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Tetra-2,3-pyrazinoporphyrazines with Externally Appended Pyridine Rings. 6. Chemical and Redox Properties and Highly Effective Photosensitizing Activity for Singlet Oxygen Production of Penta- and Monopalladated Complexes in Dimethylformamide Solution

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Tetrakis-2,3-[5,6-di-(2-pyridyl)pyrazino]porphyrazinatopalladium(II) [$Py_8TPyzPzPd$] (**1**) and the corresponding pentapalladated species [$(PdCl_2)_4Py_8TPyzPzPd$] (**2**), dissolved ($c \approx 10^{-5}-10^{-6}$ M) in preacidified dimethylformamide ([HCl] $\approx 10^{-4}$ M), behave as potent photosensitizing agents for the production of singlet oxygen, $^1O_2$, with Φ_Δ values of 0.89 ± 0.04 and 0.78 ± 0.05, respectively. The related octacation [$(2\text{-Mepy})_8TPyzPzPd]^{8+}$ (**3**), examined under similar experimental conditions, exhibits lower Φ_Δ values, that is, 0.29 ± 0.02 (as an iodide salt) and 0.32 ± 0.02 (as a chloride salt). In view of the very high values of Φ_Δ, the photophysics of complexes **1** and **2** has been studied by means of pump and probe experiments using ns laser pulses at 532 nm as excitation source. Both complexes behave like reverse saturable absorbers at 440 nm because of triplet excited-state absorption. The lifetimes of the triplet excited states are 65 and 96 ns for the penta- and mononuclear species, respectively. Fluorescence quantum yields (Φ_f) are ~ 0.1% for both **1** and **2**. Such low Φ_f values for the two complexes are consistent with the high efficiency of triplet excited-state formation and the measured high yields of $^1O_2$. Time-dependent density-functional theory (TDDFT) calculations of the lowest singlet and triplet excited states of the mono- and pentapalladated species help to rationalize the photophysical behavior and the relevant activity of the complexes as photosensitizers for the $^1O_2$ ($^1\Delta_g$) generation.

Introduction

We have previously reported the synthesis and general physicochemical characterization of the novel free-base porphyrazine macrocycle tetrakis-2,3-[5,6-di(2-pyridyl)pyrazino]porphyrazine, [$Py_8TPyzPzH_2$],[1] its metal derivatives [$Py_8TPyzPzM$] (M = $Mg^{II}(H_2O)$, Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}; Scheme 1A),[2] and the related octacations [$(2\text{-Mepy})_8TPyzPzM]^{8+}$[3] (neutralized by I^- anions; Scheme 1B). In more recent work,[4] the synthesis, IR, UV−visible and ^1H NMR spectral behavior, and density-functional theory (DFT) calculations of the pentanuclear species [$(PdCl_2)_4Py_8TPyzPzPd$], the monopalladated complex [$Py_8TPyzPzPd$], and its related octacation [$(2\text{-Mepy})_8TPyzPzPd]^{8+}$ (neutralized by I^- anions) were reported in detail. It was shown that

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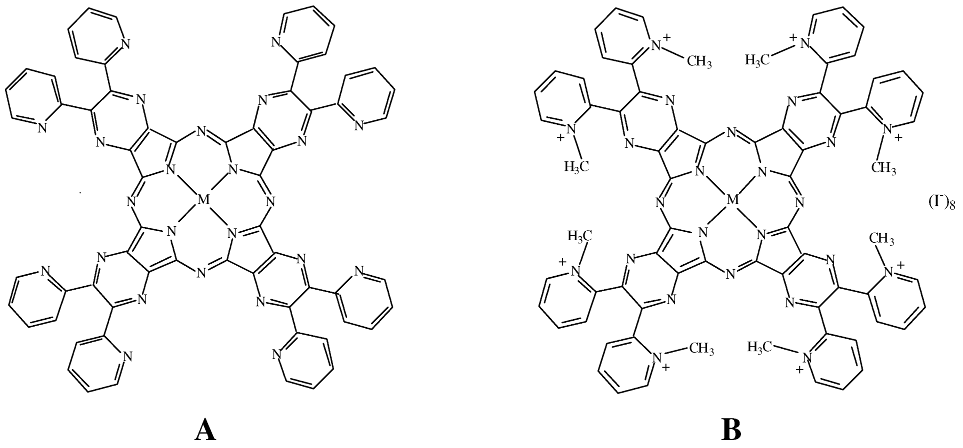

Scheme 1. Schematic Representation of (A) the Neutral Complexes [Py$_8$TPyzPzM]^{1,2} and (B) Their Corresponding Octacations [(2-Mepy)$_8$TPyzPzM]$^{8+}$ (Salted by I$^-$ Ions)^3

the octapyridinated "pyrazinoporphyrazine" macrocycle can be the site of both central and exocyclic metal coordination with the formation of mono- and pentametallic species. The pentanuclear complex [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] is quite a rare example of exocyclic metal binding by the four PdCl$_2$ groups at the N atoms of the external pyridine rings ("py-py" coordination). The square planar N$_2$PdCl$_2$ moieties are oriented outside of the pyrazinoporphyrazine plane, lying almost perpendicular to it. Two of the expected four structural isomers have been identified by ^{1}H NMR spectra. On the basis of NMR data and DFT calculations, the prevailing isomeric species has the four external N$_2$PdCl$_2$ moieties on the same side of the porphyrazine macrocycle (C_{4v} symmetry) as shown in Figure 1.

It was also established by electrochemical studies[4] that all three Pd$^{\text{II}}$ species undergo four reversible to quasi-reversible ligand-centered one-electron reductions in nonaqueous solvents (pyridine, dimethylsulfoxide (DMSO), dimethylformamide (DMF)) at potentials remarkably less negative than those found for their phthalocyanine analogues, and the half-wave potentials are close to values found for a series of related [Py$_8$TPyzPzM]^{1,2a} and [(2-Mepy)$_8$TPyzPzPd]$^{8+3}$ species, approaching 0.0 V versus SCE for the first reduction.

