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Photophysical and photochemical studies of zinc(II) phthalocyanine derivatives—effects of substituents and solvents

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The effects of substituents and solvents on the photophysical and photochemical parameters of zinc(II) phthalocyanines are reported. The complexes studied are zinc phthalocyanine (ZnPc), zinc tetra(*tert*-butylphenoxy)phthalocyanine [$ZnPc(TBPh)_4$], zinc octa(methylphenoxy)phthalocyanine [$ZnPc(MPh)_8$], zinc tetranitrophthalocyanine [$ZnPc(NO_2)_4$], zinc octachlorophthalocyanine ($ZnPcCl_8$), zinc tetrasulfophthalocyanine [$ZnPc(SO_3^-)_4$], a mixture of zinc mono-, di-, tri- and tetrasulfophthalocyanine [$ZnPc(SO_3^-)_{mix}$] and zinc naphthalocyanine (ZnNPc). It was found that the presence of peripheral substituents on the macrocycle enhances the yield of the triplet state. Among the different substituents, the sulfonated derivative, $ZnPc(SO_3^-)_{mix}$, has the longest triplet lifetime (τ_T) and the highest singlet oxygen quantum yield (ϕ_Δ). The near infra-red absorptions of the solvents reveal that solvents that absorb around 1100 nm (triplet energy level) and around 1270 nm (singlet oxygen energy level), quench the triplet state of the ZnPc derivative as well as singlet oxygen. Although water has a high singlet oxygen quenching effect, the ϕ_Δ value for $ZnPc(SO_3^-)_{mix}$ in water is still reasonably high at 0.48, which may provide an explanation for the efficient photosensitization by this molecule in photodynamic studies.

Introduction

Singlet oxygen has been implicated in photosensitized oxidation reactions. Such reactions have been exploited in, for example, photodamage of viruses,[1,2] photodynamic therapy (PDT),[3,4] photocarcinogenesis[5,6] and photodegradation of pollutants.[7,8] The enormous reactivity of singlet oxygen also finds applications in bleaching and disinfection reactions as well as in many chemical syntheses, such as the reaction of singlet oxygen with aromatic compounds, which leads to the formation of endoperoxides.[9,10] Singlet oxygen is produced by an isoenergetic quenching of the triplet excited states of photosensitizers by ground state (triplet) molecular oxygen.

Many groups of compounds have been shown to possess photosensitizing tendencies. Metallophthalocyanines (MPcs), in particular, have proved to be highly promising in this respect, due to their intense absorption in the red region of visible light. High triplet state quantum yields and long lifetimes are required for efficient sensitization and these criteria may be fulfilled by the incorporation of a diamagnetic metal such as zinc, aluminum or silicon into the phthalocyanine macrocycle. This automatically excludes phthalocyanine compounds containing paramagnetic transition metals such as copper, cobalt and iron from photosensitizing activity.

Zinc phthalocyanine complexes have attracted much interest because of their appreciably long triplet lifetimes.[11–13] Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with lifetime of the excited state. The introduction of peripheral substituents onto the MPc ring is expected to affect both the triplet quantum yield and lifetime, hence it is desirable to carry out studies on the effects of substituents on these parameters. As different solvents display different quenching abilities towards the excited triplet state of photosensitizers, the latter's lifetime should vary as the solvent is changed. Solvent effects on photosensitizing ability could be due to relative shifts in the positions of the photosensitizer's singlet and triplet excited states. In some solvents, the separation between the singlet and triplet may be maximal, resulting in a low intersystem crossing rate.[14]

In this work, we report on the effects of peripheral ring substituents and solvents on the photophysical parameters of zinc(II) phthalocyanine derivatives, shown in Fig. 1. The photophysics as well as singlet oxygen production by $ZnPc(SO_3^-)_{mix}$ in water will be investigated due to the use of this mixed complex in PDT. Studies in water are of importance for practical applications.

