Photophysical properties of metal complexes of meso-tetrakis(4-sulphonatophenyl)porphyrin

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Abstract

Laser kinetic spectroscopy was used to determine the photophysical parameters (fluorescence and triplet–triplet (T–T) spectra, lifetimes of the triplet and singlet states, bimolecular constant for oxygen quenching, fluorescence quantum yield and quantum yield of formation of the triplet state) of the water-soluble complexes of Ag(II), Cd(II), Co(II), Cu(II), Mg(II), Ni(II), Pd(II), Pt(II) and Zn(II) with the tetrasodium salt of meso-tetrakis(4-sulphonatophenyl)porphyrin (H_2TPPS_4). The complexes of metals with d^0 and d^{10} electron configurations (Cd(II), Mg(II) and Zn(II)) are characterized by high triplet quantum yields and strong fluorescence in the red spectral region and are thus more efficient photosensitizers than the ligand alone.

Keywords: Laser kinetic spectroscopy; Photophysical properties; Metal complexes; Meso-tetrakis(4- sulphonatophenyl)porphyrin

1. Introduction

The photosensitizing effects of porphyrins have been the subject of extensive studies [1] because of their potential use in photomedicine, e.g. in the photodynamic therapy (PDT) of tumours [2]. PDT involves the selective accumulation of photosensitizers in tumour cells. The mechanism of destruction of these cells involves the formation of the triplet excited state of the photosensitizer and the direct transfer of energy to the target or collision energy transfer with the formation of reactive singlet oxygen, which preferentially attacks the target double bonds (e.g. of the cell membranes [3]).

Although haematoporphyrin derivative is most commonly used in human medicine, extensive research has been concerned with the preparation of new photosensitizers [2]. In addition to the prerequisite of selective bonding to the tumour tissue, new photosensitizers must fulfil certain photophysical criteria, including the efficient formation of triplet states [4] and the singlet state of oxygen [5].

The metalloporphyrins constitute an important group of sensitizers with a porphyrin skeleton. Their photophysical properties are significantly affected by the nature of the central metal ion [6]. The properties of regular porphyrins containing metal ions with a d^0 or d^{10} configuration are determined essentially by the π electrons of the porphyrin ring, with only minor perturbations from the electrons of the central substituent. In contrast, in porphyrins containing a transition metal with incomplete d orbitals (irregular porphyrins), the electrons of these orbitals can significantly integrate with the π and π^* orbitals of the porphyrin ring. The singlet and triplet excited states of irregular porphyrins are usually short lived and the quantum yields of triplet state formation are very low.

Of the artificial derivatives of the porphyrin skeleton with good photophysical parameters, frequent studies have been carried out on the tetrasodium salt of meso-tetrakis(4-sulphonatophenyl)porphyrin (H_2TPPS_4), which has been used in human medicine for PDT [7] and whose central hydrogen atoms can be replaced by a metal. Far less is known about the photophysical properties of metal complexes with this ligand, which are water soluble. The photophysical properties of complexes of Sn(IV), Zn(II), Pd(II), Mn(III) and Co(III) with $TPPS_4^{2-}$ have been reported [8,9]. The measured quantum yields Φ_T of triplet formation of $SnTPPS_4Cl_2$ [8] and $PdTPPS_4$ [9] approach unity. The reported Φ_T value of $ZnTPPS_4$ (0.84) [9] is greater than for H_2TPPS_4. Studies of the Mn(III) and Co(III) complexes did not reveal the formation of triplet states or fluorescence in the red spectral region.

In this study, we report the preparation of the complexes of Ag(II), Cd(II), Co(II), Cu(II), Mg(II), Ni(II), Pd(II),

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Pt(II) and Zn(II) with the $TPPS_4^{2-}$ ligand and determine the photophysical parameters of these complexes.