In the present paper, we describe the photophysical behavior of the three Pd$^{\text{II}}$ compounds in DMF. Their efficiency as photosensitizers for the production of singlet oxygen, ^{1}O$_2$, and the fluorescence quantum yield were measured. DMF was chosen as the solvent for the following reasons: (a) the complexes are insoluble in water and in nonaqueous non-donor solvents such as methanol, ethanol, toluene, benzene, and so forth; (b) they can be dissolved in pyridine, DMSO, and DMF up to a concentration of about 10^{-4} M; (c) no aggregation is observed in DMF for the pentanuclear [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] or the octacation [(2-Mepy)$_8$TPyzPzPd]$^{8+}$ at concentrations used for the quantum yield measurements (ca. $(1-5) \times 10^{-6}$ M) and aggregation is only minimally present for [Py$_8$TPyzPzPd]; (d) most importantly, DMF is a widely used solvent for measurements of singlet oxygen quantum yields, particularly for phthalocyanines and porphyrazines,[5] thus allowing comparisons among different series of macrocycles. The results of the present study indicate that the penta- and monometallic species, that is, [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd], behave as potent sensitizers with ^{1}O$_2$ quantum yields close to or above 80%, a favorable aspect, particularly if seen in the context of photodynamic therapy (PDT), a currently expanding and promising anticancer therapeutic modality.[6] With the aim of providing a possible explanation for the remarkable photosensitizing activity of the examined complexes, fluorescence spectra and quantum yields as well as triplet excited-state lifetimes have been measured. The photophysical data have been interpreted with the aid of time-dependent density-functional theory (TDDFT) calculations of the lowest singlet and triplet excited states.

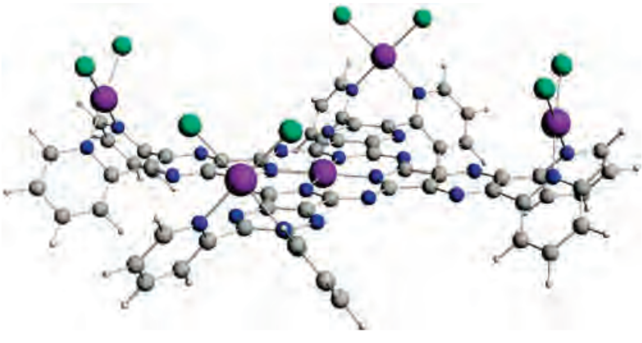

Figure 1. Predominant structural component present in the mixture of isomers of [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] having the four external N$_2$PdCl$_2$ moieties all oriented on the same side of the central pyrazinoporphyrazine core (named **1c**,[4] C_{4v} symmetry).

Experimental Section

Solvents and Reagents. Solvents and chemicals were used as purchased. DMF, from Aldrich, Carlo Erba, or Merck was of a purity >99.8%. The penta- and monopalladated complexes were

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prepared as reported in a previous publication.[4] Phthalocyaninatozinc(II), [PcZn], a commercial product from Aldrich was purified by sublimation (450 °C; 10^{-2} mmHg).

Synthesis of [(2-Mepy)$_8$TPyzPzPd](Cl)$_8$(H$_2$O)$_{16}$. The iodide complex [(2-Mepy)$_8$TPyzPzPd](I)$_8$(H$_2$O) (47.6 mg, 0.02 mmol) was dissolved in a mixture of water (10 mL) and acetone (2 mL) and the solution then passed through an ion-exchange column (Amberlite IRA 400, 1.29 g) previously washed with water, 0.5 M NaOH, H_2O, 2.0 M HCl, and then H_2O again until the washings were neutral. The eluted solution was exposed to the air, and after evaporation of the solvent, the residue was washed with acetone and dried under vacuum (25 mg, 0.013 mmol; yield 65%). Calcd for [(2-Mepy)$_8$TPyzPzPd](Cl)$_8$(H$_2$O)$_{16}$, $C_{72}H_{88}Cl_8N_{24}O_{16}Pd$: C 44.68, N 17.37, H 4.58%. Found: C 44.09, N 17.86, H 3.95%. The IR spectrum of the solid in the region 4000−200 cm^{-1} and the UV−visible solution spectrum in pyridine (300−800 nm) are identical to the spectra of the corresponding iodide.

Physical Measurements. Quantum Yields (Φ_Δ) of Singlet Oxygen ($^1O_2$). The irradiation apparatus was a Teclas PTL-Penta, equipped with a halogen lamp (Osram Xenophot HLX 64653 ELC, 24 V, 250 W), a dicroic filter R-61, used to select the 600−900 nm range and an optical fiber unit for conveying the light beam to the sensitizer solution. The latter was contained in a 1 cm quartz cell (1.00 × 1.00 cm^2 section). During each experiment, the cell was always kept in the cell compartment of the spectrophotometer (Varian, Cary 50 scan) and the solution was irradiated continuously while measuring the absorbances at selected wavelengths. The optical fiber was positioned just above the free surface of the solution. Because the amount of photons reaching the solution considerably depends on the cell−light beam system geometry, great care was paid to ensure reproducibility of the relative positions of the optical fiber and the solution. Homogeneity of the latter during irradiation was maintained by continuous magnetic stirring while constant temperature circulating water (20.0 °C) assured temperature control.

Singlet oxygen quantum yields were measured in DMF in the presence of air following a procedure described in the literature,[7] using [PcZn] as reference[8] and dimethylanthracene (DMAN) as the $^1O_2$ scavenger. A DMF solution of DMAN and of the Pd^{II} species, to which previously had been added a moderate excess of HCl (1×10^{-4} M), proved to be stable both in the dark and under irradiation (as to the suggested role of HCl, see below). The solutions used for the irradiation experiments, formed by mixing equal volumes (1.000 ± 0.001 mL) of solutions containing separately DMAN and the sensitizer in the quartz cell, were also stable in the dark. The concentration of the sensitizer, that is, the Pd^{II} species or the reference [PcZn], was such that, after mixing of the reagents, the absorbance at the Q-band maximum (630−640 and 669 nm for the Pd^{II} species and [PcZn], respectively), was in the range 0.2 to 0.4, corresponding to a concentration of about $(1-5) \times 10^{-6}$ M, with DMAN about 1×10^{-5} M.

For each sensitizer, including the [PcZn] reference, the first-order rate constant of the DMAN decay was measured under constant light illumination following continuously the decrease of absorbance of the 379 nm peak of the scavenger. The absorption at the Q-band maximum of the sensitizers was also monitored simultaneously to check their stability under illumination conditions.

The $^1O_2$ quantum yield, Φ_Δ^S, of the present Pd^{II} sensitizers was calculated by means of eq 1

$$\Phi_\Delta^S = \frac{k^S \cdot \alpha^R}{k^R \cdot \alpha^S}\Phi_\Delta^R \tag{1}$$

where k^S and k^R are the DMAN bleaching first-order rate constants and α^S and α^R the fractions of photons actually absorbed by the solutions, estimated on the basis of the filter transmittance and the solutions absorption spectra (the apexes S and R refer to the Pd^{II} sensitizers and the [PcZn] reference, respectively). The value $\Phi_\Delta{}^R = 0.56$[8] was assumed for the quantum yield of [PcZn].

