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Photophysical and photochemical parameters of octakis (benzylthio) phthalocyaninato zinc, aluminium and tin: Red shift index concept in solvent effect on the ground state absorption of zinc phthalocyanine derivatives

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ABSTRACT

This paper addresses the synthesis of octa-substituted benzylthio metallophthalocyanines (OBTMPcs) that contain the central metal ions of Zn^{2+} , Al^{3+} and Sn^{4+} . The ground state absorption of $ZnPc(SR)_8$ (OBTZnPc) along with the ZnPc derivatives, well documented in literature were used to study a new concept called the red shift index (R_sI). The concept is based on the empirical values of R_sI of the different complexes in solvent media. Unequivocally, parameters used in this paper show strong correlations that are consistent with the results obtained. For instance, R_sI of the complexes tend to increase as the refractive index, n_D , and solvent donor, DN, of solvent increases. Photodegradation (photobleaching) quantum yield, ϕ_d measurements of these compounds show that they are highly photostable, ϕ_d (0.03–0.33 × 10⁻⁵). The triplet quantum yield, ϕ_T (0.40–0.53) and the triplet lifetime, τ_T (610–810 µs) are within the typical range for metallophthalocyanines in DMSO. The photosensitisation efficiency, S_Δ , is relatively high for all the molecules (0.74–0.90).

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1. Introduction

Metallophthalocyanines (MPcs) are among the class of organic dyes that show an intense blue-green colour, with extinction coefficients greater than 10⁵ M⁻¹ cm⁻¹. They have two distinct bands; the Q-band in the visible region (650-700 nm) and the B (Soret) band in the UV region (300-350 nm). These bands are transitions that arise from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), where the Q and B bands depend largely on the nature of metallic substitution and the type of group present at the periphery of the phthalocyanine (Pc) compound. Structurally, MPcs have a well-ordered macrocyclic backbone that contains 18 π -electron systems. The π - π ^{*} stacking interactions, coupled with the facile substitution at the periphery of the phthalocyanine ring, and the nature of central metal ions introduced during cyclotetramerisation of the phthalocyanine (Pc) can indeed have an overall effect on the chemical and physical properties. Thus MPcs can be tailored to a wide variety of applications. For example, in recent years they have received extensive study in catalysis [1,2], photocatal-

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ysis [3–5], photoactivation and photosensitisation [6–9], non-linear optics (NLO) [10,11], and gas sensing devices [12,13].

MPcs aggregate in solutions [14–17] and aggregation diminishes their photosensitising abilities. In some cases, aggregation may result in low singlet oxygen production or reduced lifetime. Aggregation in MPc complexes is caused by electronic interactions between neighbouring rings. The addition of electron donating groups to the periphery of the macrocycle increases the distance between the planar macrocycle rings carrying the π -electrons, thereby making the solvation process easier. Thioether substitution (SR) in the phthalocyanine moiety is particularly suited for this purpose, as they are highly electron rich. Recently, the aggregation effect in MPcs has also been documented, showing some interesting optical uses. Kenta Adachi et al. [18a-d] documented a series of reports of thioether MPc complexes in the aggregated state in mixed solvents. In one of their reports, (OBTMgPcs) was shown as a complex resource that can be tuned optically when induced by Pd²⁺-BINAP complex at the liquid-liquid interface. Despite interesting findings by Kenta Adachi et al. and other literature work on thioether MPcs in the last decade [19-22], to our knowledge, little is known about the solvent parameters that affect their ground state absorption, photophysics and photochemistry.

This work investigates the photophysical and photochemical properties of octa-substituted benzylthio metallophthalocyanines (OBTMPcs) in DMSO. The ground state absorption of (OBTZnPcs)

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along with the ZnPc derivatives, which is well documented in literature are also investigated in different solvent media. The red shift index (R_sI), an entirely a new concept, explains the solute–solvent interactions as a macroscopic entity, thus enabling good empirical deductions. The R_sI values may provide a useful empirical guide in the selection of compounds intended for use in optical chemical sensing materials, and may also find use as solvent indicators.