2. Experimental details

2.1. Laser kinetic spectroscopy

Aqueous solutions of the metal complexes with $TPPS_4^{2-}$ were excited using an FL-3002 dye laser ($\lambda = 420$ nm; pulse length, 30 ns; pulse energy, up to 10 mJ) pumped by an XeCl excimer laser (both from Lambda Physik). The experimental set-up (Applied Photophysics) and the method of measurement of the time-resolved triplet–triplet (T–T) and emission spectra have been described previously [10,11]. The bimolecular constants of triplet excited state quenching of the photosensitizers by oxygen were calculated from the known oxygen concentrations [12] and the measured rate constants of deactivation of the triplet states for solutions saturated with oxygen, air and argon. Each decay curve was obtained by averaging 64 individual traces. Error limits are given throughout the text, the errors being calculated from the statistical treatment of averaged sets of data.

To calculate the extinction coefficients, solutions were prepared with identical absorbance at the excitation wavelength ($A_{420} = 0.5$). The relative extinction coefficients of the triplet states were estimated by the complete conversion method [4]. This method is applicable only for systems in which the quantum yield of the triplet state is high, the lifetime of the triplet state is long and the singlet lifetime is short compared with the duration of the exciting pulse. Focused laser radiation with an energy of 9 mJ was used for excitation. No change in the amplitude of the triplet state with increasing excitation energy density was observed at this energy density. The quantum yield of the triplet state Φ_T at low excitation energy density was calculated by the comparative method using the relationship [13,14]

$$\Phi_T = \Phi_T^{ST} \times \frac{\epsilon_T \Delta A_T^{ST}}{\epsilon_T^{ST} \Delta A_T}$$

where $\Delta A_T / \epsilon_T$ is the initial concentration of the triplet state. H_2TPPS_4 was chosen as the standard, with $\Phi_T^{ST} = 0.76$, an extinction coefficient for T–T absorption at a wavelength of 460 nm of $\epsilon_{460} = 130\,000$ l mol^{-1} cm^{-1} and a fluorescence quantum yield $\Phi_f^{ST} = 0.16$ [6,9].

All the experiments were carried out at laboratory temperature in aqueous solutions and, for $MgTPPS_4$ and $CdTPPS_4$, in 0.01 N NaOH, to avoid demetallization of these unstable complexes in non-alkaline media.

2.2. Preparation of the complexes

The preparation of the dodecahydrate of the tetrasodium salt of H_2TPPS_4 was carried out by sulphonation of meso-tetraphenylporphyrin, prepared by condensation of pyrrole

with benzaldehyde in refluxing propionic acid by the method of Adler et al. [15]. H_2TPPS_4 was purified by the method of Jirsa and Kakáč [16].

The complexes of Mg(II), Ni(II), Pd(II), Ag(II) and Cd(II) were prepared using the method of Adler et al. [17] for the preparation of metalloporphyrins. This involved heating anhydrous H_2TPPS_4 with an excess of the corresponding anhydrous metal salt in refluxing N,N-dimethylformamide (DMF). The formation of the complex was monitored by measuring the absorption spectrum. The raw reaction mixture was obtained by distilling off the DMF under vacuum or by precipitation with excess $CHCl_3$ and subsequent filtration. Excess metal salt was then removed from the mixture by dissolving in 0.01 N NaOH with subsequent filtering off of the undissolved metal hydroxides. The filtrate was then adjusted to pH 8–9 with dilute HCl and desalted by the gel chromatographic method on Sephadex G-50 flushed with distilled H_2O. The Co(II), Cu(II), Zn(II) and Pt(II) complexes were prepared in a similar manner in aqueous medium. The desalting of the reaction mixtures was carried out in a similar manner to the complexes prepared in DMF medium.

The identity of H_2TPPS_4 was confirmed by measuring the ^{1}H-NMR, UV–visible and IR spectra and comparison with those described in the literature [16]. The identity of the complexes was confirmed by comparison with the analogous complexes described in the literature using UV–visible and IR spectra and elemental analysis for C, H, N and S [18,19]. The content of the given central metal was determined by atomic absorption spectroscopy.