Results and discussion

Spectroscopic studies

The absorption spectra of zinc phthalocyanine (ZnPc), zinc octa(methylphenoxy)phthalocyanine [$ZnPc(MPh)_8$], zinc tetra(*tert*-butylphenoxy)phthalocyanine [$ZnPc(TBPh)_4$] and zinc naphthalocyanine [ZnNPc] in DMSO are typical for monomeric phthalocyanines (Fig. 2, Table 1). The Q bands of $ZnPc(TBPh)_4$ (trace ii in Fig. 2) and $ZnPc(MPh)_8$ are not as sharp as those of ZnPc and ZnNPc (traces i and iii in Fig. 2); they exhibit some broadening, even at very low concentrations. The broadening of bands and formation of an extra band, called the X band, have been attributed to a slight reduction in the symmetry of the molecule due to the presence of bulky groups at the non-peripheral positions.[15] The observation of broadening in spectra of compounds having bulky peripheral substituents may suggest that steric effects of the substituents in these positions could also cause some lowering in symmetry. A flexible σ bond connects the phenyl rings to the local MPc ring. Twisting of the phenyl ring about this σ bond distorts the molecule and so a slight loss of symmetry occurs.[15] Zinc

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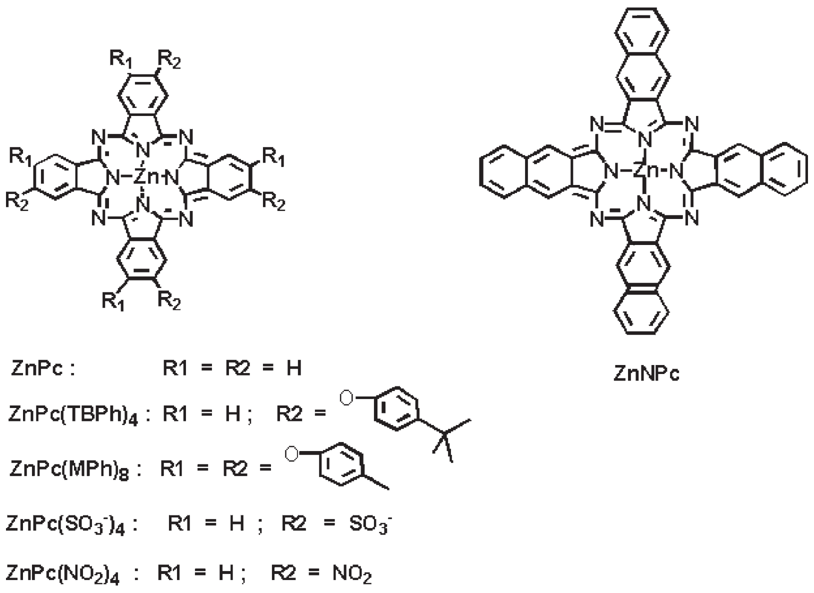

Fig. 1 Structure of zinc(II) phthalocyanine derivatives.

tetranitrophthalocyanine [ZnPc(NO_2)$_4$] (trace iv in Fig. 2) and zinc octachlorophthalocyanine (ZnPcCl_8) are known[12,16] to be cofacially aggregated in DMSO. The presence of two non-vibrational bands (the low energy and high energy bands for monomer and dimer, respectively), are typical of aggregation behaviour in MPc complexes.[17] In a recent paper,[16] we determined the extinction coefficients for monomeric and dimeric species of ZnPc(NO_2)$_4$. The spectra of dilute solutions of zinc tetrasulfophthalocyanine [ZnPc(SO_3^-)$_4$] and of a mixture of zinc mono-, di-, tri- and tetrasulfophthalocyanine [ZnPc(SO_3^-)$_{mix}$] in DMSO show strong Q bands at 680 and 675 nm, respectively, implying that monomeric species are predominant. In all the solvents studied, ZnPc showed monomeric behaviour up to ~1×10^{-5} mol L^{-1}.