Excited State Lifetimes by Pump and Probe Experiments. Determination of excited-state lifetimes for [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd] was accomplished by means of pump and probe experiments as previously described.[2b] These experiments were carried out on preacidified ([HCl] = 1×10^{-4} M) and deaerated DMF complex solutions ($5 \times 10^{-5} \leq c < 1 \times 10^{-4}$ M) and an incident fluence (F_{in}) higher than 0.15 J cm^{-2}, using 2 mm glass cells from Hellma (Type No. 110-OS). Linear optical spectra of the solutions were recorded with a Varian Cary 5 UV−visible spectrophotometer before and after pump and probe measurements for every analyzed wavelength to evaluate possible photodegradation during sample pumping. The pump radiation was generated by a doubled Nd:YAG laser (Quantel YG980E) which produced 9 ns long pulses at 532 nm. The energy of the pump radiation was controlled with a $\lambda/2$ wave-plate and a polarizing cube beam-splitter. A pyroelectric detector (Scientech, Mod. SPHD25) was used for determining the energy of the pump radiation. The latter was focused on the sample to control the variation of the illuminated area (0.196 cm^2). The repetition rate of pumping was 2 Hz, and 250 responses were recorded at every wavelength to increase the signal-to-noise ratio. The (continuous) probe was a Xe lamp from Spectra-Physics (Oriel Instruments, Mod. 66902) with 150 W as output power. The area of the sample illuminated by the probe lamp was 0.075 cm^2 and was adjusted by means of a plane-convex lens. The variation of the sample transient transmission was detected by a Jobin-Yvon Horiba TRIAX 320 spectrometer equipped with an Hamamatsu phototube (R2257). Time variation of the phototube response was recorded and averaged by a 1 GHz digital oscilloscope (LeCroy LC564A) on a microsecond time scale with nanosecond resolution.

Fluorescence Quantum Yields (Φ_f). Fluorescence and excitation spectra for [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd] were also recorded in preacidified ([HCl] = $\sim 10^{-4}$ M) DMF solutions with a Jobin Yvon-Spex spectrofluorometer (Mod. Fluoromax-2) using 10 mm quartz SUPRASIL cells. For the excitation spectra a Baird Atomic BA 660 filter was used. The determination of fluorescence quantum yields was accomplished by means of the comparative method using a solution of [PcZn] in 1-propanol as fluorescence standard ($\Phi_{f[PcZn]} = 0.45$ with $\lambda_{exc} = 600$ nm).[9] The formula used for the determination of the fluorescence quantum yields Φ_f is:[9b]

$$\Phi_f^S = \frac{G^S \cdot n_{DMF}^2 \cdot A_{600}^R}{G^R \cdot n_{1-prop}^2 \cdot A_{600}^S}\Phi_f^R \tag{2}$$

where G is the integrated emission area, n is the refractive index of the solvent, A is the absorbance (≤ 0.02) at the wavelength of

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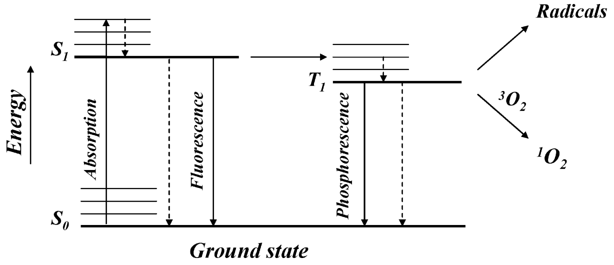
excitation, S and R indicate the sample and the reference, and Φ_f^R = 0.45 for [PcZn].

Quantum Chemical Calculations. Vertical excitation energies were computed using TDDFT methods.[10] For the exchange-correlation (xc) potential, which appears in the zeroth-order Kohn–Sham equations, we employed the hybrid B3LYP[11] functional. TDDFT/B3LYP calculations were performed with Turbomole version 5.7.1[12] using the Karlsruhe split-valence basis set[13] augmented with polarization functions[14] (SVP). Relativistic effective core potential (ecp-28-mwb) was used for Pd.[15] Solvent effects on the excitation energies were modeled by the conductor-like continuum solvent model (COSMO).[16] In the TDDFT calculations the ground-state geometries optimized at the DFT/BP86 level of theory in DMSO were employed.[4]

Results and Discussion

Chemical Stability and Redox Behavior in DMF Solution. As reported in a recent paper,[4] the examined Pd^{II} complexes, namely, the pentanuclear [$(PdCl_2)_4Py_8TPyzPzPd$], the mononuclear [$Py_8TPyzPzPd$], and its related iodide salt [$(2\text{-}Mepy)_8TPyzPzPd$]$(I)_8$, all exist as redox-stable species in pyridine or DMSO at all examined concentrations, although it should be noted that the pentapalladated species in pyridine releases the external $PdCl_2$ groups forming [$Py_8TPyzPzPd$] plus a pyridine complex of $PdCl_2$.[4] DMF solutions of all three Pd^{II} complexes are stable only if the concentration of the complexes is about 10^{-4} M or higher, while at lower concentrations (ca. 10^{-5}–10^{-6} M), these compounds undergo a one-electron reduction, as clearly indicated by UV–visible spectral variations, identical to those already observed for the same process by spectroelectrochemical measurements.[4] Reduction very likely takes place because of trace amounts of an impurity present in the solvent which acts as a reducing agent, presumably dimethylamine, coming from the hydrolysis of DMF. Accordingly, it was found that by adding to the solvent a small amount of HCl (up to 10^{-4} M) we were able to prevent this reduction. It was also observed that the −1 charged species, once formed, are easily reversed to the original species by addition of HCl. Because of the $E_{1/2}$ values, close to zero (V vs SCE), for the one-electron reduction of the complexes,[4] the oxidizing agent might be the proton itself. Despite the fact that reoxidation was performed under anaerobic conditions, a residual amount of dioxygen sufficient to back oxidize the reduced complexes cannot be excluded.

Scheme 2. Schematic Diagram of Energy Transfer from the Sensitizer to the Dioxygen Molecule



Quantum Yields of Singlet Oxygen ($^1O_2$). As is well-known, singlet oxygen, $^1O_2$, is a highly cytotoxic agent widely studied in diverse areas and especially for its involvement in the field of photodynamic therapy (PDT) of cancer.[5,6] $^1O_2$ is formed by energy transfer from a photoexcited sensitizer to $^3O_2$ oxygen, for the process $^3O_2$ ($^3\Sigma_g$) → $^1O_2$ ($^1\Delta_g$). In early and more recent times, the most investigated photosensitizers for the production of singlet oxygen were various natural or chemically modified hematoporphyrins (among them Photofrin, the first commercially accepted photosensitizer for clinical use), core-modified porphyrins, chlorins, bacteriochlorins, phthalocyanines, naphthalocyanines, and texaphyrins, all in the series having single components in various stages of evaluation as therapeutic agents in PDT.[5,6a,b] Among the different classes of tetrapyrrolic systems, porphyrazines, macrocycles of increasing general interest,[17] have been comparatively much less studied as photosensitizers in PDT (see more on this point below).

