Syntheses and photophysics of new phthalocyanine derivatives of zinc, cadmium and mercury

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The syntheses of novel tetra{2,(3)-pyridyloxyphthalocyaninato} complexes of zinc, cadmium and mercury (TPyZnPc, TPyCdPc and TPyHgPc) are presented. Their spectral and photophysical properties (as well as those of their unsubstituted counterparts: ZnPc, CdPc and HgPc) are investigated. TPyZnPc and TPyCdPc are aggregated in non-coordinating solvents such as chloroform, while TPyHgPc is demetallated, as evident from their respective absorption spectra. The trends in fluorescence (Φ_F), triplet (Φ_T) and singlet oxygen (Φ_Δ) quantum yields are explained in terms of relative strengths of spin–orbit coupling induced by the respective central metal ions in the complexes. The effect of the pyridyloxy substituents is a decrease in Φ_F and an increase in Φ_T values. The complexes are less fluorescent in DMSO but possess higher Φ_T, triplet lifetimes (τ_T) and Φ_Δ therein.

Introduction

Metallophthalocyanine (MPc) molecules are diverse and robust materials, which are useful for a variety of applications ranging from medicine (*e.g.* as photosensitizers in photodynamic therapy, PDT) to molecular electronics.[1–7] It is believed that in PDT the photosensitizer generates singlet oxygen which then destroys the cancer cells. The generation of singlet oxygen *via* photosensitization (by an MPc) requires the existence of the metastable MPc excited triplet state, the typical lifetime of which ranges between the microsecond (μs) and millisecond (ms) time scales. Such a metastable state could be rapidly "quenched" in the presence of features that promote charge (electron) transfer, and this excludes MPcs containing electroactive transition metal centers from photosensitizing activity. This work reports on MPc derivatives containing diamagnetic metals: zinc(II), cadmium(II) and mercury(II). Much energy has been invested into studies on ascertaining the potential photosensitizing and photocatalytic abilities of zinc(II) phthalocyanine derivatives,[8–11] but literature is scanty for studies on cadmium(II) and mercury(II) phthalocyanine derivatives. Worth stressing is the fact that zinc, cadmium and mercury, being heavy atoms, would induce spin–orbit coupling and therefore populate the excited triplet state of the MPc molecules in which they reside. A high population of triplet state molecules should increase the number of diffusional encounters with ground state molecular oxygen, thereby leading to a high rate of singlet oxygen generation. The presence of substituents on the MPc ring brings about sizeable modification of the spectral, photophysical and photochemical behaviour of MPcs; a comparison of the photophysicochemical properties of unsubstituted and substituted MPcs is therefore desirable in the development of new materials for photocatalysis and photosensitization. Thus, the photochemical and photophysical properties of tetra{2,(3)-pyridyloxyphthalocyaninato} complexes of zinc, cadmium and mercury (TPyZnPc, TPyCdPc and TPyHgPc) are presented in this work. The synthesis of the zinc complex, TPyZnPc, has been reported before,[12] but no photochemical or photophysical data were reported. The use of pyridyl substituents on MPc complexes allows for derivatization of these complexes into water soluble species by quaternization and coordination of metal complexes on the pyridyl ligand.[12] The study of the photophysical and photochemical properties of the new Hg and Cd complexes reported in this work is of importance for the use of these complexes as photocatalysts in, for example, phototransformation of alkenes.

Results and discussion

Syntheses and characterizations

The substitution reaction of a nitro derivative with a phenol derivative to give a monosubstituted phthalonitrile derivative such as compound **2** has been well documented and has been shown to proceed *via* a base catalyzed nucleophilic displacement reaction mechanism.[13] Treatment of the derivative **2** with various metal salts, *i.e.* $Zn(OAc)_2$, $CdCl_2$ or $HgCl_2$, in the presence of a high boiling point solvent such as 1-pentanol allows its cyclotetramerization to afford the peripherally tetrasubstituted complexes TPyZnPc, TPyCdPc and TPyHgPc, respectively (Scheme 1). The purification procedure involved Soxhlet extraction of impurities and yields obtained vary between 40 and 60%.

Unsubstituted MPc derivatives are insoluble in most organic solvents; however, with the introduction of various substituents on the periphery of the ring, solubility tends to increase.[14] All of the complexes (substituted and unsubstituted) are soluble in highly polar solvents (*i.e.* DMF and DMSO). The substituted derivatives (TPyZnPc, TPyCdPc

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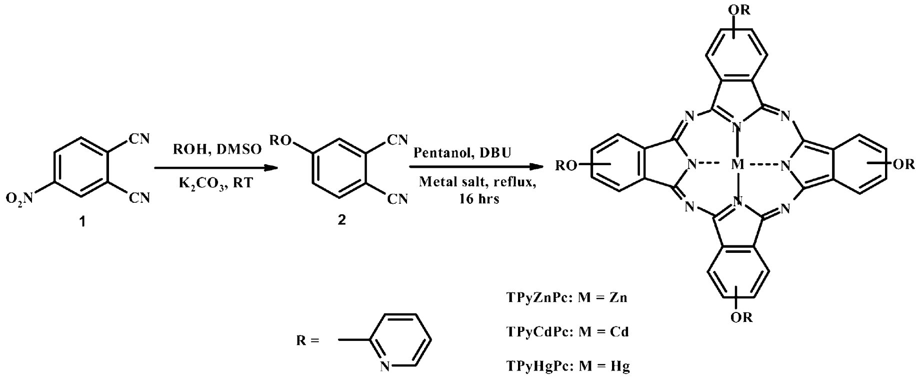