The purity of the prepared H_2TPPS_4 and its complexes was verified by capillary zone electrophoresis, carried out using the apparatus described previously [10]. The background electrolyte was borate buffer, pH 9.14 (0.05 M H_3BO_3, 0.025 M NaOH). The separation was carried out at a working potential of $U = 17$ kV, constant current of $I = 8$ μA and laboratory temperature. The fractions were detected using a UV spectrophotometric detector at $\lambda = 206$ nm. The electropherograms of all the test substances contained only one peak, corresponding to the pure substance.

3. Results and discussion

3.1. Singlet states

The measured lifetime of the singlet excited state of H_2TPPS_4 (6.0 ns) is in agreement with information given in the literature (5.2 ns [14] or 10.4 ns [6]). The determined lifetime of the $MgTPPS_4$ singlet state is shorter (5.4 ns), while the lifetimes of the other complexes (less than 3.0 ns) are significantly affected by the presence of a transition metal atom and cannot be determined because of the pulse length of the excitation source (30 ns). The trend in the lifetimes of the singlet excited states is comparable with the observations for unsulphonated metal complexes with tetraphenylporphyrin [6].

The fluorescence spectra of solutions of the individual complexes in the red spectral region (Fig. 1) are very different; higher fluorescence quantum yields are expected for MgTPPS$_4$ (0.18, Fig. 1(b)), ZnTPPS$_4$ (0.17, Fig. 1(c)), H$_2$TPPS$_4$ (0.16 [6], Fig. 1(a)) and CdTPPS$_4$ (0.08, Fig. (d)). PdTPPS$_4$ (0.04, Fig. 1(e)) and PtTPPS$_4$ (0.02, Fig. (f)) complexes are characterized by lower fluorescence quantum yields in the red region.

Differences in the aggregation of the individual species compared with published data [6,8,9] were found on the basis of the fluorescence and absorption spectra. MgTPPS$_4$ Fig. 1(b)), ZnTPPS$_4$ (Fig. 1(c)) and H$_2$TPPS$_4$ (Fig. 1(a)) exist primarily as monomeric species under the conditions used here. In contrast, the broadening of the Soret band (Fig. 2(a)) and the presence of two peaks in the PdTPPS$_4$ emission spectrum (Fig. 1(e)) indicate a marked tendency to form aggregates.

The transition metalloporphyrins of groups VIII and IB are characterized by low fluorescence quantum yields associated with the filling of the e$_g$(d$_\pi$) orbitals [6]. CoTPPS$_4$ is characterized by a lack of emission, similar to its unsulphonated analogue CoTPP [6]. NiTPPS$_4$ (Fig. 1(g)), with a marked fluorescence shift into the near-IR, CuTPPS$_4$ and AgTPPS$_4$ have Φ_f values below 0.01.
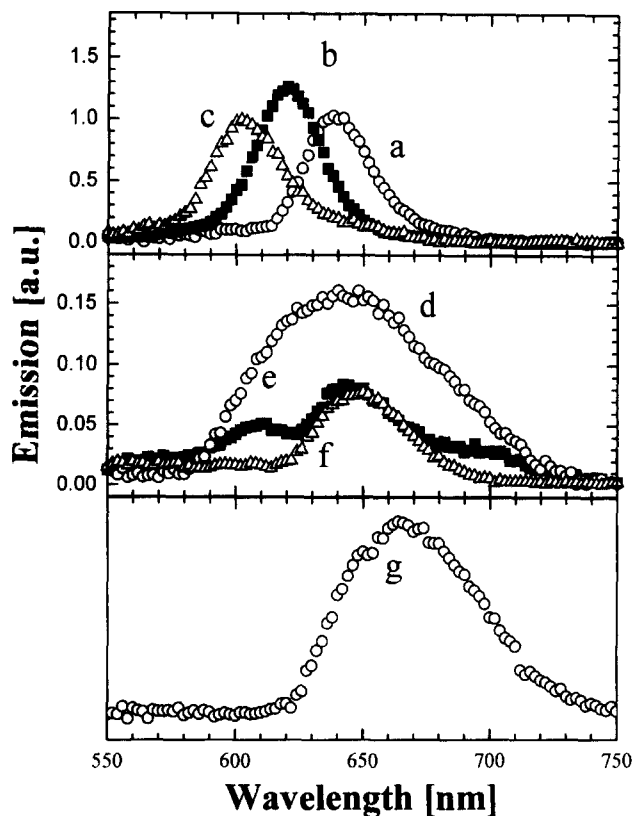