Triplet quantum yields, triplet lifetimes and fluorescence

Table 1 shows the values of the triplet quantum yield (ϕ_T) and triplet lifetime (τ_T) for the various ZnPc derivatives. Fig. 3 shows the singlet depletion curves for ZnPc and ZnPc(TBPh)$_4$. For all derivatives except ZnNPc, ϕ_T values are larger than for the unsubstituted ZnPc complex. This suggests that the presence of these substituents encourages intersystem crossing from excited singlet to triplet state. The increase in ϕ_T values is complemented by a decrease in fluorescence quantum yield (ϕ_F) values for all the derivatives except ZnPc(MPh)$_8$. In the case of ZnNPc, both the excited singlet and triplet states probably suffer from substantial internal conversion, such that the rate constant for internal conversion would be high for both states, resulting in low ϕ_T. Also, ZnNPc is known to degrade fast upon photolysis,[16] hence reducing the number of molecules in the excited state. Due to a lack of suitable data in different solvents for ZnPc, only a very few values of ϕ_T are compared in Table 2. However, the available data shows that the values of ϕ_T are slightly higher in pyridine and toluene compared to DMSO.

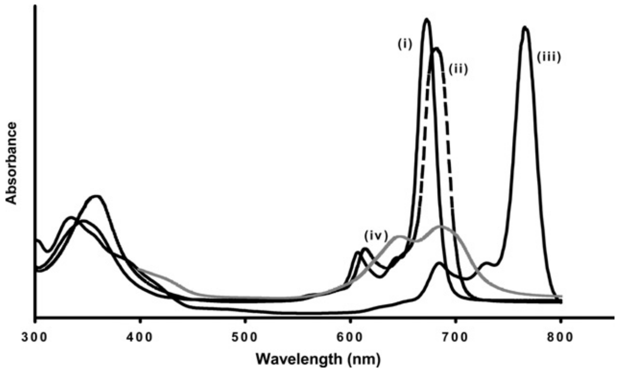

Fig. 2 Electronic absorption spectra of (i) ZnPc (4×10^{-6} mol dm^{-3}), (ii) ZnPc(TBPh)$_4$ (6×10^{-6} mol dm^{-3}), (iii) ZnNPc (6×10^{-6} mol dm^{-3}) and (iv) ZnPc(NO_2)$_4$ (2×10^{-5} mol dm^{-3}) in DMSO.

There is no particular trend in the variation of τ_T with substituent type. However, it is striking from Table 1 that sulfonation brings about a longer triplet lifetime. This implies that the anionic complexes are less efficient at dissipating the energy of the excited triplet state. Also of interest is the relatively low τ_T value for ZnPc(TBPh)$_4$. It appears that the σ C–H bonds of the *tert*-butyl substituents may exhibit the so-called "loose bolt" effect,[14] associated with the vibration of bonds set off by the parent molecule in a similar manner as a loose bolt in a moving part of the machine, which tends to be set in motion by other moving parts of the machine. The "loose bolt" effect accelerates internal conversion since electronic energy "leaks out" through C–H vibrations. The "loose bolt" effect is expected to be less pronounced in ZnPc(MPh)$_8$ molecules since there are fewer C–H bonds than in ZnPc(TBPh)$_4$. The fact that the τ_T value of ZnPc(MPh)$_8$ is more than twice that of ZnPc(TBPh)$_4$ suggests that the triplet state of the former is probably being stabilized by some other factors. ZnNPc showed the shortest triplet lifetime. Naphthalene itself is known to be an efficient triplet state quencher.[18,19] The triplet lifetimes for ZnPc in Table 2 do not change much as the solvent is changed, with ZnPc in THF and benzonitrile showing marginally shorter lifetimes than in the other solvents.

ZnPc(SO_3^-)$_{mix}$ is of current interest for PDT, such that photophysical and photochemical studies in aqueous media are essential. Table 3 shows that the τ_T value for ZnPc(SO_3^-)$_{mix}$ is very low in water compared to that in non-aqueous solvents or D_2O. The reason for this can be explained in terms of the near IR spectra of the solvents, shown in Fig. 4 for three solvents, DMSO, DMF and H_2O, and how these affect the triplet and singlet oxygen lifetimes in solution. The triplet energy of ZnPc and many of its derivatives in solution is ~1.12 eV,[20,21] which corresponds to an absorption wavelength of ~1108 nm. The intensity and broadness of the solvent's absorption in this wavelength region should have considerable effect on the triplet lifetime. H_2O shows a very broad absorption near 1108 nm, which implies that