Scheme 1 Syntheses of TPyZnPc, TPyCdPc and TPyHgPc.

and TPyHgPc) exhibit limited solubility in solvents of weaker polarity, *i.e.* $CHCl_3$, DCM and THF. This may be attributed to the polar nature of the pyridyloxy substituents attached to the MPc ring as well as the presence of positional isomers which tend to occur as a result of the unsymmetrical orientation of the substituents at the ring periphery.[15]

The new complexes were characterized by various spectroscopic methods, IR, UV-Vis, MALDI-TOF and ^1H NMR, and are in agreement with the predicted structures. The IR spectra show the loss of the characteristic nitrile stretch at ~2284 cm^{-1} (indicative of phthalonitriles) on formation of the various metal substituted Pcs. ^1H NMR spectra for the unsubstituted derivatives (ZnPc, CdPc and HgPc) were similar, showing the 8 non-peripheral protons as a singlet between 9.37 and 9.55 ppm, while the peripheral protons resonate upfield as a broad singlet, integrating for 8 protons, between 7.99 and 8.28 ppm. For the pyridyloxy derivatives (TPyZnPc, TPyCdPc and TPyHgPc) peaks corresponding to the non-peripheral protons are observed between 8.94 and 9.47 ppm and integrate for a total of 8 protons. The 4 peripheral protons of the Pcs occur between 8.18 and 8.20 ppm and the pyridyloxy protons, which integrate to give 16 protons, are observed between 7.68 and 7.80 ppm as an unresolved multiplet.

Ground state electronic absorption and fluorescence spectra

The absorption spectra of ZnPc, CdPc and HgPc show monomeric behaviour in DMSO and DMF (Fig. 1). These complexes remain monomeric up to ~2 × 10^{-5} mol dm^{-3}. CdPc and HgPc are insoluble in $CHCl_3$, DCM and THF, while ZnPc is soluble in all, though sparingly so in $CHCl_3$ and DCM. The shift to longer wavelengths with the increase in size of the central metal is due to an increase in electron density. The substituted TPyZnPc and TPyCdPc are monomeric in DMSO, DMF and THF, but aggregated in $CHCl_3$ (Fig. 2) and DCM. The aggregating tendencies of MPc complexes in non-coordinating solvents are well documented,[16,17] and are attributed to the formation of π–π interactions between adjacent MPc rings. Coordinating solvents are axially ligated to the central metals in the MPc complexes, thereby preventing columnar aggregation. Addition of a surfactant, Triton X-100 (1 × 10^{-4} mol dm^{-3}), to a $CHCl_3$ (or DCM) solution of TPyZnPc or TPyCdPc results in partial disaggregation into monomers, as seen in Fig. 2. TPyHgPc is also monomeric in DMSO and DMF, but is demetallated in $CHCl_3$ (Fig. 3) and DCM, as evidenced by a split in the Q band, typical of demetallation in MPc complexes.[18] Studies have shown that, in chlorinated solvents, MPcs undergo oxidation with the formation of HCl as a by-product,[19] which in certain cases reacts with the MPc to cause demetallation. The diagonal N–N distance of the Pc core is 396 pm.[18] The Hg^{2+} ion, with a radius of 110 pm,[20] is expected to be out of the plane of the Pc ring since a smaller metal ion such as Mg^{2+}, with a radius of 71 pm,[20] is out of the plane of the Pc ring.[18] Thus, the mercury

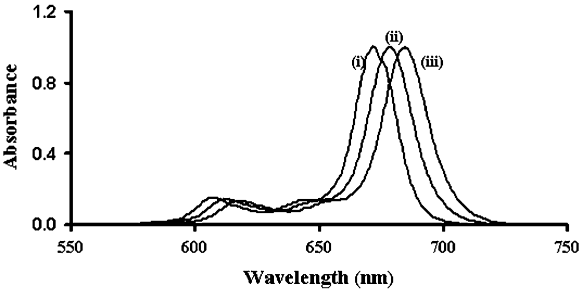

Fig. 1 Ground state electronic absorption spectra of ZnPc (i), CdPc (ii) and HgPc (iii) in DMSO. Concentrations: ZnPc = 1.5 × 10^{-5} M, HgPc and CdPc = 1.0 × 10^{-5} M.

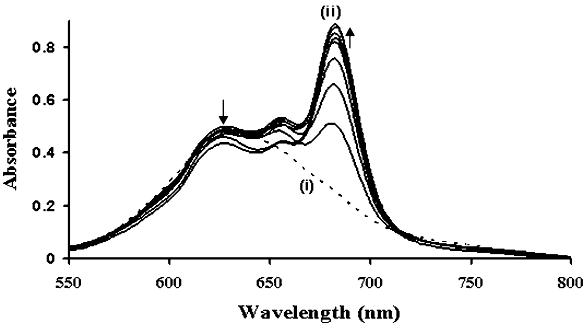

Fig. 2 TPyCdPc disaggregation absorption spectra using different concentrations of Triton X-100 and a constant concentration of TPyCdPc = 2.4 × 10^{-6} M in $CHCl_3$. Triton X-100 concentrations: (i) 0, 0.2 × 10^{-4}, 0.3 × 10^{-4}, 0.4 × 10^{-4}, 0.5 × 10^{-4}, 0.6 × 10^{-4}, 0.8 × 10^{-4}, 0.9 × 10^{-4} and (ii) 1 × 10^{-4} M.