Because the efficiency of a photosensitizer depends on the photophysical properties of its ground-to-excited states pathway, that is, singlet ground state (S_0) → first singlet excited state (S_1) → first triplet excited state (T_1) (Scheme 2), the triplet state T_1 should be generated with a high quantum yield and have an appropriate energy and lifetime long enough to make the energy transfer to an oxygen molecule highly probable for the process $^3O_2 \rightarrow {}^1O_2$.

The photoefficiency of a sensitizer also strongly depends on the presence and type of central metal ion. Tetrapyrrolic macrocycles containing closed shell central metal ions, for instance Zn^{II} and Mg^{II}, are normally highly photoactive sensitizers, with the heavier metal ion being more efficient, that is, Zn^{II} > Mg^{II}.[5,6a,b] A large number of macrocyclic chromophores (porphyrins, phthalocyanines) containing these two metal centers are able to generate singlet oxygen with high quantum yield values (Φ_Δ).[5,6] Although much less numerous, macrocyclic chromophores with centrally incorporated Pd^{II}, an open shell d^8 metal center which can take

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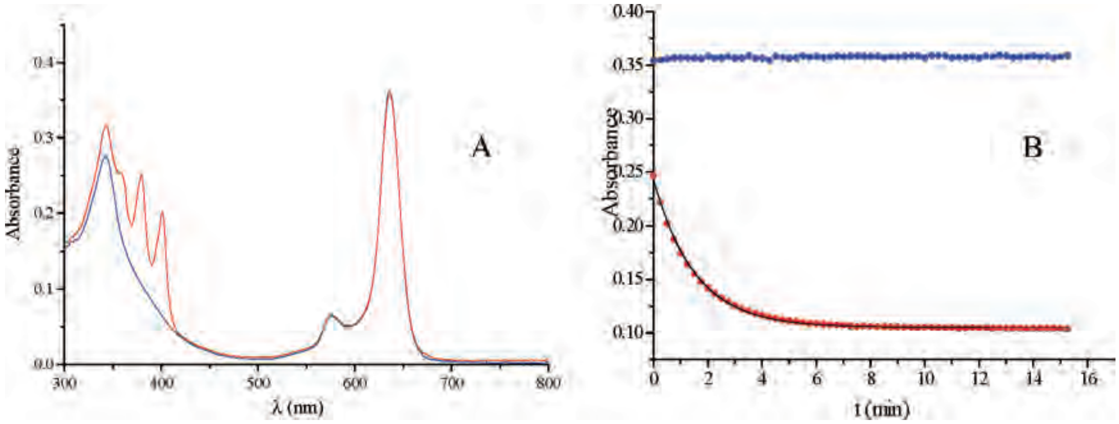

Figure 2. (A) UV−visible spectra of a DMF solution containing [$(PdCl_2)_4Py_8TPyzPzPd$] (ca. 1 × 10^{-6} M), DMAN (ca. 1 × 10^{-5} M), and HCl (ca. 1 × 10^{-4} M) before (red line) and after irradiation (blue line). (B) Plot of the absorbances of DMAN at 379 nm (red dots) (and associated first-order fit) and of the sensitizer at 635 nm (blue dots) during irradiation.

advantage in PDT of the “heavier atom effect”,[6a] generally show to be efficient sensitizers for the production of singlet oxygen. Potential photochemotherapeutic agents are Pd^{II}-bacteriochlorophylls,[18] and in comparative studies of different bacteriochlorophyll-metal derivatives, the Pd^{II} complexes behave as the most photoactive sensitizers.[18c,d,f] Turning to Pd^{II}porphyrin or phthalocyanine derivatives, a value of $\Phi_\Delta = 0.88$ was found for [(TPP)Pd] (TPP = tetraphenylporphyrinato dianion) measured by the time-resolved luminescence technique (0.78 by the steady state technique).[19] Five substituted Pd^{II} porphyrins with different peripheral steric demands were shown to generate singlet molecular oxygen with a quantum yield Φ_Δ of about 0.85 in all cases.[20] Whereas we are not aware of any measurements on the simple Pd^{II} phthalocyanine, [PcPd], Pd^{II}-octabutoxyphthalocyanine, [$(BuO)_8PcPd$], has comparatively the highest value of Φ_Δ (0.64) within the series of H_2-, Al^{III}-, Zn^{II}-, Ga^{III}-, Ge^{IV}-, Ru^{II}-, Pd^{II}-, Sn^{IV}-octabutoxyphthalocyanines,[21] and, similarly, for two parallel series of free-base, Zn^{II} and Pd^{II} (*t*-butyl)substituted symmetrical and low-symmetry phthalocyanine derivatives, Φ_Δ moves in the direction $H_2 < Zn^{II} < Pd^{II}$.[19] Within this overview, there appear to be no studies, to our knowledge, on porphyrazinato-palladium(II) species concerning the determination of singlet oxygen quantum yields. This encouraged our study of the photoactivity of the present Pd^{II} species, and the results on the quantum yields of the production of singlet oxygen are discussed below.

Measurements of singlet oxygen quantum yields for the present Pd^{II} complexes were carried out by using the methodology described in the Experimental Section. Figure 2 exemplifies the results of an experiment with the pentapalladated species [$(PdCl_2)_4Py_8TPyzPzPd$]. Figure 2A shows the initial UV−visible spectrum of the solution containing the sensitizer (red line, Q band at 635 nm) and the peaks of DMAN in the region 300−400 nm superimposed with the Soret band of the complex. Irradiation of the solution causes a complete disappearance of the DMAN peaks within 10 min, leaving the spectrum of the Pd^{II} complex unmodified. Figure 2B shows the variation of absorbance at 379 nm (DMAN) which can be fitted according to a first-order law, thus allowing determination of the related *k* value. As can also be seen in Figure 2B, the absorbance of the Q band of the sensitizer remains constant during the experiment, indicating that the sensitizer is not undergoing photobleaching. The *k* values measured for coupled experiments on the Pd^{II} species and the reference [PcZn] were used in eq 1 to calculate quantum yields of the present Pd^{II} species as described above. [Because hydrolysis of DMF generates trace amounts of formic acid and dimethylamine (the supposed reducing agent for the Pd^{II} complexes), the latter present as its hydrochloride in the acidic medium, experiments were conducted with a deliberately added excess of each one of the two species in separate experiments. No effects were observed on the kinetic constants and related quantum yield values of singlet oxygen.]

Table 1 lists the average values of Φ_Δ obtained for the examined Pd^{II} complexes. The quantum yields of [$(PdCl_2)_4Py_8TPyzPzPd$] (0.89 ± 0.04) and [$Py_8TPyzPzPd$] (0.78 ± 0.05) are remarkably high, thus suggesting that these complexes can act as potent photosensitizers for the production of singlet oxygen. The slightly lower Φ_Δ value of [$Py_8TPyzPzPd$] can be due to, at least in part, the interfering presence of aggregation, as detected by the systematic presence in the UV−visible spectrum of a small shoulder at about 660 nm, which only rarely and very slowly (days) disappears. In one case, an experiment was conducted on a solution for which this shoulder was no longer present.