Fig. 2. UV–visible absorption spectra of the ground state of a 10^{-5} M solution of PdTPPS$_4$ (a), CdTPPS$_4$ in 0.01 N NaOH (b) and ZnTPPS$_4$ (c).

3.2. Triplet states

The photophysical parameters of the triplet states of the MgTPPS$_4$, CdTPPS$_4$, PdTPPS$_4$, PtTPPS$_4$, ZnTPPS$_4$ and H$_2$TPPS$_4$ complexes are given in Table 1. The T–T spectra of the metal complexes are similar to that of H$_2$TPPS$_4$; the maximum absorption in the blue spectral region lies in the range 440–480 nm for all the complexes and differs only in the extinction coefficient (Table 1). The triplet states of these compounds are efficiently quenched by oxygen; the rate constant for oxygen quenching k_{O2} is greater than 10^9 l mol^{-1} s^{-1} and is controlled by the diffusion of oxygen.

The measured transient spectrum of AgTPPS$_4$ coincides with the T–T spectrum of the ligand, but the absorbance changes in a 10^{-5} M solution are more than 20-fold lower. Although the formation of the triplet state occurs with a low quantum yield, or the triplet state has a low extinction coefficient in the blue spectral region, this state is very stable, with a lifetime of greater than 300 μs (Table 1). These similarities in the lifetimes and T–T spectra are not due to traces of H$_2$TPPS$_4$, since the initial sample of AgTPPS$_4$ does not contain a measurable concentration of H$_2$TPPS$_4$ according to capillary zone electrophoresis, and no changes in the UV spectra or amplitudes of the time profiles of the triplet state are observed after several tens of laser pulses.

No transient absorption in the 300–650 nm region, corresponding to T–T transitions, is observed for the other irregular complexes (CoTPPS$_4$, CuTPPS$_4$ and NiTPPS$_4$), although the triplet state of the unsulphonated analogue CuTPP, with a lifetime of 40 ns, has been found in toluene solution at room temperature [6]. In analogy with Cu(II) and Ag(II), which have identical d^9 electron configurations, it seems probable that CuTPPS$_4$ is not detected due to the weak spectral transient and not as a result of the low stability of this complex.

The lifetime of the triplet state of H$_2$TPPS$_4$ (414 μs) is in good agreement with the value given in the literature (400 μs) for H$_2$TPPS$_4$ in neutral aqueous medium [14]. Compared with the free ligand, all the other complexes with

Fig. 1. Fluorescence spectra of H$_2$TPPS$_4$ (a), MgTPPS$_4$ in 0.01 N NaOH (b), ZnTPPS$_4$ (c), CdTPPS$_4$ in 0.01 N NaOH (d), PdTPPS$_4$ (e), PtTPPS$_4$ (f) and NiTPPS$_4$ (g) in the red region, corrected for the sensitivity of the photomultiplier. Solution absorbance measured at a wavelength of 420 nm, $A_{420} = 0.5$.
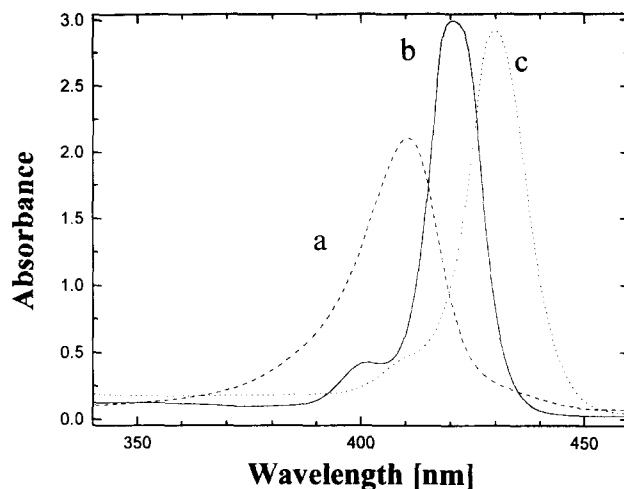
Table 1