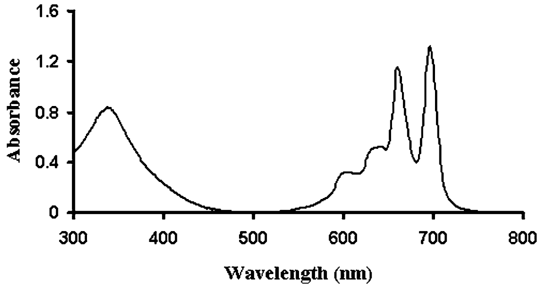

Fig. 3 Ground state electronic absorption spectrum of TPyHgPc in $CHCl_3$. Concentration of TPyHgPc = 8.7×10^{-6} M.

atom in the TPyHgPc molecule protrudes out of the planar phthalocyanine ring, making the molecule highly susceptible to demetallation. The positions of the Q bands are red-shifted with the introduction of the pyridyloxy ring substituents, which is a result of the electron donating nature of the substituents. This is evident in all the solvents in which studies were carried out, and Table 1 shows the trend in DMSO and DMF.

The effect of changing the central metal ion on the Q band position is as expected, *i.e.* the order of Q band positions is TPyHgPc > TPyCdPc > TPyZnPc, which is the order of extent of destabilization of the highest occupied molecular orbital (HOMO) in the complexes. Mercury, having more electrons in its atomic structure (more reducing), destabilizes the HOMO more than cadmium and zinc do, hence bringing about a shorter HOMO–LUMO separation and consequently the most red-shifted spectra. For a particular MPc complex, the Q band position changes with the solvent. We have previously suggested that the Q band position of an MPc complex is a function of the solvent's refractive index.[21] Fig. 4 shows the variation of the Q band position of TPyZnPc with solvents' refractive indices. On the grounds of having a lower refractive index, the Q band position in DMF is expected to be blue-shifted relative to that of $CHCl_3$. However, the values of Q band maxima are similar in both solvents, Table 1. This observation is ascribed to the interaction of DMF (a coordinating solvent) with the MPc ring, which stabilizes the LUMO of the MPc complexes. In Table 1, it can be observed that the molar extinction coefficients of the MPcs vary with the size of the central metal ion, with the value being highest for Zn(II) complexes and least for Hg(II) complexes. We attribute this observation to the phenomenon of spin–orbit coupling, which becomes more significant as the size of the central metal ion increases. The interaction of an electron's spin magnetic moment with its orbital magnetic moment introduces a new term into the Hamiltonian operator which operates on both spin and space variables. As a result of the introduction of this new term, the zero order wave functions of the excited singlet state, which were hitherto pure singlets, now possess some triplet character, and the $S_0 \rightarrow S_1$ transition becomes somewhat forbidden.

The fluorescence excitation and emission spectra of the Zn(II), Cd(II) and Hg(II) complexes are typical of phthalocyanine complexes, with Stokes' shifts ranging from 8 nm to 15 nm. For Zn and Cd derivatives, the fluorescence excitation spectra are mirror images of the emission spectra and are similar to the absorption spectra (Fig. 5). In the case of the Hg(II) complexes, however, the fluorescence emission spectrum is different from the absorption spectrum in that the emission spectrum is broad, Fig. 6, suggesting loss of symmetry in the fluorescing molecule.

Table 1 Absorption and fluorescence data for MPc derivatives in different solvents

Solvent	MPc	Q band λ_{max}/nm	Log ε^a	Fluorescence emission^b λ_{max}/nm	Fluorescence excitation^c λ_{max}/nm
DMSO	ZnPc	672	5.38	682	672
	CdPc	679	5.36	691	679
	HgPc	684	5.25	698	670
	TPyZnPc	680	5.36	686	680
	TPyCdPc	685	5.30	698	685
	TPyHgPc	690	5.18	704	676
DMF	ZnPc	670	5.37	676	670
	CdPc	674	5.38	683	674
	HgPc	681	5.11	700	675
	TPyZnPc	673	5.18	684	673
	TPyCdPc	682	5.11	695	682
	TPyHgPc	685	5.08	702	677
$CHCl_3$	ZnPc	673	—	680	673
	TPyZnPc	674	—	702	674
	TPyCdPc	673	—	701	673
	TPyHgPc	661, 697	—	702	661, 697
DCM	ZnPc	671	—	681	671
	TPyZnPc	673	—	702	673
	TPyCdPc	672	—	676	672
	TPyHgPc	661, 697	—	702	661, 697
THF	ZnPc	668	5.48	672	668
	TPyZnPc	672	—	681	672
	TPyCdPc	677	—	684	677
	TPyHgPc	661, 697	—	703	661, 697

[a] Some values undetermined due to limited or inadequate solubility. [b] Excitation at 630 nm for ZnPc and CdPc derivatives and at 640 nm for HgPc derivatives. [c] Emission wavelength = Q band maximum of the fluorescence spectra.