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Table 1. Quantum Yields (Φ_Δ) for the Production of Singlet Oxygen ($^1O_2$) by the Pd^{II} Complexes

photosensitizer	Φ_Δ	aver. Φ_Δ
$[(PdCl_2)_4Py_8TPyzPzPd]$	0.84 0.92 0.90	0.89 ± 0.04
$[Py_8TPyzPzPd]$	0.81 0.81 0.71	0.78 ± 0.05
$[(2\text{-}Mepy)_8TPyzPzPd](I)_8$	0.27 0.30 0.31	0.29 ± 0.02
$[(2\text{-}Mepy)_8TPyzPzPd](Cl)_8$	0.30 0.33 0.34	0.32 ± 0.02

In this case, consistent with the explanation given above, Φ_Δ was measured to be 0.95.

The octacation $[(2\text{-}Mepy)_8TPyzPzPd]^{8+}$ has a much lower value of Φ_Δ (±0.02, Table 1). The I^- ion is known to react with $^1O_2$ in the presence of $(NH_4)_2MoO_4$ as a catalyst,[22] generating the I_3^- ion which absorbs at 351 nm. No trace of this peak was found during irradiation of the complex. Moreover, by using an ion exchange method, the I^- ion was exchanged by Cl^- (see Experimental Section) and the octachloride was irradiated under experimental conditions identical to those used for the corresponding iodide. A value very close to that of the iodide ion, $\Phi_\Delta = 0.32 \pm 0.02$, was obtained (Table 1), which means that the presence of the I^- ion has no influence on the photoactivity of the octacation. Presently, in the absence of more detailed information concerning quantum yields and lifetimes of the triplet state, no reasonable hypothesis for the quenched Φ_Δ value of the octacation can be proposed.

It must be emphasized that the observed values of $\Phi_\Delta = 0.8-0.9$ for $[(PdCl_2)_4Py_8TPyzPzPd]$ and $[Py_8TPyzPzPd]$ approach closely or are significantly higher than those found for the previously studied Pd^{II}-bacteriochlorophylls[18] or porphyrins.[19,20,22] As to the related family of phthalocyanines, the present values of Φ_Δ are $1^1/_2$ times the well-established value (0.56) reported for [PcZn] in DMF[8] (only slightly solvent dependent[7b]) and much higher than any value measured for the studied Pd^{II}-phthalocyanines.[19,21] The higher Φ_Δ values for the two present Pd^{II} species are maintained in comparison with entire classes of unmetalated ($\Phi_\Delta = 0.2-0.5$)[5,6a,b] and metalated phthalocyanines and naphthalocyanines (Al^{III}, Ga^{III}, Si^{IV}, Ge^{IV}, Zn^{II}, Mg^{II}) for which the Φ_Δ values are normally in the range 0−0.5, in rare cases approaching 0.6−0.7.[5,6a,b] The comparison holds as well with several classes of substituted phthalocyanines[23] and naphthalocyanines,[24] benzonaphthoporphyrazines,[8] azaphthalocyanines,[25] and secoporphyrazines.[26] Noticeably, the measured Φ_Δ values of the present Pd^{II} complexes are much higher than the value (0.53) reported for the Zn^{II} analogue $[Py_8TPyzPzZn]$ in pyridine,[27] a rarely used solvent for quantum yield measurements of $^1O_2$ formation.[5a] In summary, the presently examined penta- and monopalladated species are among the most active sensitizers of related macrocycles and are very promising candidates for applications in different fields, including photodynamic therapy.

An adequate understanding of the observed high Φ_Δ values for the examined Pd^{II} complexes is provided by the photophysical and theoretical data reported on the following pages.

Determination of Triplet Excited-State Lifetimes. Irradiation with 9 ns laser pulses at 532 nm of preacidified ($[HCl] = 1 \times 10^{-4}$ M) and deaerated DMF solutions of $[(PdCl_2)_4Py_8TPyzPzPd]$ and $[Py_8TPyzPzPd]$, induces formation of excited states with larger optical density than their ground states in the wavelength range 400−580 nm. This is in line with previous findings for the Mg^{II} analogue[2b] and similar macrocycles,[28] which show that triplet states are populated at low fluence.[2b] Such a result indicates the occurrence of reverse saturable absorption (RSA)[29] for the present Pd^{II} complexes.

Figure 3 reports the time dependent optical density ΔO.D. at 440 nm for $[(PdCl_2)_4Py_8TPyzPzPd]$ and $[Py_8TPyzPzPd]$. Pump intensities were kept low to prevent that other phenomena, like charge transfer processes[2b] or macrocycle decomposition, would obscure detection of the triplet state. Also, concentrations were low to minimize aggregation which might lead to different excited-state dynamics. Therefore, pump and probe signals are noisy but their exponential decay can be easily recognized and fitted.

It has been verified that the fast transient signals can be fitted with a monoexponential decay. The values of the time constant τ were found to be 65 ns for $[(PdCl_2)_4Py_8TPyzPzPd]$ and 96 ns for $[Py_8TPyzPzPd]$. These values are relatively low when compared to the triplet excited-state lifetimes of analogous complexes like phthalocyanines, naphthalocyanines, and porphyrins,[2b,28,30,31] which generally display $\tau >$

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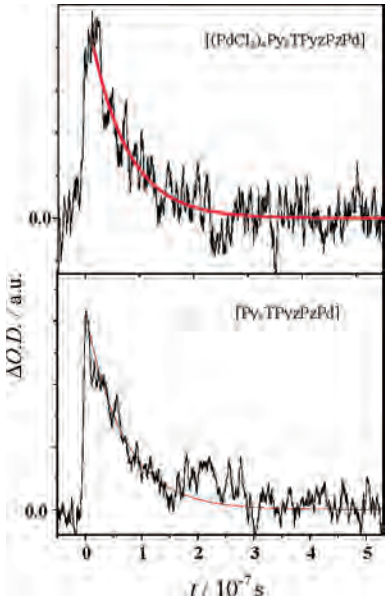

Figure 3. Time dependent optical density difference with respect to the ground state (ΔO.D.) at 440 nm for [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] (above, $c = 7.4 \times 10^{-5}$ M; $F_{\text{in}} = 0.17$ J cm^{-2}) and [Py$_8$TPyzPzPd] (below: $c = 5.0 \times 10^{-5}$ M; $F_{\text{in}} = 0.47$ J cm^{-2}) in preacidified ([HCl] = 1×10^{-4} M) deaerated DMF upon excitation with ns laser pulses at 532 nm. Red lines indicate the monoexponential fittings of the decay curves. The evaluated time constants of the monoexponential fittings are 65 and 96 ns for [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd], respectively.