Overall, this work shows three key ways in which this class of dyes may be employed, namely: as photocatalysts due to their low photodegradation yields and high triplet lifetime; as photosensitisers due to the calculated values of their photosensitisation efficiency and the photon yields per molecule they generate; and lastly as advanced optical chemical sensing materials based on the excellent spectroscopic trends of OBTZnPc in both single and mixed solvents.

2. Experimental procedures

2.1. Materials

4,5-dichloro-1,2-dicyanobenzene, zinc acetate, anhydrous tin(IV)chloride, aluminium monoacetate ((HO)₂AlC₂H₃O₂), dimethylsulfoxide (DMSO), 1,3-diphenylisobenzofuran (DPBF), and aluminium oxide (Type WN-3, neutral) were purchased from Sigma– Aldrich. N,N' dimethylformamide (DMF), ammonium hydroxide (25% and 35% solutions), lithium metal, and glacial acetic acid were purchased from SAARChem. Potassium carbonate (anhydrous), sodium sulphate (anhydrous) and diazabicyclo[2.2.2]octan (DABCO) were purchased from Merck. Phenylmethanethiol and 1-pentanol were purchased from Fluka. DMSO was dried over alumina, and DMF was freshly distilled before use.

2.2. Methods

UV-vis. spectra were recorded on a Varian 500 UV/Visible/NIR spectrophotometer. Nitrogen gas was purchased from Afrox. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Photo-irradiation was done using a General Electric Quartzline 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. A 700 nm interference filter, with a bandwidth of 40 nm, was also placed in the light path before the sample. Light intensities were measured with a PowerMax 5100 (Molelectron Detector Inc.) power meter. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, and the excitation pulses were produced by Nd: YAG laser (Quanta-Ray, 1.5 J/90 ns) pumping a tunable dye laser (Lambda Physic FL 3002, pyridine 1 dye in methanol). The analysing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses.

2.3. Synthesis and characterisation

2.3.1. Synthesis of 1,2-(benzylthio)-4,5-dicyanobenzene (2)

Compound **1**, 4,5-dichloro-1,2-dicyanobenzene was synthesised according to literature methods [22]. Compound **2** was a modification of the previously procedure reported in the literature [23]. Phenyl methanethiol (8420 mg, 68 mmol) was dissolved in dry DMSO (35 cm³) under nitrogen, and compound **1** (5 910 mg, 30 mmol) was added while gently stirring the mixture under inert nitrogen condition. The mixture was then stirred for additional 30 min after compound **1** was completely added. Finely ground anhydrous potassium carbonate (15,000 mg, 109 mmol) was

added in portions over a period of 2 h while maintaining the inert atmosphere and with constant stirring to obtain a homogenous mixture. The reaction mixture was stirred under nitrogen at ambient temperature for additional 12 h. The reaction mixture was quenched with water ($\sim 110 \text{ cm}^3$) and the aqueous phase extracted with chloroform. The chloroform portion was then treated with 5% sodium carbonate solution to remove the excess phenyl methanethiol, followed by additional treatment with water to remove unreacted potassium carbonate and potassium chloride. The resulting product was then dried over anhydrous sodium sulphate to yield an oily product. The oily product was dried by evaporating the inherent chloroform. The final product (compound **2**) was crystallised from absolute ethanol and dried in a dessicator (silica gel) to yield golden yellow needle-like crystals: yield: 10.1 g (80%) m.p. 190–191°C. IR (KBr) v/cm⁻¹: 2228 (C=N_{str}) prominent peak, ¹H NMR (DMSO-d₆)/ppm: 8.20 (s, 2 H, benzyl), 7.30 (m, 10 H, phenyl), 4.30 (s. 4 H. methylene).