Table 1 Photophysical parameters of zinc(II) phthalocyanine derivatives in DMSO

	λ_{max} (Q band)/nm	Log ε	ϕ_Δ	$10^5/\phi_p$	ϕ_F	ϕ_T	S_Δ	τ_T/μs
ZnPc	672	5.38	0.67[a]	2.61	0.20	0.50[b]	1.34	350
$ZnPc(TBPh)_4$	681	5.15	0.60	3.33	0.14	0.85	0.71	160
$ZnPc(MPh)_8$	679	5.12	0.51	2.12	0.24	0.63	0.81	370
$ZnPc(SO_3^-)_4$	680	4.54	0.46	4.03	0.07	0.88	0.52	470
$ZnPc(SO_3^-)_{mix}$	675	4.66	0.72	13.65	0.14	0.86	0.84	530
$ZnPc(NO_2)_4$	645, 682	4.67, 4.87	0.11	—	0.02	—		310
$ZnPcCl_8$	641, 683	—	0.34	—	0.02	—		370
ZnNPc	766	5.24	0.19	16.35	0.07	0.37	0.51	126

[a] From ref. 34. [b] From ref. 12.

non-radiative decay and quenching of the sensitizer's triplet state would be more rapid in H_2O than in DMSO or DMF for which the 1108 nm absorption in minimal. Thus, τ_T values are lower in water when compared to DMSO or DMF (Table 3). The low value of τ_T for $ZnPc(SO_3^-)_{mix}$ in *n*-butylamine could be a result of the quenching of the triplet state by the amine group. The fluorescence quantum yield (ϕ_F) values reported in Tables 1 and 3 are generally low, as is typical for most phthalocyanine complexes. Fig. 5 shows that it is mainly the monomeric species that fluoresce. Aggregation lowers the photoactivity of molecules through dissipation of energy by the aggregates. In light of this, aggregated species like $ZnPc(NO_2)_4$ and $ZnPcCl_8$ have unsurprisingly low ϕ_F values (Table 1). The variation of ϕ_F values for $ZnPc(SO_3^-)_{mix}$ with solvent is given in Table 3. The highest value of ϕ_F was observed in *n*-butylamine in which the complex exists mainly in the more fluorescent monomeric form, as judged by the UV-Vis spectra. One would expect the amine part of the molecule to quench the complex's fluorescence, but it is known[22] that organic amines are inactive as quenchers of the singlet excited states of metallophthalocyanine complexes. The effect of solvents on ϕ_F for ZnPc has been discussed in detail before.[23]

Singlet oxygen and photobleaching quantum yield studies

The singlet oxygen quantum yield (ϕ_Δ) is a measure of the photosensitizer's ability to generate singlet oxygen. In a particular solvent, the value of ϕ_Δ could depend on a number of factors: (i) triplet quantum yield ϕ_T, (ii) triplet lifetime τ_T, (iii) triplet energy E_T, (iv) ability of substituents to quench singlet oxygen and (v) the efficiency of energy transfer from the excited triplet state to ground state molecular oxygen. It is difficult to actually identify which of these factors is predominant in explaining the observed trends in ϕ_Δ values. The unsubstituted ZnPc shows a higher singlet oxygen quantum yield than all of its derivatives studied [except $ZnPc(SO_3^-)_{mix}$], despite the fact that it possesses a lower triplet quantum yield than most of these complexes (Table 1). For substituted derivatives [except for $ZnPc(SO_3^-)_{mix}$], it is possible that intramolecular vibrations associated with introduction of certain substituents quench singlet oxygen as soon as it is formed. Some aggregation in $ZnPc(SO_3^-)_4$ cannot be ruled out. ZnNPc in particular has a low ϕ_Δ value due to its low values of ϕ_T and τ_T. In addition, because the triplet energy of ZnNPc is very low compared to that of ZnPc, this may result in a less efficient energy transfer from this state to ground state molecular oxygen. $ZnPc(NO_2)_4$ and $ZnPcCl_8$ also show very low ϕ_Δ values. This is due to these complexes' well-documented tendency to form aggregates in dilute solution.[12,16] Aggregates take up electronic energy and convert it into vibrational motion. As a result, molecular interaction with singlet oxygen is reduced drastically. The high value of ϕ_Δ for $ZnPc(SO_3^-)_{mix}$ could reflect the monomeric nature of this molecule; it is known that MPc complexes containing a larger variety of differently substituted sulfonated derivatives are less aggregated than those containing fewer (or only one) isomers.[8]

