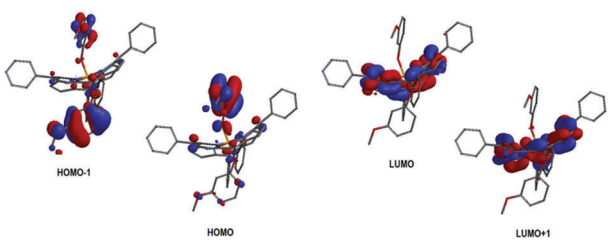


Fig. 4 Molecular orbitals, calculated for **4b**.

Thus, a CT-state is strongly anticipated for such a molecule. Optimized structures with calculated frontier MO for other studied complexes are presented in the ESI† (Fig. S36–S43).

In conclusion, the experimental and theoretical investigations clearly demonstrated the possibility of tuning photochemical properties of P(v) porphyrins. The photochemical properties of P(v) porphyrin derivatives strongly depend on the nature of axial ligands. Indeed, the introduction of aromatic ligands at the two apical positions on the P atom activates CT processes and turns off SO generation and quenches fluorescence. In the absence of this type of ligands, fluorescent P(v) porphyrins are effective photosensitizers in water as well as in organic media.

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Conflicts of interest

There are no conflicts to declare.

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