2.3.2. Synthesis of octakis(benzylthio)phthalocyaninato lithium, OBTLiPc (3)

Lithium metal (12 mg, 0.0081 mmol) was suspended in 8 mL n-pentanol under nitrogen and was refluxed at 90 °C, while being stirred, for 2 h until a homogeneous mixture containing lithium pentanoalate was formed. The mixture was allowed cooled to room temperature followed by addition of 30 mg (0.081 mmol) of compound **2** (1,2-(benzylthio)-4,5-dicyanobenzene) which was previously suspended in n-pentanol. The temperature was steadily raised to 135 °C while stirring. The reaction mixture was stirred for an additional 2 h and monitored at intervals using a UV–vis. spectrophotometer for the formation of the Q-band for the lithium complex, compound **3**. The complex was not isolated but employed in the formation of compounds **4–6**, as explained in the following sections.

2.3.3. Synthesis of octakis(benzylthio)phthalocyaninato zinc, OBTZnPc (4)

To the mixture containing OBTLiPc, compound **3**, a solution of anhydrous zinc acetate (64 mg, 3.488×10^{-4} mol) in dry DMSO was added and refluxed for 45 min until a deep green colour of OBTZnPc, compound 4 was observed. The formation of compound **4** was monitored with a UV-vis. spectrophotometer, and the reaction was deemed complete when the Q-band position of compound **3** disappeared and a new Q-band position due to compound 4 was formed. The reaction mixture was cooled to room temperature. The Pentanol was removed under reduced pressure and hexane (1 mL) was added to the mixture to precipitate the compound. The product was collected by vacuum filtration and washed with hot EtOH (2 \times 5 mL) and then dried in under vacuum. Compound 4: Yield: 65%. IR (KBr) v/cm⁻¹: 2916 (C-C_{str}), 1589 (C=C_{str}), 695 (C-S_{str}). UV-vis. (DMSO) λ_{max} (nm) (log ε): 373 (4.87), 634 (4.48), 710 (5.33). ¹H NMR (DMSO-d₆)/ppm: 8.29 (s, 8 H, Pc), 7.99 (*m*, 40 H, phenyl), 4.48 (*m*, 16 H, methylene). MALDI-TOF (m/z): Molecular mass of 4: 1555.42 g/mol, found: {{M + 1}⁺, 1556.42 g/mol, (100).

2.3.4. Synthesis of octakis(benzylthio)phthalocyaninato aluminium, OBTAIPcOH (5)

A solution of aluminium acetate (25 mg, 0.0162 mmol) in npentanol was added to the mixture containing compound **3**, and the solution was refluxed for 1 hour until a deep blue colour was observed. The complete formation of the OBTAIPc was confirmed by monitoring the disappearance of the split Q-bands related to the metal free Pc with the simultaneous formation of a well defined Q-band corresponding to OBTAIPcOH. The mixture was cooled to room temperature. The solid product was washed in hot EtOH (2×3 mL) collected by centrifuge, and dried in a desiccator. Compound **5**: yield: 69%. IR (KBr) ν/cm^{-1} : 3461 (**O**-**H**_{str}), 2959 (C-C_{str}), 1543 (C=C_{str}), 669 (C-S_{str}). UV-vis. (DMSO) λ_{max} (nm) (log ε): 379 (4.807), 627 (4.31), 699 (5.14). ¹H NMR (DMSO-d₆)/ppm: 9.18 (*s*, 8 H, Pc), 7.70 (*m*, 40 H, Phenyl), 4.76 (*m*, 16 H, meth-ylene). MALDI-TOF (*m*/*z*): Molecular mass of 4: 1551.06 g/mol, found: {{M + 2}⁺, 1553.06 g/mol.