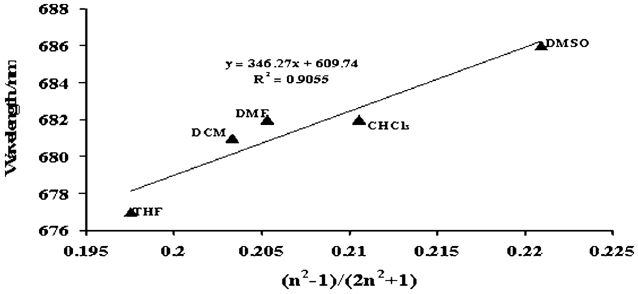

Fig. 4 Dependence of Q band positions on refractive indices of various solvents.

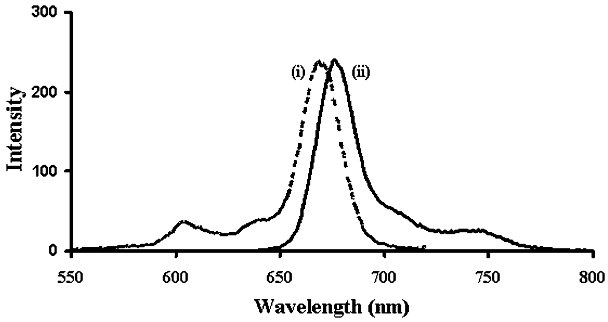

Fig. 5 Fluorescence excitation (i) and emission (ii) spectra of ZnPc in DMF. Concentration of ZnPc = ~1.5 × 10^{-6} M. Emission wavelength for excitation spectrum was 677 nm. λ_{exc} for emission = 630 nm.

Fluorescence quantum yields and lifetimes

The order of fluorescence quantum yield (Φ_F) values is ZnPc > CdPc > HgPc and TPyZnPc > TPyCdPc > TPyHgPc. This order is expected on the grounds of the spin–orbit coupling induced by the respective central metal ions. Hg(II), being the heaviest of the three metal ions, brings about the strongest spin–orbit coupling, thereby increasing the likelihood of the spin-forbidden intersystem crossing and an attendant decrease in the spin-allowed fluorescence and internal conversion. Under this circumstance, the Hg(II) derivatives are also expected to give the highest triplet quantum yield values, and the Zn(II) derivatives, the lowest. In general, the effect of introducing pyridyloxy substituents to peripheral positions on the MPc ring is a reduction in Φ_F values, compared to those of the unsubstituted analogues (Table 2). The substituents perhaps encourage the deactivation of the excited singlet state *via* non-radiative means (intersystem crossing and internal conversion) rather than *via* fluorescence. However, the substituent effect on Φ_F values of TPyZnPc (in DMF) and TPyCdPc (in DMSO) are negligible. In Table 2, Φ_F values are generally higher in DMF than in DMSO, which could be explained by the premise that DMSO itself contains heavy atoms (sulfur compared with nitrogen in DMF), which could promote intersystem crossing to the triplet state, thereby reducing the likelihood of fluorescence. The effect of the pyridyloxy substituents on the respective MPc rings is a decrease in fluorescence lifetime (τ_F) (Table 3), except for CdPc. This implies that the excited singlet states in the pyridyloxy-substituted derivatives are deactivated more *via* non-radiative means (*i.e.* intersystem crossing and internal conversion), rather than *via* fluorescence emission. Considering the effect of the central metal ion on τ_F values, there is obviously a shortening of fluorescence lifetime with an increase in size of the central metal ion. We believe that intersystem crossing to the triplet state should be the major pathway through which the excited singlet state is being deactivated.

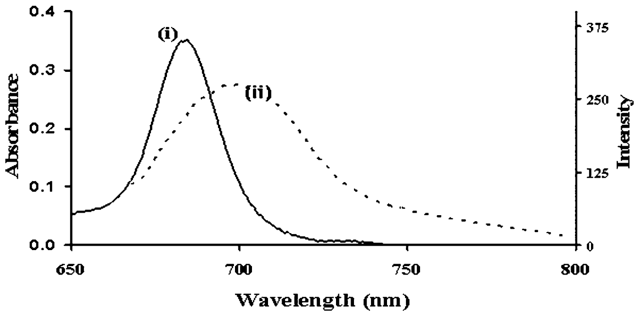

Fig. 6 Absorption (i) and fluorescence emission spectra (ii) of TPyHgPc in DMSO. Concentration = ~2.3 × 10^{-6} M. λ_{exc} for emission = 640 nm.

Triplet quantum yields and lifetimes

The lowest excited triplet states of light-absorbing molecules are populated as a result of intersystem crossing from the lowest excited singlet states. The fact that this spin-forbidden process takes place at all is as a result of spin–orbit coupling. Consequently, species in which the strongest spin–orbit coupling is induced should have the highest triplet quantum yield (Φ_T) values. In Table 2, the order of variance of Φ_T values is consistent with the strengths of the induced spin–orbit coupling in the complexes, *i.e.* Hg(II) complexes show the highest values while Zn(II) complexes show the lowest values. The presence of the pyridyloxy ring substituents also brought about increases in Φ_T values, implying that these substituents, as well, induce spin–orbit coupling. These trends are the reverse of what was observed for the Φ_F values of the complexes, which means that, in these complexes, molecules that do not fluoresce undergo intersystem crossing (rate of internal conversion should be lower than that of intersystem crossing). Φ_T values are higher in DMSO than in DMF for the unsubstituted ZnPc and for TPyZnPc, but the values are almost the same in both solvents for TPyCdPc, TPyHgPc and HgPc. The higher values in DMSO could be ascribed to the stronger inducement of spin–orbit coupling by DMSO than DMF, since the former contains heavier atoms than the latter. However, the fact that the values in some cases are almost the same in both DMSO and DMF suggests that there are other factors (such as the viscosity of the solvents) which affect the Φ_T values apart from the spin–orbit coupling effects of DMSO. The transient absorption spectrum of TPyCdPc (as an example) and the triplet decay curve in DMSO are shown in Fig. 7. Worthy of note is the appearance of a broadened peak centered near 700 nm in the transient absorption spectrum, while the absorption spectrum of this complex in DMSO was