Table 1 shows that in DMSO the value of ϕ_Δ for $ZnPc(SO_3^-)_{mix}$ is higher than that of unsubstituted ZnPc. This suggests that $ZnPc(SO_3^-)_{mix}$ should be a better sensitizer than ZnPc in all applications involving singlet oxygen. Singlet oxygen absorbs at ~1267 nm and, as argued above, the solvent's

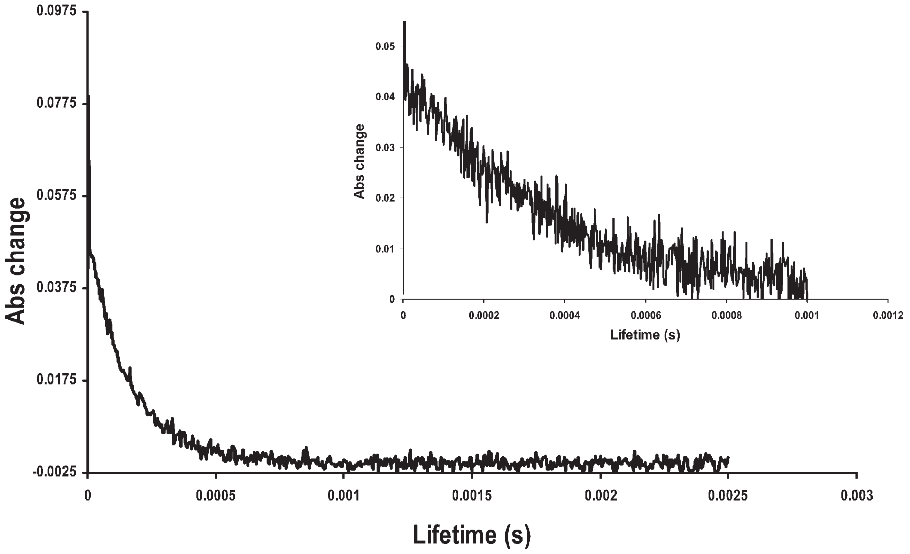

Fig. 3 Singlet depletion curve for 2×10^{-5} mol dm^{-3} $ZnPc(TBPh)_4$ in DMSO (inset: ZnPc in DMSO). $\lambda_{exc} = 680$ nm.

Table 2 Photophysical parameters of unsubstituted zinc(II) phthalocyanine (ZnPc) in various solvents

Solvent	ϕ_Δ	ϕ_T	S_Δ	τ_T/μs
DMSO	0.67	0.5	1.34	350
DMF	0.56	—	—	330
THF	—	—	—	230
Benzonitrile	—	—	—	260
n-Butylamine	—	—	—	300
Pyridine	0.61	0.65[b]	0.94	340
Toluene	0.58[a]	0.65[c]	0.89	

[a] Value from ref. 23. [b] Value from ref. 40 (general value for organic solvents). [c] Value from ref. 13.

absorption around this wavelength should have a great effect on singlet oxygen lifetime (Fig. 4). For example, the broad absorption of water near 1267 nm could explain the short lifetime of singlet oxygen (τ_Δ) in this solvent (Table 3) . DMSO, pyridine and DMF exhibit little absorption in the 1267 nm region, leading to longer τ_Δ. D_2O does not have the O–H vibration, hence singlet oxygen suffers less quenching with D_2O than with H_2O.

S_Δ, given in eqn. (1),[24] is the fraction of the triplet state quenched by triplet state oxygen:

$$S_\Delta = \phi_\Delta/\phi_T \qquad (1)$$

In Table 1 we see that the S_Δ is less than unity for the substituted ZnPc derivatives. This suggests that not all triplet quenching by triplet state oxygen leads to singlet oxygen formation, but the quenching is efficient since the values are not too far from unity, with the exception of ZnNPc and $ZnPc(SO_3^-)_4$. The low value of S_Δ for the former may be attributed to either the fast degradation of ZnNPc (see below) or the inefficient transfer of energy by this molecule, discussed above. It was also not possible to determine ϕ_T for $ZnPc(NO_2)_4$ and $ZnPcCl_8$ due to aggregation. For ZnPc a value higher than unity was obtained for S_Δ as calculated from the literature data, this could reflect incompatibilities in data from different laboratories. S_Δ values slightly larger than one have been reported before.[24]