2.3.5. Synthesis of octakis(benzylthio)phthalocyaninato tin, OBTSnPcCl₂ (6)

A solution of tin (II) chloride (105 mg, 0.0647 mmol) in n-pentanol was added to the mixture containing compound **3** and refluxed for one hour until a deep green colour was observed. The reaction was monitored with a UV–vis. spectrophotometer, as for compound **4** above. The mixture was cooled to room temperature. Hexane (1 mL) was added and the solid product precipitated out. The resultant product (Compound **6**) was collected by vacuum filtration, washed with hot methanol (1 × 4 mLs) and immediately dried in a dessicator. Compound **6**: Yield: 73%. IR (KBr) ν/cm^{-1} : 2915 (C–C_{str}), 1562 (C=C_{str}), 687 (C–S_{str}), 327 (Sn–Cl_{str}). UV–vis. (DMSO) λ_{max} (nm) (log ε): 377 (4.56), 6304 (3.97), 703 (4.86). ¹H NMR (DMSO-d₆)/ppm: 9.18 (*s*, 8 H, Pc), 7.76 (*m*, 40 H, phenyl), 4.76 (*m*, 16 H, methylene). MALDI-TOF (*m*/*z*): Molecular mass of 4: 1657.5 g/mol, found: {{M + 2}⁺, 1659.5 g/mol.

3. Results and discussion

3.1. Synthesis and characterisation

The synthesis of the octakis (benzylthio) phthalocyanato zinc, aluminium and tin were carried out using established procedure in the literature [23] illustrated in Scheme 1.

Compound **2** was synthesised according to the procedure described in literature [23] involving the conversion of 4,5-dichloro-1,2-dicyanobenzene (**1**) with an 80% yield. The MPc 2complexes were characterised by several methods including UV–vis., IR, and ¹H NMR spectroscopies and MALDI-TOF mass spectroscopy. As shown in the experimental section, the mass spectral data (Maldi-TOF) for all the MPcs showed prominent molecular ion peaks.

The UV–vis. spectra of OBTMPcs: **4**, **5** and **6** are shown in Fig. 1. The Q-bands occurred at 710 nm (for compound **4**, OBTZnPc), 699 nm (for compound **5**, OBTAIPcOH) and 703 nm (for compound **6**, OBTSnPcCl₂). The compounds obeyed Beer's law at concentrations less than 1×10^{-5} mol dm⁻³.

Disappearance of the characteristic CN stretch at 2228 cm⁻¹ (from compound **2**, Fig. 2) for all the OBTMPcs indicates complete cyclotetramerisation of the Pc ring (Fig. 3).

The ¹H NMR spectra of OBTMPcs (4–6) in deuterated DMSO-d⁶ exhibit patterns consistent with metallophthalocyanines. The ¹H NMR peaks of compounds: **4**, OBTZnPc; **5**, OBTAlPcOH and **6**, OBTSnPcCl₂ of the aromatic protons on the phenyl groups appeared at 8.29, 9.18, and 9.18 ppm, and methylene protons appeared at 4.48, 4.76 and 4.76 ppm, respectively. The large upfield shift in the proton is caused by the influence of the diamagnetic ring currents of OBTMPc, in the shielding core. Consequently, signals are shifted upfield and the magnitude depends on the distance between a given proton and the Pc moiety. This effect is particularly pronounced in OBTZnPc because of the relative net contribution of electronegativity changes and $P\pi$ - $d\pi$ back donation between the Pc ring and the central atom (Zn). The $P\pi$ - $d\pi$ back donation is explained in reference [24].

3.2. Solvent effects of the UV-vis absorption spectra of OBTZnPc

The electronic absorption spectrum of an organic dye is primarily dependent on the type of chromophore, the nature of transition (in MPc: $\pi \rightarrow \pi^*$ (Q-band), $n \rightarrow \pi^*$ (Soret or B band) and charge transfer absorptions. Solvent effects on electronic absorption spec-



Scheme 1. Synthesis of complexes 4: OBTZnPc; 5: OBTAIOH; 6: OBTSnPcCl₂.