Table 2 Photophysical data of MPc derivatives in DMSO and DMF[a]

Solvent	MPc	Φ_F	Φ_T[b]	Φ_{IC}	Φ_Δ[c]	S_Δ
DMSO	ZnPc	0.20	0.65 (30)	0.15	0.67 (33)	1.03
	CdPc	0.015	0.70	0.285	0.78	1.11
	HgPc	0.010	0.87	0.12	0.82	0.94
	TPyZnPc	0.077	0.80	0.123	0.46	0.57
	TPyCdPc	0.013	0.83	0.157	0.74	0.89
	TPyHgPc	0.005	0.89	0.105	0.78	0.88
DMF	ZnPc	0.17	0.58 (31)	0.25	0.56 (32)	0.96
	CdPc	0.021	0.77	0.209	0.58	0.75
	HgPc	0.017	0.86	0.123	0.57	0.66
	TPyZnPc	0.17	0.68	0.151	0.40	0.59
	TPyCdPc	0.017	0.85	0.133	0.64	0.75
	TPyHgPc	0.009	0.90	0.091	0.56	0.62

[a] Φ_F = quantum yield of fluorescence; Φ_T = quantum yield of triplet excited state; Φ_{IC} = quantum yield of internal conversion; Φ_Δ = quantum yield of singlet oxygen and $S_\Delta = \Phi_\Delta/\Phi_T$. [b] Excitation at the Q band maxima of the complexes. References for literature values are in brackets. [c] Using an interference filter, the excitation wavelength was from 630 to 710 nm (see experimental section). References for literature values are in brackets.

Table 3 Lifetimes and kinetic data of MPc complexes in DMF and DMSO[a]

Solvent	MPc	τ_F/ns	τ_T/μs	$k_F/10^{-7}$ s^{-1}	$k_{ISC}/10^{-9}$ s^{-1}	$k_{IC}/10^{-8}$ s^{-1}
DMSO	ZnPc	4.73	350	4.23	0.14	0.32
	CdPc	0.32	30	4.64	2.17	8.82
	HgPc	0.27	40	3.68	3.20	4.42
	TPyZnPc	1.22	350	6.32	0.66	1.01
	TPyCdPc	0.29	30	4.48	2.86	5.41
	TPyHgPc	0.11	20	4.45	7.92	9.34
DMF	ZnPc	4.26	5.00	3.99	0.14	0.59
	CdPc	0.51	4.70	4.08	1.49	4.06
	HgPc	0.84	4.40	2.02	1.02	1.46
	TPyZnPc	1.09	7.30	1.55	0.67	0.14
	TPyCdPc	0.70	5.20	2.42	1.21	1.89
	TPyHgPc	0.31	3.90	2.87	2.87	2.90

[a] τ_F = fluorescence lifetime; τ_T = triplet life time; k_F = rate constant for fluorescence; k_{ISC} = rate constant for intersystem crossing; k_{IC} = rate constant for internal conversion.

observed at 685 nm, Table 1. We believe that the changes in spectra are a result of symmetry loss following photoexcitation. Symmetry loss is usually depicted by splitting or broadening of bands. A flexible σ bond connects the pyridino ring to the local MPc ring. Twisting of these pyridino rings about the σ bonds distorts the molecule and so a slight loss of symmetry occurs.[22] Recently, we observed a similar effect for octaphenoxy zinc phthalocyanine, in which case the twisting of the ring substituents resulted in ground state absorption spectral changes.[21] The absorption spectra of the solutions used for triplet quantum yield and lifetime determinations were recorded after the experiments and it was observed that the unsubstituted complexes had been partly degraded. In the case of the pyridyloxy-substituted derivatives, broadening and shifting of the spectra were observed (Fig. 8), which we ascribe to photoinduced twisting of the pyridino groups about the flexible σ bonds that attach them to the local MPc ring. As higher light doses are applied, the extent of the twisting becomes greater. The possibility of oxidation or reduction of the complex was ruled out by adding reducing or oxidizing agents after laser irradiation. The original spectra could not be regenerated by exposure of the final solution to air, or by addition of reducing or oxidizing agents or by a change in temperature.

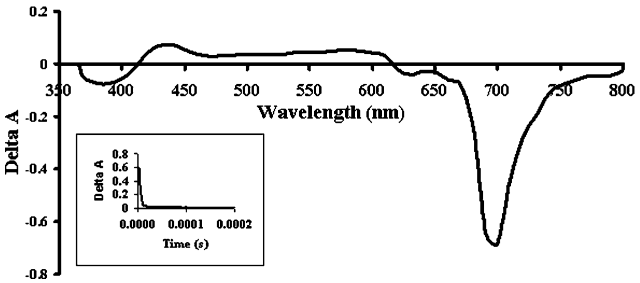

Fig. 7 Transient absorption spectrum for TPyCdPc in DMSO (inset: TPyCdPc triplet decay curve). Concentration = ~3.4 × 10^{-6} M. λ_{exc} = 690 nm.