Photophysical properties of the triplet states of the metal complexes of $TPPS_4^{2-}$: natural lifetime τ_T and bimolecular constant for oxygen quenching k_{O_2} in 10^{-5} M solution, extinction coefficient of triplet state at 460 nm ϵ_{460} and estimated quantum yield of triplet state formation Φ_T

Compound	$\tau_T{}^a$ (μs)	$10^9 k_{O_2}$ (l mol^{-1} s^{-1})	$\epsilon_{460}{}^a$ (10^{-5} l mol^{-1} cm^{-1})	$\Phi_T{}^a$
H_2TPPS_4	414	2.0 ± 0.1	1.30 [b]	0.76 [b]
$AgTPPS_4$	301	1.8 ± 0.1	–	–
$CdTPPS_4{}^{c,d}$	149	1.4 ± 0.1	0.80	0.88
$MgTPPS_4{}^d$	467 (43%)			
	2640 (57%)	1.2 ± 0.3 [e]	0.43 [e]	0.85 [e]
$PdTPPS_4$	268	2.2 ± 0.1	1.32	0.63
$PtTPPS_4$	12.7	2.9 ± 0.9	1.71	0.40
$ZnTPPS_4$	2040	1.3 ± 0.1	1.61	0.86

[a] $\pm 10\%$.
[b] Literature value [11].
[c] At 480 nm.
[d] In 0.01 N NaOH.
[e] Second process.

metals, with the exception of $MgTPPS_4$ and $ZnTPPS_4$, exhibit lower lifetimes of the triplet states. The long lifetime of $ZnTPPS_4$ is in agreement with earlier measurements by Kalyanasundaram and Neumann-Spalart [9]. The biexponential quenching kinetics found for $MgTPPS_4$ indicate the formation of two excited species. The species with a lifetime of 2.65 ms is apparently the triplet state of $MgTPPS_4$, which can be expected to have a long lifetime, similar to complexes with other ligands [6]. The second species has a lifetime similar to the ligand alone H_2TPPS_4; however, the UV–visible spectrum of the ground state of $MgTPPS_4$ does not exhibit any changes even after 100 laser pulses.

The following three effects are apparently combined here.

3.2.1. The effect of the electronic configuration of the central metal atom

Metalloporphyrins with electronic configurations of d^0 and d^{10} ($MgTPPS_4$, $ZnTPPS_4$ and $CdTPPS_4$) have regular electronic absorption spectra, indicating that significant spin–orbital interaction (decreasing the lifetimes of the excited states), caused by the overlap of the $e_g(d_\pi)$ orbitals of the porphyrin with the nd orbitals of the central metal, does not occur. Metalloporphyrins with Mg(II), Zn(II) or Cd(II) as the central ion are fluorescent metalloporphyrins which, in addition to fluorescence, also exhibit high quantum yields and long triplet excited state lifetimes [6,21]. Thus it is not surprising that high quantum yields and long triplet excited state lifetimes were found for Mg(II), Zn(II) and Cd(II) complexes of $TPPS_4^{2-}$.

Metalloporphyrins with d^6–d^9 electron configurations (all the other studied metalloporphyrins) have hypso-type electronic spectra. This indicates partial overlap of the $e_g(d_\pi)$ orbitals of the porphyrin with the nd orbitals of the central metal ion, leading to increased spin–orbital interaction, which decreases the lifetimes of the excited states [6,21].