Fig. 1. Electronic absorption spectra in DMSO: 4 = OBTZnPc (λ_{max} = 710 nm); 5 = OBTAIPcOH (λ_{max} = 699 nm); 6 = OBTSnPcCl₂ (λ_{max} = 703 nm). Concentration = $\sim 1 \times 10^{-6}$ mol dm⁻³.

tra of donor-substituted thioether derivatives of OBTZnPc were investigated in eight selected solvents. The data (Table 1) were evaluated following literature methods [25–27]. The refractive indices of the solvent mixture were calculated using the equation below:

$${}^{mix}n_D = \frac{n_1 V_1 + n_2 V_2 + \dots + n_n V_n}{V_1 + V_2 + \dots + V_n}$$
(1)

where $^{mix}n_D$ is the refractive index of the solvent mixture and n_1 and n_2 are the refractive indices of solvents 1 and 2 respectively. V_1 and V_2 are the volumes of solvents 1 and 2 respectively. OBTZnPc spectra in single and mixed solvents showed monomer peaks at the Q-bands with concentrations as low as $<1 \times 10^{-6}$ mol dm⁻³, except in a water/pyridine mixture, where aggregation behaviour was noticed (not shown as a figure legend). In the search for a solvent

mixture where OBTZnPc exhibits the highest monomeric behaviour, the following criteria discussed in reference [28] were partly used: (1) the solvent component of the higher refractive index should be a very good solvent of the given polymer (OBTZnPc), while the lower refractive index should be an effective participant in the polymer; (2) the solvent with the higher refractive index should exhibit a better affinity for the polymer; (3) linear relationships exist between the refractive index measurements of single solvent and mixed solvents at 20 °C [29]; (4) hydrogen-bonding interaction between solvent and polymer is assumed to be absent.

Bayliss et al. [25] qualitatively described three factors that could possibly affect the ground state electronic absorption spectra. These are: dipole, polarisation and hydrogen-bonding forces, which they summarised as the momentary transition dipole during the optical absorption process, the difference between the permanent dipole moment(between the ground and the excited states of the solute) and the effect of the Franck-Condon principle. The latter two factors are assumed to be non-operative in the ground state electronic absorption spectra of the complex investigated, or are negligible factors that can be ignored. The only operative force is assumed to be the momentary polarisation that is induced in the solvent by the transition dipole of OBTZnPc, which can be interpreted as the red shift and is a function of the solvent refractive index. The polarisation red shift of ZnPc has been reported [26] but for the purpose of this study, the absorption spectra at the Qband of ZnPc were determined in nine selected solvents using a UV-vis spectrophotometer.

Table 1 shows the polarisation red shift behaviour of OBTZnPc in different solvents. The polarisation red shift of a substituted MPc can be calculated, provided the Q-band (λ_{max}) of the unsubstituted MPc is known in the vapour phase. In addition, the Q-band of the unsubstituted MPc in solution for any given solvent must be



Fig. 2. (a) Polarisation red shift of OBTZnPc in single solvents. Solvents: 1: pyridine; 2: DMSO; 3: DMF; 4: THF. $F = \frac{p^2 - 1}{2n^2 + 1}$, *n* is the refractive index of solvent and (b) polarisation red shift of OBTZnPc in mixed solvents. Solvents: a: benzene/pyridine; b: toluene/pyridine; c: chloroform/pyridine; d: petroleum ether/pyridine.



Fig. 3. (a) Q-band dependence on the refractive index of single solvents (OBTZnPc in single solvents) and (b) Q-band dependence on the refractive index of mixed solvents. a: petroleum ether/pyridine; b: chloroform/pyridine; c: toluene/pyridine; d: benzene/pyridine (OBTZnPc in mixed solvents).

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Solvent effects on the electr	onic absorption sp	pectra of OBTZnPc in var	ious solvents. λ_m	_{ax} (at the Q-band) fo	or the unsubstituted ZnI	°c in vapour =	660 nm [30].	
Solvent	Refractive index, n _{D²⁰}	Solvent donor number (DN)	Dipole moment, μ	Q-band λ _{max} (nm) ZnPc	Q-band λ _{max} (nm) OBTZnPc	$\Delta\lambda_a (nm)$ ZnPc	$\Delta \lambda_b (nm)$ OBTZnPc	$F = \frac{n^2 - 1}{2n^2 + 1}$
DMSO	1.479	29.8	3.96	672	710	12	50	0.2209
DMF	1.430	26.6	3.79	670	705	10	45	0.2053
THF	1.406	20.0	1.69	667	704	7	44	0.1972
Pyridine	1.509	33.1	2.21	674	713	14	53	0.2299
Benzene/pyridine (2:1)	1.504 ^a	_e	(0.00, 2.21)	672 ^b	711	12	51	0.2285
Chloroform/pyridine (2:1)	1.462 ^a	_ ^e	(1.90, 2.21)	673 ^c	710	13	50	0.2157
Toluene/pyridine (2:1)	1.501 ^a	_e	(0.38, 2.21)	671 ^d	711	11	51	0.2276
Petroleum ether/ pyridine (2:1)	1.413 ^a	_e	(- ^e , 2.21)	666	708	6	47	0.1996
$H_2O/pvridine(2.1)$	1 3915 ^a	Ασσ	(187 221)	Ασσ	Ασσ	_e	_e	_e