The photobleaching quantum yield (ϕ_p) is a measure of the photostability of a molecule. It is indicated by a reduction in the absorbance intensity without the emergence of new peaks on photo-irradiation. Different substituents exhibit different effects on the ϕ_p values of ZnPc. While some substituents stabilize the ring against photodegradation, some make it more vulnerable to oxidative attack. ZnNPc is readily photodegraded, as has been reported before.[16] $ZnPc(SO_3^-)_{mix}$ also degraded easily compared to other substituted ZnPc derivatives (Table 1). ϕ_p values of ZnPc in different solvents have been discussed in detail elsewhere.[23] The ϕ_p value of $ZnPc(SO_3^-)_{mix}$ is solvent dependent as evident from Table 3 and Fig. 6. The observation that photostability increases with solvent basicity is attributed to the screening of the MPc ring from oxidative attack by the solvent's donor ability.

Table 3 Photophysical parameters of $ZnPc(SO_3^-)_{mix}$ in various solvents

Solvent	SB[a]	τ_D/μs	τ_T/μs	ϕ_Δ	ϕ_F	$10^5/\phi_P$
DMSO	0.647	30[b]	530	0.72	0.14	13.65
DMF	0.613	19[c]	290	0.58	0.18	15.97
H_2O	0.025	4.2[d]	190	0.48	0.16	—
D_2O	—	68[d]	420	0.53	0.19	—
Pyridine	0.581	20[e]	250	0.62	0.23	16.38
n-Butylamine	0.944	—	200	—	0.27	9.03

[a] Solvent basicity, values from ref. 41. [b] Value from ref. 42 [c] Value from ref. 43 [d] Values from ref. 44 [e] Value from ref. 45.

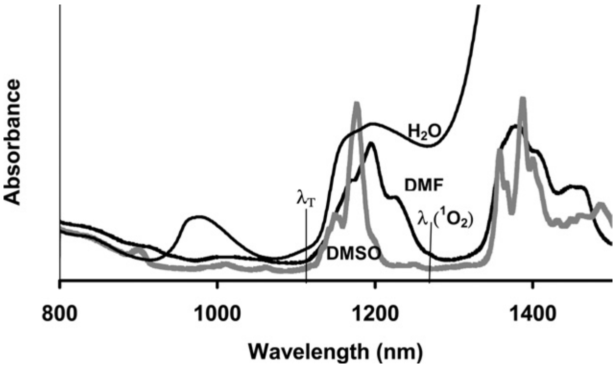

Fig. 4 Near IR absorption spectra of some common solvents: DMSO, DMF and water.

Conclusion

In conclusion, this work shows that the presence of ring substituents leads to the enhancement of intersystem crossing as evident from the higher values of the triplet quantum yield compared to that of unsubstituted ZnPc. $ZnPc(TBPh)_4$ gave a lower value of the fluorescence quantum yield and a shorter triplet lifetime than the unsubstituted ZnPc. Most of the ZnPc derivatives studied gave lower values of singlet oxygen quantum yields compared to unsubstitued ZnPc, due to the probable quenching of singlet oxygen by vibrations in the substituents. The anionic sulfonated derivatives gave the longest lifetimes and higher triplet state yield compared to the rest of the complexes, probably due to the poor ability of anionic species to dissipate energy nonradiatively. $ZnPc(MPh)_8$ has a high lifetime of the triplet state and a reasonable triplet state quantum yield, whereas $ZnPc(TBPh)_4$ has a low triplet life time, even though it has a high triplet yield. Since it is desirable for molecules to have both ϕ_T and τ_T reasonably high, the design of new photosensitizers should take into consideration the charge and the flexibility of the molecules. Solvent studies revealed that strong near-IR absorption of some solvents is responsible for the short singlet oxygen lifetime in such solvents and that photostability of the complexes is a function of solvent basicity.