Metalloporphyrins with central metal ions from the first transition metal series of the periodic system (with hypso-

type electronic spectra) are radiationless metalloporphyrins. They are characterized by very short triplet state lifetimes. This is explained by the rapid non-radiant de-excitation of the π–π^* states via low-lying ligand field d–d or ring $\rightleftharpoons$ metal charge transfer excited states (π–d or d–π^*) [6]. Thus measurable triplet state lifetimes are not observed for $CoTPPS_4$, $NiTPPS_4$ and $CuTPPS_4$.

Metalloporphyrins with Pd(II), Pt(II) and Ag(II) central metal ions are fluorescent metalloporphyrins which, relative to the radiationless species, have longer triplet state lifetimes. The non-emisisive de-excitation is far less important here. In agreement with theory, H_2TPPS_4, $PtTPPS_4$ and $AgTPPS_4$ have longer triplet excited state lifetimes than the radiationless metal complexes.

3.2.2. The effect of a "heavy" central metal atom

The presence of atoms with high proton numbers leads to rapid transitions between states with different multiplicities, and thus also a rapid transition from the triplet state back to the ground singlet state [22]. The effect of the heavy atom can be followed (however, it is combined with the previous effect) by comparing the lifetimes of the triplet excited states: $H_2TPPS_4 > PdTPPS_4 = AgTPPS_4 > PtTPPS_4$ (aqueous medium) or $H_2TPPS_4 > CdTPPS_4$ (0.01 M NaOH). Thus the lifetime of the triplet state decreases with increasing metal proton number.

3.2.3. The effect of the aggregation of porphyrins and metalloporphyrins in aqueous medium

Water-soluble porphyrins and metalloporphyrins readily aggregate even at low concentrations. The formation of aggregates leads to a decrease in the lifetime of the triplet excited state [23]. The longer lifetimes of $MgTPPS_4$ and $ZnTPPS_4$ may therefore be a consequence of the fact that these complexes do not form dimers. A similar explanation has been given for the longer triplet state lifetime of the Zn complex of tetrakis(trimethylaminophenyl)porphyrin

compared with the free ligand [6]. The large difference between the literature value of the quantum yield of the triplet state of the PdTPPS$_4$ complex [9] and our result ($\Phi_T = 1$ compared with $\Phi_T = 0.56$) is apparently caused by the conditions used in this study due to the shift in the monomer ⇌ aggregate equilibrium in favour of the aggregate, which is mostly photochemically inactive.

The assumption of the existence of an aggregate species in aqueous solution is in agreement with the observation that the UV–visible bands of the PdTPPS$_4$ complex are sensitive to the presence of non-ionogenic tenside. After the addition of tenside (Triton X-100, supercritical concentration 2×10^{-3} M), the Soret band is red shifted and narrows while the Q band in the visible region is blue shifted. These changes in the UV–visible bands are typical of the incorporation of porphyrins or metalloporphyrins into micellar assemblies accompanied by disruption of the non-covalent aggregates [6].

The highest Φ_T values were measured for the Zn(II), Cd(II) and Mg(II) complexes with central metal electron configurations of d^0 or d^{10}. The calculated Φ_T value for ZnTPPS$_4$ (0.86) is in good agreement with the literature value (0.84 [9]). The sum $\Phi_f + \Phi_T$ for these complexes is close to unity, indicating that a minimum of the absorbed energy is converted into heat. This trend is characteristic of the Mg(II) and Zn(II) complexes and of free ligands of the porphyrin type, where $\Phi_f + \Phi_T > 0.95$ [6]. However, the usefulness of these complexes is limited by their stability. While ZnTPPS$_4$ is stable in neutral medium, demetallization of MgTPPS$_4$ occurs after several tens of minutes and CdTPPS$_4$ is stable only in alkaline medium (pH > 12).

Acknowledgements

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