 $\Delta \lambda_a$ polarisation red shift of ZnPc. Values calculated using; $\Delta \lambda_a = \lambda_{max}^{ZnPc_{solution}} - \lambda_{max}^{Zn$

 $\Delta \lambda_b$ polarisation red shift of OBTZnPc. Values calculated using; $\Delta \lambda_b = \lambda_{max}^{OBTZ_{solution}} - \lambda_{max}^{ZnPc}$

Agg = aggregation.

Table 1

Refractive index of solvent mixture calculated using Eq. (1).

 λ_{max} for ZnPc measured in benzene.

 λ_{max} for ZnPc measured in chloroform.

d λ_{max} for ZnPc measured in toluene.

Not found.

greater than the Q-band in the vapour phase. The values obtained are approximate. Ideally the polarisation red shift is the difference between the Q-band in solution and the Q-band in the vapour phase. The equations below show an empirical method for calculating the polarisation red shift of any given substituted MPc.

$$\Delta \lambda^{\text{MPc}(\text{substituted})_{\text{solution}}} = \lambda_{\text{max}}^{\text{MPc}(\text{substituted})_{\text{solution}}} - \lambda_{\text{max}}^{\text{MPc}(\text{unsubstituted})_{\text{vapour}}}$$
(2)

$$\lambda_{\max}^{\text{MPC}(\text{substituted})_{\text{solution}}} = \left(\lambda_{\max}^{\text{MPC}(\text{unsubstituted})_{\text{solution}}} - \lambda_{\max}^{\text{MPC}(\text{unsubstituted})_{\text{vapour}}}\right) + \Delta\lambda' \quad (3)$$

$$\Delta \lambda' = \lambda_{\max}^{\text{MPC}(\text{substituted})_{\text{solution}}} - \lambda_{\max}^{\text{MPC}(\text{unsubstituted})_{\text{solution}}}$$
(4)

where $\Delta \lambda'$ is the increased value brought about by the interaction of the solvent and the substituted electron donating group in the MPc moiety. Substituting Eq. (4) for Eq. (3) gives Eq. (2). The polarisation red shift of OBTZnPc is therefore the difference between the Q-band of OBTZnPc in solution and the Q-band of unsubstituted ZnPc in the vapour phase.

$$\begin{aligned} \Delta\lambda &= -12.807F + 108.25 \text{ with } R^2 &= 0.972 \\ (\text{OBTZnPc})(\text{in single solvents}) \end{aligned} \tag{5a} \\ \Delta\lambda &= -6.3289F + 78.89 \text{ with } R^2 &= 0.9745 \\ (\text{OBTZnPc})(\text{in mixed solvents}) \end{aligned} \tag{5b}$$

The two plots (Fig. 2a and b) suggest that the polarisation red shifts are largely due to solvation, and are expressed by the equations above ((5a) and (5b)). R is the correlation coefficient and F(OBTZnPc) is a constant for a particular solvent or solvent mix at a given volume ratio. A linear variation of the Q-band with

refractive index was also observed in both single and mixed solvents, indicating a Q-band dependence on the solvent's refractive index, as shown in Eqs. (6a) and (6b) (Fig. 3a and b).