Experimental

Materials

Zinc(II) phthalocyanine (ZnPc) was obtained from Aldrich. The synthesis and characterization of the following complexes:

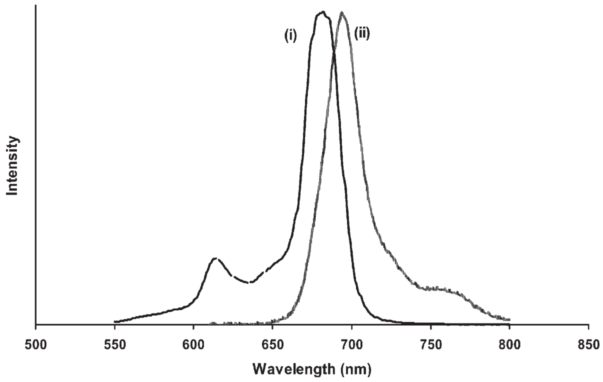

Fig. 5 Electronic absorption (i) and fluorescence (ii) spectra of 2×10^{-6} mol dm^{-3} $ZnPc(TBP)_4$ in DMSO.

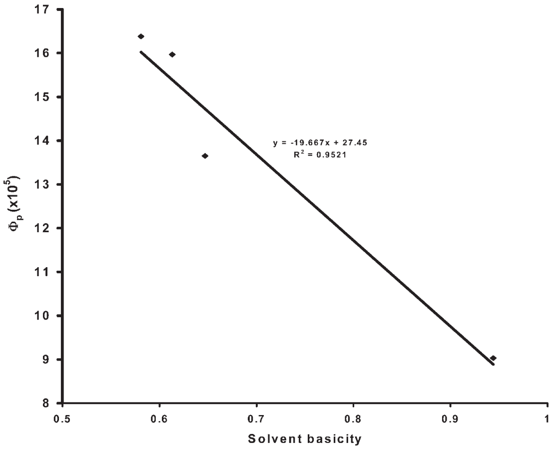

Fig. 6 Dependence of $ZnPc(SO_3^-)_{mix}$ photostability as ϕ_p on solvent basicity.

zinc tetra(*tert*-butylphenoxy)phthalocyanine $[ZnPc(TBPh)_4]$,[25] zinc octa(methylphenoxy)phthalocyanine $[ZnPc(MPh)_8]$,[26] zinc tetranitrophthalocyanine $[ZnPc(NO_2)_4]$,[27] zinc octachlorophthalocyanine $(ZnPcCl_8)$,[28] zinc tetrasulfophthalocyanine $[ZnPc(SO_3^-)_4]$,[29] the mixture of zinc mono-, di-, tri- and tetrasulfophthalocyanine $[ZnPc(SO_3^-)_{mix}]$[30] and zinc naphthalocyanine (ZnNPc)[31] have been reported before in the references cited for each complex. The synthesized complexes were only used if their characterization data was similar to that reported in the literature. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Aldrich and used as received. *N*,*N*′-dimethylformamide (DMF, SAARCHEM) was freshly distilled, dimethylsulfoxide (DMSO, SAARCHEM) was dried over alumina before use. Benzonitrile, *n*-butylamine, tetrahydrofuran (THF) and pyridine were from Aldrich and were used as obtained.

Photobleaching and singlet oxygen studies

Photobleaching (or photodegradation) of the ZnPc complexes and quantum yields for singlet oxygen generation were determined as has been previously explained in detail.[26,32,33] Typically, 2 ml of the reaction solution was introduced into the cell and photolyzed in the Q band region of the respective ZnPc derivative with a General Electric quartz line lamp (300 W). A 600 nm glass cut-off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiation. An interference filter (Intor, 700 nm with a band width of 20 nm) was additionally placed in the light path before the sample. Quantum yields of singlet oxygen photogeneration were determined in air (no oxygen bubbled) using the relative method with unsubstituted ZnPc as reference and DPBF as chemical quencher for singlet oxygen, from eqn. (2):

$$\phi_\Delta = \phi_\Delta^{\mathrm{PcZn}} \frac{W \times I_{\mathrm{abs}}^{\mathrm{PcZn}}}{W^{\mathrm{PcZn}} \times I_{\mathrm{abs}}} \tag{2}$$

where $\phi_\Delta^{\mathrm{PcZn}}$ is the singlet oxygen quantum yield for the standard, ZnPc in DMSO (0.67).[34] W and W^{PcZn} are the DPBF photobleaching rates in the presence of the ZnPc derivative under investigation and the standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{PcZn}}$ are the rates of light absorption by the ZnPc derivative and the standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen,[35] the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}$ mol L^{-1}. Solutions of sensitizer (absorbance below 0.5 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 7×10^{16} photons s^{-1} cm^{-2}. The error in the determination of ϕ_Δ was ~10% (determined from several ϕ_Δ values).