300 ns. The main reason for these results is related to the heavy-atom effect[31] produced by the presence of palladium atoms which shorten the lifetime of the excited triplet state thus produced.[32] Confirmation of this effect is the shorter lifetime of the first excited triplet state for the pentametallic [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] (65 ns) with respect to that of the monometallic complex [Py$_8$TPyzPzPd] (96 ns), which can be explained with the larger number of palladium atoms present in the pentanuclear complex. As a consequence, one can also expect that the yield of triplet formation is high because of the same heavy-atom effect.[30,31] The measured high yields of $^1O_2$ formation by [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd] clearly indicate that favorable factors are encountered in terms of high rates and large yields of formation and long enough lifetimes of the photogenerated T_1 state, and, according to TDDFT results (vide infra), give a good match between the T_1 state energy and the first excitation energy of the molecular oxygen.

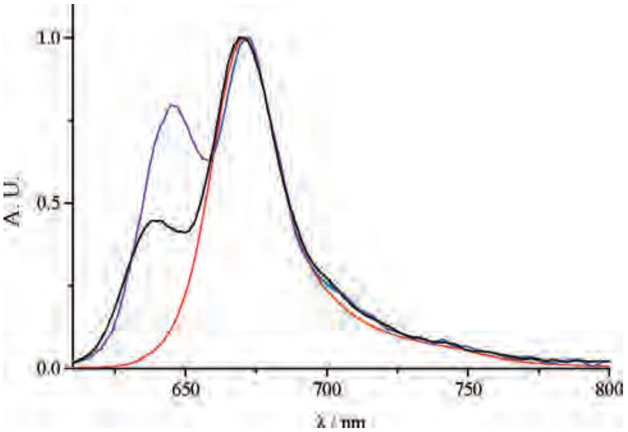

Figure 4. Fluorescence spectra of [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] (blue line), [Py$_8$TPyzPzPd] (black line), and [Py$_8$TPyzPzH$_2$] (red line) in acidified DMF ($\lambda_{\text{exc}} = 600$ nm).

Fluorescence Quantum Yields. The fluorescence spectra of [(PdCl$_2$)$_4$Py$_8$TPyzPzPd] and [Py$_8$TPyzPzPd] show the presence of two bands of emission upon excitation at 600 nm in preacidified DMF (Figure 4). One band is located at 670 nm for both species, while the other appears at 646 and 637 nm for the penta- and monometallic complex, respectively.

Repeated fluorescence measurements performed on different solutions from the same batch for each one of the two complexes show a variation in the relative intensity of these two bands. Such a feature strongly suggested the presence of small amounts of an unknown macrocyclic contaminant in the two Pd^{II} materials with presumably stronger emission than that of the Pd^{II} species. Considering that the contaminant might be the corresponding unmetalated species, [Py$_8$TPyzPzH$_2$], its fluorescence spectrum was also recorded (red line, Figure 4).

As can be seen, the spectrum of [Py$_8$TPyzPzH$_2$] shows a peak at 670 nm, coincident with that observed in the same position for the two Pd^{II} samples. In the light of this, it is reasonable to assign the 646 and 637 nm peaks to the fluorescence response of the Pd^{II} macrocycles. To confirm such an interpretation, the excitation spectra at 646 and 637 nm for the penta- and monopalladated complexes, respectively, were recorded and compared to their corresponding absorption spectra (Figures 5 and 6, respectively).

The close resemblance between excitation and absorption spectra is encouraging evidence for the assignment of the peaks observed at 646 and 637 nm to the fluorescence response of the two Pd^{II} macrocycles in the samples examined.

To get further confirmation of the above assignments, excitation spectra of the unmetalated species and of the two Pd^{II} complexes in the range 300−690 nm were acquired at 700 nm (Figure 7) (a wavelength where the contribution in terms of fluorescence emission by the Pd^{II} macrocycles is likely to be very close to zero, as suggested by the spectra in Figure 4). The very good correspondence of the spectrum of the two Pd^{II} samples with that of the free-base macrocycle definitely supports the assignments made for the bands at 670 nm (free-base) and 646/637 nm (Pd^{II} macrocycles). On the basis of these results, the fluorescence quantum yield, Φ_F, for the two complexes was calculated by estimating the

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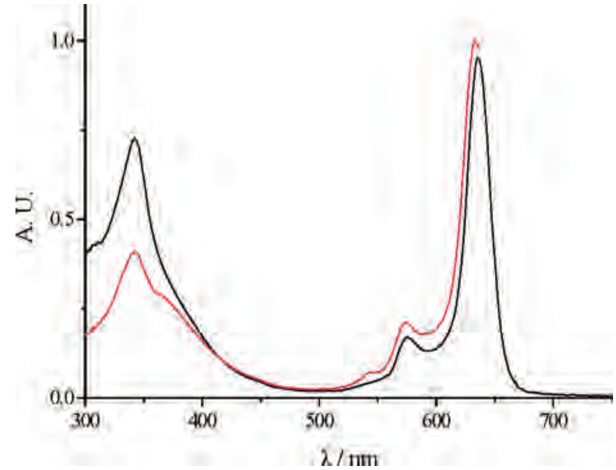

Figure 5. Excitation (red line) and absorption spectra (black line) of [$(PdCl_2)_4Py_8TPyzPzPd$] in acidified DMF (λ_{em} = 646 nm).

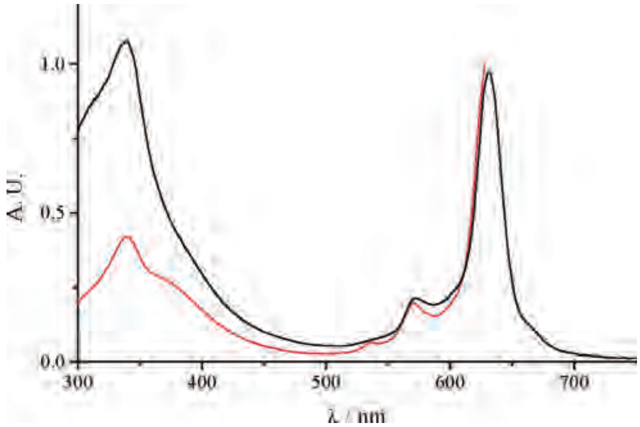

Figure 6. Excitation (red line); and absorption spectra (black line) of [$Py_8TPyzPzPd$] in acidified DMF (λ_{em} = 637 nm).