$$\lambda_{\text{max}} = 90.421n + 576.35 \text{ with } R^2 = 0.9863$$
(OBTZnPc)(in single solvents)
(6a)

$$\lambda_{\text{max}} = 43.462n + 645.86 \text{ with } R^2 = 0.9541$$
(OBTZnPc)(in mixed solvents) (6b)

Linear expressions are also shown for the following parameters in Eqs. (7a) and (7b) (Figs. 4a and b):

$$\Delta \lambda = 0.6973 \text{DN} + 28.912 \quad \text{with } R^2 = 0.8432$$
(OBTZnPc)(in single solvents)
$$\lambda_{\text{max}} = 0.6973 \text{DN} + 688.91 \quad \text{with } R^2 = 0.8432$$
(7a)

but there was no direct correlation between the polarisation red shift (or the Q-band) and the solvent's dipole moment.

3.3. Interpretation of the photophysical and photochemical data

The photophysical and photochemical parameters of photosensitising dyes can be measured in terms of the light harvesting property of the dye (i.e. molar extinction coefficient (ε), fluorescence quantum yield (ϕ_F), fluorescence lifetime (τ_F), triplet quantum yield (ϕ_T), triplet lifetime (τ_T), singlet oxygen quantum yield (ϕ_{Δ}) , phosphorescence quantum yield (ϕ_p) , photosensitising



Fig. 4. (a) Variation of red shift at the Q-band with solvent's coordination no. (DN) (OBTZnPc) and (b) variation of the Q-band with solvent's coordination no. (DN) (OBTZnPc).

efficiency (S_{Δ}). All three complexes were measured in dimethyl sulphoxide (DMSO) at the room temperature and the solutions

were further filtered before transferring into a standard spectrophotometer cell.



Fig. 5. (a) Polarisation red shift vs. red shift index $(R_s I)$ (OBTZnPc) and (b) Q-band vs. red shift index $(R_s I)$ (OBTZnPc).



Fig. 6. (a) Scale control chart. DMSO represents the universal solvent for the five complexes and it also the highest polarity index of solvent (7.2). $ZnPc(SR)_8$ is OBTZnPc, (b) polarity index chart of single and mixed solvents (2:1 volume ratio). PET: petroleum ether; Py: pyridine; Tol: toluene; Bz: benzene; THF: tetrahydrofuran; Chl: chloroform; DMF: dimethyl formamide; DMSO: dimethyl sulphoxide. Red bars represent solvents employed in OBTZnPc only, (c) relative red shift index (R_sI) in DMF: ZnOEPc > OBTZnPc > ZnOPc > ZnOPc > ZnPc (py)ZnPc, (d) relative red shift index (R_sI) in THF: OBTZnPc > ZnOEPc > ZnOPc > ZnPc, (e) relative red shift index (R_sI) in pyridine: ZnC= ZnOEPc > ZnOPc > OBTZnPc, (f) relative red shift index (R_sI) in Bz (or Bz/Py): ZnOEPc > OBTZnPc > ZnPc = (py)ZnPc, (g) relative red shift index (R_sI) in Chl(or Chl/ Py): ZnOEPc > OBTZnPc, (h) relative red shift index (R_sI) in Tol (or Tol/Py): ZnOEPc > OBTZnPc > ZnPc = (py)ZnPc, (g) relative red shift index (R_sI) in Tol (or Tol/Py): ZnOEPc > ZnPc = (py)ZnPc, (d) relative red shift index (R_sI) in Tol (or Tol/Py): ZnOEPc > ZnPc = (py)ZnPc, (g) relative red shift index (R_sI) in DET/Py: OBTZnPc > ZnPc = (py)ZnPc, (g) relative red shift index (R_sI) in Tol (or Tol/Py): ZnOEPc > ZnPc = (py)ZnPc, and (i) relative red shift index (R_sI) in DET/Py: OBTZnPc > ZnPc = (py)ZnPc, (h) relative red shift index (R_sI) in Tol (or Tol/Py): ZnOEPc > DRTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) in PT/Py: OBTZnPc > ZnPc = (py)ZnPc, (p) relative red shift index (R_sI) i