Triplet lifetimes (τ_T) for the Cd(II) and Hg(II) complexes are generally lower than those for the Zn(II) derivatives; this is attributed to the heavy atom effect, which induces intersystem crossing from the excited triplet state to the ground state. Values in DMSO are much higher than those in DMF, which may be attributed to the higher viscosity of DMSO than that of DMF. Diffusion-like movements (which enhance non-radiative deactivation of excited states) are less frequent in

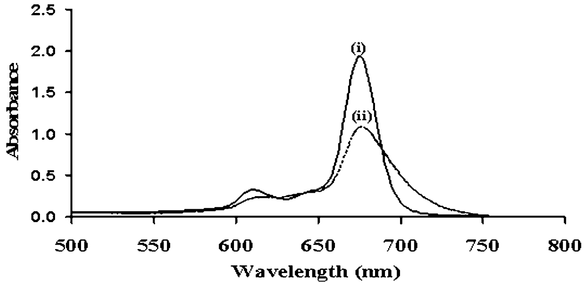

Fig. 8 TPyCdPc absorption spectra, in DMSO, before (i) and after (ii) laser photolysis. Concentration of TPyCdPc = ~9.7×10^{-5} M. λ_{exc} for emission = 630 nm.

DMSO than in DMF; as a result, triplet lifetimes are longer in DMSO than in DMF. Table 3 shows that the order of triplet lifetimes with respect to the central metal ions is Zn(II) > Cd(II) > Hg(II), with HgPc in DMSO presenting an exception. The reason that fluorescence lifetimes become shorter as the size of the central metal ion in the MPc increases should also suffice in explaining the observed trend in the variation of τ_T. Spin–orbit coupling enhances intersystem crossing, hence the non-radiative decay from T_1 to S_0 is encouraged by heavy metal ions.

The quantum yield of internal conversion (Φ_{IC}), which deactivates the excited singlet states, offers no well-defined trend among the complexes (Table 2).

Singlet oxygen quantum yields and rate constants

Singlet oxygen quantum yield (Φ_Δ) is defined as the number of singlet oxygen molecules formed per photon absorbed. Singlet oxygen is formed *via* energy transfer from the triplet state of a photosensitizer to ground state (triplet) molecular oxygen. Consequently, Φ_Δ values should vary with the population and lifetime of triplet state molecules. It is clear from Table 2 that Cd- and Hg-containing derivatives show higher Φ_Δ values than their Zn-containing counterparts, which could be ascribed, in principle, to the higher triplet state population in Cd- and Hg-containing derivatives. Values for the Hg-containing derivatives (HgPc and TPyHgPc) are in some cases lower than those of the Cd-containing derivatives. Comparing values in DMSO and DMF, Φ_Δ are higher in DMSO than in DMF, which is attributed to solvent-induced spin–orbit coupling in DMSO, as indicated above.

S_Δ (eqn (8)) values, the fraction of excited triplet state molecules quenched by ground state molecular oxygen $\{O_2(^3\Sigma_g^-)\}$ are listed in Table 2. S_Δ is actually the efficiency of energy transfer from the triplet state of the complexes to ground state molecular oxygen. The closer the value of S_Δ to unity, the higher the efficiency of energy transfer. The S_Δ values for ZnPc and CdPc are slightly larger than 1 in Table 2, but within experimental error these values are close to unity. The presence of pyridyloxy substituents decreases S_Δ values, except in the case of the Cd(II) derivatives in DMF, which show similar values. S_Δ values are higher in DMSO than in DMF, which could be related to the lifetimes of the triplet states in the respective solvents. In DMSO, triplet lifetimes are longer; hence, there is more time for diffusional collisions with $O_2(^3\Sigma_g^-)$ than in DMF, resulting in more efficient energy transfer.

Rate constant values for the intrinsic processes deactivating the excited singlet states of the MPc derivatives (k_F, k_{ISC} and k_{IC}) are listed in Table 3. The values do not follow any particular pattern; however, it could be observed that k_F and k_{IC} values are generally higher in DMSO than in DMF.

Conclusions

The synthesized complexes, TPyZnPc, TPyCdPc and TPyHgPc, are soluble in highly polar solvents (DMF and DMSO), but have limited solubility in solvents of weaker polarity ($CHCl_3$, DCM and THF). All the complexes are monomeric in DMSO, DMF and THF. TPyZnPc and TPyCdPc aggregate in non-coordinating solvents such as $CHCl_3$ and DCM, while TPyHgPc is demetallated in these solvents. The effect of introducing pyridyloxy substituents to peripheral positions on the MPc ring is a reduction in Φ_F values, compared to those of the unsubstituted analogues. The effects of pyridyloxy substituents on the host ZnPc, CdPc or HgPc are an increase in triplet quantum yield and decreases in triplet lifetime and singlet oxygen quantum yield. Cd- and Hg-containing derivatives show higher Φ_Δ values than their Zn-containing counterparts due to the heavy atom effect. The Φ_Δ are higher in DMSO than in DMF due to solvent-induced spin–orbit coupling in the former solvent. The photophysical parameters of the complexes studied show that they have potential as photocatalysts.