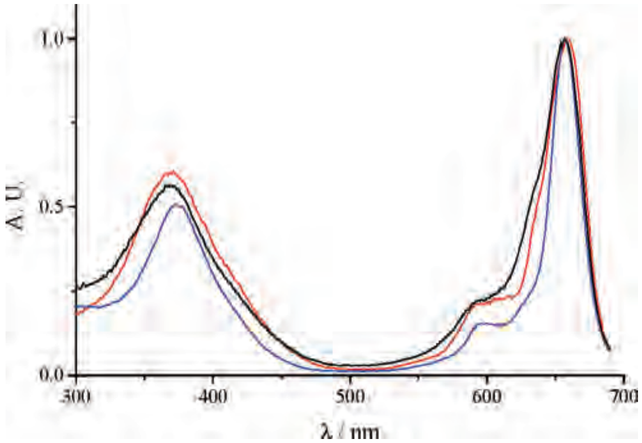

Figure 7. Excitation spectra (λ_{em} = 700 nm) of [$(PdCl_2)_4Py_8TPyzPzPd$] (blue line), [$Py_8TPyzPzPd$] (black line), and of [$Py_8TPyzPzH_2$] (red line) in acidified DMF.

related integrated area of the peak at 646 nm for [$(PdCl_2)_4Py_8TPyzPzPd$] and at 637 nm for [$Py_8TPyzPzPd$]. Φ_F was found to be ~0.1% for both species, well in keeping with the calculated values of the related singlet oxygen quantum yields presented above. From the just discussed fluorescence data, an estimation of the average amount of the contaminant [$Py_8TPyzPzH_2$] present in the batches of both Pd^{II}complexes could also be obtained. In every sample tested, the contaminant was always well within the 3−5% range in weight. If account is taken for the low value of singlet oxygen quantum yield measured for [$Py_8TPyzPzH_2$] (0.11 ± 0.02 in preacidified DMF) it can be concluded that the contaminant only negligibly affects the values of singlet oxygen quantum yields measured for the Pd^{II} complexes.

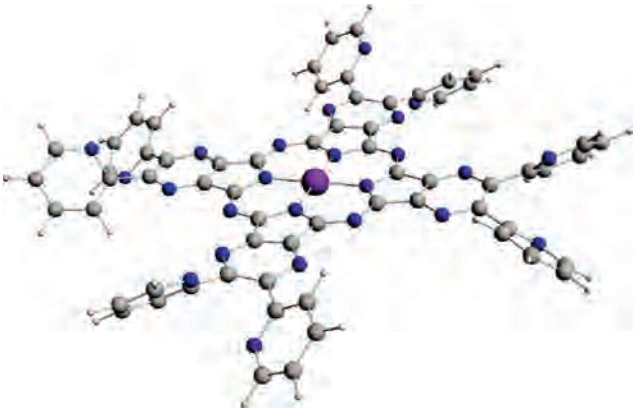

Figure 8. DFT-optimized structure of the [$Py_8TPyzPzPd$] **2b** conformer. For the details see ref 4.

Table 2. Vertical Excitation Energies Computed for the Lowest Singlet and Triplet Excited States of [$(PdCl_2)_4Py_8TPyzPzPd$] in DMF

state	character	E (eV/nm)[a]	expt[b] (eV/nm)
S_2	π,π^*	2.21/561 (0.560)	1.95/636
S_1	π,π^*	2.21/561 (0.560)	Q
T_6	$\pi_{Pd-Cl},\sigma^*_{Pd-N_2Cl_2}$	2.07/599	
T_5	$\pi_{Pd-Cl},\sigma^*_{Pd-N_2Cl_2}$	2.07/599	
T_4	$\pi_{Pd-Cl},\sigma^*_{Pd-N_2Cl_2}$	2.07/599	
T_3	$\pi_{Pd-Cl},\sigma^*_{Pd-N_2Cl_2}$	2.07/599	
T_2	π,π^*	1.39/892	
T_1	π,π^*	1.39/892	

[a] Oscillator strengths in parentheses. [b] Present work.

Nature and Energy of the Lowest Excited States. To gain greater insights into the photophysical and photochemical behavior of the investigated complexes, the nature and energy of the lowest singlet and triplet excited states of [$(PdCl_2)_4Py_8TPyzPzPd$] and [$Py_8TPyzPzPd$] were examined through TDDFT calculations using the hybrid B3LYP functional. Since the photophysical properties have been explored in DMF, this solvent was employed in the TDDFT calculations. Concerning the pentapalladated species, the excited-state calculations were restricted to the structural isomer **1c** (C_{4v} symmetry) shown in Figure 1 since this isomer is the predominant species among the four possible isomers of the complex.[4] As to the monopalladated species, TDDFT calculations were performed for the C_1 symmetry conformer (denoted elsewhere[4] as **2b**) shown in Figure 8. According to DFT calculations (ref 4), this is the most stable among the four [$Py_8TPyzPzPd$] conformers generated by different orientations of the eight external pyridine rings with respect to the pyrazinoporphyrazine macrocycle.

Table 3. Vertical Excitation Energies Computed for the Lowest Singlet and Triplet Excited States of [$Py_8TPyzPzPd$] in DMF

state	character	*E* (eV/nm)[a]	expt[b] (eV/nm)
T_3	$\pi_{\text{pyz-py}},\pi^*$	2.25/550	
S_2	π,π^*	2.21/561 (0.544)	1.96/631 Q
S_1	π,π^*	2.20/564 (0.545)	
T_2	π,π^*	1.38/898	
T_1	π,π^*	1.37/905	

[a] Oscillator strengths in parentheses. [b] Present work.

The vertical absorption energies (*E*) calculated for the lowest singlet and triplet excited states of the **1c** conformer of the pentapalladated species and the **2b** conformer of the monopalladated species are listed in Tables 2 and 3, respectively. In the tables the character of the excited states is also indicated.

According to the TDDFT/B3LYP results in Table 2, the lowest singlet excited states of [$(PdCl_2)_4Py_8TPyzPzPd$] are the nearly degenerate S_1 and S_2 states computed at 2.21 eV and with a summed oscillator strength of 1.120 (note that for technical reasons the symmetry of the molecule has been lowered from C_{4v} to C_1. In the actual C_{4v} symmetry of the molecule, the S_1 and S_2 states correspond to the degenerate 1^1E states). On the basis of their vertical excitation energies and oscillator strengths the S_1 and S_2 excited states are responsible for the intense Q band appearing in the electronic absorption spectrum of the complex at 635 nm (see Table 4). The S_1 and S_2 states have a π,π^* character as they involve transitions between the HOMO and LUMO Gouterman orbitals (for an extensive discussion of the ground-state electronic structure of the target complexes we refer the reader to ref 4). The corresponding triplets are the degenerate T_1 and T_2 excited states (1^3E in the actual C_{4v} symmetry of the molecule) located vertically at 1.39 eV. Because these are the lowest triplet states of the complex, they are involved in the energy-transfer reaction with the ground-state molecular oxygen, $^3O_2$ ($^3\Sigma_g$). As previous theoretical studies on nickel phthalocyanines and naphthalocyanines have indicated that the triplet π,π^* excited states undergo a minor geometrical relaxation,[33] it is reasonable to assume that the adiabatic energies of the T_1 and T_2 excited states are only slightly lower than the vertical excitation energies, that is, still sufficiently higher than the $^3O_2$ ($^3\Sigma_g$) $\rightarrow$ $^1O_2$ ($^1\Delta_g$) excitation energy (0.98 eV).[21] The favorable match between the pentapalladated triplet-state energy and the first excitation energy of the molecular oxygen certainly plays a key role in determining the observed high efficiency of the complex as a $^1O_2$ ($^1\Delta_g$) photosensitizer.