For the determination of the photobleaching quantum yields, the usual eqn. (3) was employed:

$$\phi_{\mathbf{p}} = \frac{(C_{\mathbf{o}} - C_t) \times V \times N_{\mathbf{A}}}{I_{\mathbf{abs}} \times S \times t} \tag{3}$$

where C_o and C_t in mol L^{-1} are the Pc concentrations before and after irradiation, respectively. V is the reaction volume, S the irradiated cell area (1.4 cm^2), t is the irradiation time, N_A is Avogadro's number and I_{abs} is the overlap integral of the radiation source intensity and the absorption of the Pc (the action spectrum) in the region of the interference filter transmittance.[32,33] UV-Vis spectra were recorded on a Varian 500 UV/visible/NIR spectrophotometer.

Fluorescence, triplet quantum yield and triplet lifetime studies

Fluorescence quantum yields were determined by the comparative method,[36,37] eqn. (4), using chlorophyll a in ether ($\phi_F = 0.32$)[38] as the reference:

$$\phi_F = \phi_F(\mathrm{std}) \frac{F(\mathrm{x}) \cdot A(\mathrm{std}) \cdot \eta^2(\mathrm{x})}{F(\mathrm{std}) \cdot A(\mathrm{x}) \cdot \eta^2(\mathrm{std})} \tag{4}$$

where F(x) and F(std) are the areas under the emission curves of the sample and standard, respectively. A(x) and A(std) are the absorbances of the sample and standard, respectively, and η(x) and η(std) are the refractive indexes of the solvents used for sample and standard, respectively. The error in the determination of ϕ_F was 10% (determined from several ϕ_F values). Both the sample and reference were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05. The refractive indices of the solvents were employed in calculating ϕ_F in different solvents. At least three independent experiments were performed for the quantum yield determinations. Fluorescence spectra were recorded on a Varian Eclipse spectrofluorometer.

The transient absorption spectra and decay kinetics were recorded with a flash photolysis system. The excitation pulse was provided by a Nd-Yag laser, providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye laser. Single pulse energy was 7 mJ. A 300 W xenon arc lamp (Thermo Oriel) provided the analyzing light. The kinetic curves were averaged over 256 laser pulses using a Tektronix TDS 360 digital oscilloscope. The triplet lifetimes were determined by exponential fitting of the kinetic curves using the program ORIGIN. The solutions for triplet state lifetimes and yields were introduced into a 0.2 mm path length UV/visible spectrophotometric cell, deaerated using nitrogen and photolyzed at the Q band maxima. Triplet (ϕ_T) state quantum yields of the substituted ZnPc derivatives were determined by the singlet depletion method, since triplet absorption gave much weaker signals under our experimental conditions. A comparative method[39] using zinc phthalocyanine as a standard was employed for the calculations, eqn. (5):

$$\phi_T^{\mathrm{Sample}} = \phi_T^{\mathrm{Std}} \frac{\Delta A_S^{\mathrm{Sample}} \varepsilon_S^{\mathrm{Std}}}{\Delta A_S^{\mathrm{Std}} \varepsilon_S^{\mathrm{Sample}}} \tag{5}$$

where $\Delta A_S^{\mathrm{Sample}}$ and $\Delta A_S^{\mathrm{Std}}$ are the changes in the singlet state absorbance of the substituted ZnPc derivative and ZnPc standard, respectively. $\varepsilon_S^{\mathrm{Sample}}$ and $\varepsilon_S^{\mathrm{Std}}$ are the singlet state extinction coefficients for the substituted ZnPc derivatives and ZnPc standard, respectively. ϕ_T^{Std} is the triplet state quantum yield for the standard, ZnPc in DMSO ($\phi_T = 0.50$).[12]

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