Experimental

Materials

Chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol and 1-pentanol were dried and distilled prior to use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), deuterated dimethyl sulfoxide (DMSO-d_6), Triton X-100 (*tert*-octylphenoxypolyethoxyethanol), 2-hydroxypyridine, 4-nitrophthalonitrile, phthalonitrile, cadmium chloride, mercury chloride and zinc acetate were all purchased from Sigma-Aldrich. The metal salts were dried in the oven prior to use. Zinc phthalocyanine (ZnPc), cadmium phthalocyanine (CdPc) and mercury phthalocyanine (HgPc) were synthesized according to literature methods.[23] Tetra{2,(3)-pyridyloxyphthalocyaninato} zinc(II) (TPyZnPc); tetra{2,(3)-pyridyloxyphthalocyaninato} cadmium(II) (TPyCdPc) and tetra{2,(3)-pyridyloxyphthalocyaninato} mercury(II) (TPyHgPc) were synthesized as described below.

Equipment

FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer. UV-Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer. ^1H NMR spectra were obtained in DMSO-d_6 using a Bruker EMX 400 NMR spectrometer. MALDI-TOF spectra were recorded with Perspective Biosystems Voyager DE-PRO

Biospectrometry Workstation and Processing Delayed Extraction at the University of Cape Town, Cape Town, South Africa. Fluorescence spectra were recorded on a Varian Eclipse spectrofluorimeter.

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Nd:YAG laser (Quanta-Ray, 1.5 J per 90 ns) pumping a dye laser (Lambda Physic FL 3002, Pyridine 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as the detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. Photoirradiations were done using 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 radiations, respectively. Additionally, an interference filter (Intor, 670 nm with a band width of 40 nm) was placed in the light path before the sample. Light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter.

Synthesis and characterization

4-(2-Pyridyloxy)phthalonitrile (2). In the presence of a steady flow of nitrogen, 2-hydroxypyridine (7.00 g, 74 mmol) and 4-nitrophthalonitrile (**1**, 8.50 g, 49 mmol) were suspended in dry DMSO (70 ml). Anhydrous K_2CO_3 (13.50 g, 98 mmol) was added and the mixture stirred at room temperature. Further aliquots of K_2CO_3 (0.63 g, 4.6 mmol) were added portion-wise after 4 and 24 h of stirring. After 48 h total reaction time, the mixture was poured into H_2O (250 ml), thus resulting in a precipitate that was recrystallized from methanol to give a brownish-yellow product (**2**). Yield: 10.3 g (95%). IR (KBr) ν_{max}/cm^{-1}: 2284 (ν_{CN}), 1220 (ν_{C-O-C}). ^1H NMR (400 MHz, DMSO-d_6) δ/ppm: 8.34 (1H, s, Ar–H), 8.25–8.27 (1H, d, Ar–H), 8.02–8.04 (1H, d, Ar–H), 7.70 (1H, d, Ar′–H), 7.52 (1H, t, Ar′–H), 6.49–6.52 (1H, d, Ar′–H), 6.37 (1H, t, Ar′–H).

Tetra{2,(3)-pyridyloxyphthalocyaninato} zinc(II) (TPyZnPc). Compound **2** (2.5 g, 14.6 mmol) was dissolved in 1-pentanol (15 ml). Zinc acetate (0.60 g, 2.8 mmol) and DBU (10 mmol) were then added to the solution and the reaction mixture was refluxed at 100 °C for about 16 h. The resultant dark-green coloured precipitate was then added to methanol, filtered and purified using methanol and acetone in Soxhlet apparatus to give a dark-green solid which was oven dried at 90 °C. Yield: 1.30 g (50%). UV-Vis (DMSO) λ_{max}/nm (log ε): 340 (4.50), 615 (4.32), 680 (5.36). IR (KBr) ν_{max}/cm^{-1}: 3040 (ν_{C-H}), 1583 (ν_{C-C}), 1245 (ν_{C-O}), 1135, 1096 (ν_{C-O-C}), 865, 764 (ν_{C-H}). ^1H NMR (400 MHz, DMSO-d_6) δ/ppm: 9.23–9.36 (8H, m, Pc–H), 8.20 (4H, bs, Pc′–H), 7.69–7.71 (16H, m, pyridyloxy). MALDI-TOF MS *m*/*z*: calc. 950.254 amu. Found 950.29 amu.

Tetra{2,(3)-pyridyloxyphthalocyaninato} cadmium(II) (TPyCdPc). The synthetic and purification procedure for TPyCdPc was similar to that used for TPyZnPc using the following quantities: compound **2** (2.5 g, 14.6 mmol), 1-pentanol (15 ml) and cadmium chloride (0.60 g, 2.72 mmol). Yield: 1.52 g (56%). UV-Vis (DMSO) λ_{max}/nm (log ε): 355 (4.70), 618 (4.52), 685 (5.30). IR (KBr) ν_{max}/cm^{-1}: 1614 (ν_{C-C}), 1205 (ν_{C-O}), 1133, 1090 (ν_{C-O-C}), 765 (ν_{C-H}). ^1H NMR (400 MHz, DMSO-d_6) δ/ppm: 9.37–9.47 (8H, m, Pc–H), 8.18 (4H, bs, Pc′–H), 7.69–7.71 (16H, m, pyridyloxy). MALDI-TOF MS *m*/*z*: calc. 997.264 amu. Found (M^+) 998.01 amu.