As inferred from Table 2, a set of nearly degenerate triplet excited states are located between the S_2/S_1 and T_2/T_1 pairs of the π,π^* excited states. According to their composition, these triplet states are localized on the peripheral N_2PdCl_2 moieties, as they originate from transitions out of the set of $\pi_{\text{Pd-Cl}}$ MOs into the set of the nearly degenerate $\sigma^*_{\text{Pd-N}_2\text{Cl}_2}$ MOs (cf. Figure 6 of ref 4). Given their close proximity (0.16 eV) to the S_1 state and their predominant metal character, the T_3-T_6 set of triplets are likely to open a route for an efficient $S_2/S_1 \rightarrow T_2/T_1$ ISC process. This explains the very low fluorescence emission quantum yield of this complex.

As for the monopalladated complex, TDDFT/B3LYP results in Table 3 show that the lowest singlet excited states are the nearly degenerate S_1 and S_2 states computed at 2.20 and 2.21 eV and with oscillator strength of 0.545 and 0.544, respectively. On the basis of their vertical excitation energies and oscillator strengths, the S_1 and S_2 excited states are responsible for the intense Q band with maximum at 631 nm (see Table 4). They originate from one-electron transitions out of the Gouterman HOMO into the nearly degenerate Gouterman LUMO and LUMO+1 (cf. Figure 6 in ref 4). An energy gap of 0.83 eV separates the S_1 and S_2 π,π^* states from the corresponding triplets, T_1 and T_2. Unlike in the case of the pentapalladated complex, no additional excited states are located between the S_2/S_1 and T_2/T_1 pairs of π,π^* excited states. However, a triplet state, T_3, is predicted to lie vertically immediately above the S_2/S_1 pair. This state has a multi-transition character as it originates from one electron transitions out of the nearly degenerate HOMO-1 and HOMO-2 $\pi_{\text{pyz-py}}$ MOs into the LUMO and LUMO+1 π^* MOs. The near degeneracy of the T_3 and S_2/S_1 pair of states suggests that the relaxed energy surfaces of these states are likely to cross, opening a route for an efficient intersystem crossing (ISC) process. Thus, just as in the case of the pentapalladate complex, population of the T_1 state is greatly facilitated, that is in line with the almost negligible fluorescence quantum yield and the high Φ_Δ values determined for the two complexes. According to the TDDFT results there also is a favorable match between the triplet-state energy and the first excitation energy of the molecular oxygen in the case of the monopalladated species.

Conclusions

A set of three Pd^{II} complexes of the macrocyclic porphyrazine free-base tetrakis-2,3-[5,6-di-(2-pyridyl)pyrazino]porphyrazine, namely tetrakis-2,3-[5,6-di-(2-pyridyl)pyrazino]porphyrazinatopalladium(II), [$Py_8TPyzPzPd$], its related

Table 4. UV–visible Spectral Data for the Mono- and Pentapalladated Species in DMF

	λ, nm (lg ε)	
compound	Soret region	Q-band region
[$Py_8TPyzPzPd$][a]	340 (4.65)[b] 400sh 572 (4.10)[b]	631 (4.68)[b]
[$Py_8TPyzPzPd$]$^{1-}$ [c]	340 (4.95) 400sh (4.45) 503 (4.05) 545 (4.39) 596sh (4.33)	663 (4.56) 800 (3.97)
[$(PdCl_2)_4Py_8TPyzPzPd$][a]	343 (5.00) 575 (4.37)	635 (5.11)
[$(PdCl_2)_4Py_8TPyzPzPd$]$^{1-}$ [c]	346 (4.96) 400sh (4.51) 510 (4.08) 551 (4.45)	605 (4.34) 682 (4.56) 800 (4.00)
[$(2\text{-Mepy})_8TPyzPzPd$]$(I)_8$[a]	340 (5.06) 400sh 577 (4.43)	638 (5.16)
[$(2\text{-Mepy})_8TPyzPzPd$]$^{7+}$ [c]	340 (4.97) 400sh (4.46) 510sh (4.09) 555 (4.40)	604 (4.39) 674 (4.50) 825 (3.93)

[a] In the presence of HCl (ca. 1×10^{-4} M). [b] ε values are only approximate because of the presence of aggregation. [c] ε values calculated from the spectra obtained by complete reduction of the corresponding unreduced species.

octacation $[(2\text{-Mepy})_8\text{TPyzPzPd}]^{8+}$, and the pentapalladated species, $[(\text{PdCl}_2)_4\text{Py}_8\text{TPyzPzPd}]$, the latter formed upon coordination to the external pyridine N atoms of four PdCl_2units in a quite rare arrangement, were recently reported and their structural and physicochemical properties examined.[4] Their extremely facile multiple stepwise one-electron reductions in different solvents (pyridine, DMSO, DMF) illustrate the remarkable electron-deficient properties of the basic "pyridinopyrazinoporphyrazine" macrocycle. This is incremented by the aligned contributing electronic effects because of the presence of positive charges in the octacation and the PdCl_2 units in the pentapalladated species. All three species are stable in the solid, but may be sensitive to the presence of reducing agents when in solution. It was verified that all three species at $\sim 10^{-4}$ M concentration are stable in DMF, whereas in more dilute solutions (10^{-5}-10^{-6} M) the complexes are one-electron reduced, very likely by dimethylamine released by the solvent. However, preacidification ([HCl] about 10^{-4} M) of the solvent avoids reduction. Neutral pentapalladated, $[(\text{PdCl}_2)_4\text{Py}_8\text{TPyzPzPd}]$, and monopalladated, $[\text{Py}_8\text{TPyzPzPd}]$, complexes exhibit potent photosensitizing properties for the generation of singlet oxygen, $^1\text{O}_2$.[34] This behavior finds adequate support by the measured triplet state lifetimes, the fluorescence spectral response and reasonable explanation by TDDFT calculations as to the nature and energy of the lowest singlet and triplet excited states. On the basis of their highly efficient photosensitizing activity, the $[(\text{PdCl}_2)_4\text{Py}_8\text{TPyzPzPd}]$ and $[\text{Py}_8\text{TPyzPzPd}]$ complexes should be promising materials for use in photodynamic therapy (PDT).

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