Tetra{2,(3)-pyridyloxyphthalocyaninato} mercury(II) (TPyHgPc). The synthetic and purification procedure for TPyHgPc was similar to that used for TPyZnPc using the following quantities: compound **2** (2.5 g, 14.6 mmol), 1-pentanol (15 ml) and mercury chloride (0.74 g, 2.72 mmol). Yield: 1.20 g (41%). UV-Vis (DMSO) λ_{max}/nm (log ε): 340 (4.55), 623 (4.06), 690 (5.17). IR (KBr) ν_{max}/cm^{-1}: 3045 (ν_{C-H}), 1586 (ν_{C-C}), 1270 (ν_{C-O}), 1130, 1098 (ν_{C-O-C}), 748 (ν_{C-H}). ^1H NMR (400 MHz, DMSO-d_6) δ/ppm: 8.94–9.31 (8H, m, Pc–H), 8.19 (4H, bs, Pc′–H), 7.68–7.80 (16H, m, pyridyloxy). MALDI-TOF MS *m*/*z*: calc. 1085.464 amu. Found 1085.66 amu.

Photophysical studies

Fluorescence quantum yields and lifetimes. Fluorescence quantum yields (Φ_F) were determined by the comparative method[24,25] (eqn (1)).

$$\Phi_F = \Phi_{F(Std)} \frac{F A_{Std} \eta^2}{F_{Std} A \eta_{Std}^2} \tag{1}$$

Where F and F_{Std} are the areas under the fluorescence curves of the MPc and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference, respectively, at the excitation wavelength and η and η_{Std} are the refractive indices of the solvents used for the sample and reference, respectively. Chlorophyll a in ether (Φ_F = 0.32[26]) was employed as the reference. 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 for ZnPc and CdPc derivatives and was 0.1 for HgPc derivatives. Fluorescence lifetimes were determined using the program PhotochemCAD,[27] and the determination is based on the Strickler–Berg equation.[28]

Triplet lifetimes and quantum yields. The deaerated solutions of the respective MPc complexes were introduced into a 2 mm × 10 mm spectrophotometric cell and irradiated at the Q band with the laser system described above. Triplet quantum yields (Φ_T) of the MPc complexes were determined using the triplet absorption method. A comparative method,[29] using zinc phthalocyanines (ZnPc) as the standard, was employed for the calculations, eqn (2).

$$\Phi_T = \Phi_T^{Std} \frac{\Delta A_T \varepsilon_T^{Std}}{\Delta A_T^{Std} \varepsilon_T} \tag{2}$$

Where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbances of the MPc derivative and the standard, respectively; ε_T and ε_T^{Std} are the triplet state molar extinction coefficients for the MPc derivative and the standard, respectively; Φ_T^{Std} is the triplet quantum yield for the standard (Φ_T = 0.65 for ZnPc in DMSO[30] and 0.58 for ZnPc in DMF[31]). ε_T and ε_T^{Std} were determined from the molar extinction coefficients of their respective ground singlet states (ε_S and ε_S^{Std}), the changes in absorbances of the ground singlet states (ΔA_S and ΔA_S^{Std}), and changes in the triplet state absorptions, (ΔA_T and ΔA_T^{Std}) according to eqn (3a) and (3b).

$$\varepsilon_T = \varepsilon_S \frac{\Delta A_T}{\Delta A_S} \tag{3a}$$

$$\varepsilon_T^{Std} = \varepsilon_S^{Std} \frac{\Delta A_T^{Std}}{\Delta A_S^{Std}} \tag{3b}$$

Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 supplied by OriginLab®. The triplet lifetime was calculated as the reciprocal of the first order decay constant of the excited triplet state (eqn (4)).

$$\tau = \frac{1}{k} \tag{4}$$

Quantum yields of internal conversion (Φ_{IC}) were obtained from eqn (5), which assumes that only the three intrinsic processes (fluorescence, intersystem crossing and internal conversion) jointly deactivate the excited singlet state of an MPc molecule.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \tag{5}$$

Rate constants for the excited singlet state deactivation processes, *i.e.* fluorescence (k_F), intersystem crossing (k_{ISC}) and internal conversion (k_{IC}), were calculated from the values of Φ_F, Φ_T and Φ_{IC}, respectively (eqn (6a–c)).

$$k_F = \frac{\Phi_F}{\tau_F} \tag{6a}$$

$$k_{ISC} = \frac{\Phi_T}{\tau_F} \tag{6b}$$

$$k_{IC} = \frac{\Phi_{IC}}{\tau_F} \tag{6c}$$

Singlet oxygen quantum yields. Singlet oxygen quantum yield (Φ_Δ) values were determined in air using the relative method with diphenylisobenzofuran (DPBF) acting as a singlet oxygen chemical quencher in DMSO, using eqn (7).

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R I_{abs}^{Std}}{R^{Std} I_{abs}} \tag{7}$$

Where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard (ZnPc) (Φ_Δ^{Std} = 0.56 in DMF[32]and 0.67 in DMSO[33]); R and R^{Std} are the DPBF photobleaching rates in the presence of the MPc and standard, respectively; I_{abs} and I_{abs}^{Std} are the rates of light absorption by the MPc and standard, respectively. The light intensity used for Φ_Δ determinations was found to be 4.76×10^{15} photons s^{-1} cm^{-2}, and the error in the determination was ~10% (from several Φ_Δ values).

The fraction of the excited triplet state quenched by ground state molecular oxygen, S_Δ, was calculated using eqn (8).

$$S_\Delta = \frac{\Phi_\Delta}{\Phi_T} \tag{8}$$

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