3.3.1. Fluorescence quantum yields

Fluorescence quantum yield (ϕ_F) was determined by the comparative method used in literature [31].

$$\phi_F = \phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n_D^2}{F_{\text{Std}} \cdot A \cdot n_{\text{DStd}}^2}$$
(8)

F represents the areas under the fluorescence curves of the OBTMPc ($M = Zn^{2+}$, Al^{3+} , Sn^{4+}), and F_{Std} is area under the fluorescence curve of the standard. *A* and A_{Std} are the respective absorbances of sample, OBTMPc and the standard at the excitation wavelengths, and n_D and n_{DStd} are the refractive indices of solvents used in the sample and standard respectively. Fluorescence quantum yield for standard, ZnPc in DMSO ($\phi_F^{Std} = 0.18$) [32a,b]. Both the sample and standard were excited at the same wavelength.

3.3.2. Triplet quantum yields and lifetimes

De-aerated solutions of the respective OBTMPc were introduced into a 2 mm × 10 mm spectrophotometer cell and irradiated at the Q-band maxima with the laser system described above. Triplet quantum yields (ϕ_T) were determined by the comparative method based on triplet decay in Eq. (9).

$$\phi_T^{\text{Sample}} = \phi_T^{\text{Std}} \frac{\Delta A_T \cdot \varepsilon_T^{\text{std}}}{\Delta A_T^{\text{Std}} \cdot \varepsilon_T}$$
(9)

where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbance of the OBTMPc and standard respectively; ε_T and $\varepsilon_\tau^{\text{Std}}$ are the triplet state extinction coefficients for OBTMPc and standard respectively. The triplet quantum yield for standard, zinc phthalocyanine (ZnPc) in DMSO ($\phi_T^{\text{Std}} = 0.65$ cited in Ref. [33]). Quantum yields of internal conversion (ϕ_{IC}) were obtained

Quantum yields of internal conversion (ϕ_{IC}) were obtained using Eq. (10). The assumption is based on the fact that there are only three processes that are solely responsible for the joint deactivation processes of OBTMPc, namely fluorescence, intersystem crossing and internal conversion.

$$\phi_{IC} = 1 - (\phi_F + \phi_T) \tag{10}$$

Triplet lifetimes were obtained by the exponential fitting of the kinetic curves using OriginPro 7.5 software.

3.3.3. Singlet oxygen and photodegradation quantum yields

Singlet oxygen (ϕ_{Δ}) and photodegradation (ϕ_d) quantum yield determinations were carried out using the experimental set-up described in detail in this paper [34]. Typically, a 2 mL portion of the



Table 2

Red shift index table of ZnPc derivatives. Ref. [26] indicates the literature values used to calculate the red shift indices of the different complexes. ZnOPPc: zinc octaphenoxyphthalocyanine; ZnOEPc: zinc octaestronephthalocyanine; (py) ZnPc: (pyridino) zinc phthalocyanine.

Solvent	Solvent polarity index, PI	Red shift index, ZnPc, N _{dye} = 560	Red shift index, OBTZnPc, N _{dye} = 142	Red shift index, ZnOPPc [27], <i>N</i> _{dye} = 357	Red shift Index, ZnOEPc [27], <i>N</i> _{dye} = 324	Red shift index, (py)ZnPc [27], N _{dye} = 560
DMSO	7.2	10	10	10	10	10
DMF	6.4	8.358	9.064	8.965	9.529	7.534
THF	4.0	5.877	8.875	10.500, 15.523	8.136	_d
Pyridine	5.3	11.632	10.555	11.009	11.368	_d
Benzene/pyridine (2:1)	(2.7, 5.3)	10 ^a	10.186	10.500, 15.523 ^a	10.452 ^a	10 ^a
Chloroform/ pyridine (2:1)	(4.1, 5.3)	10.817 ^b	10	_d	_d	_d
Toluene/pyridine (2:1)	(2.4, 5.3)	9.180 ^c	10.186	10.500, 15.523 ^c	9.991 ^c	10 ^c
Petroleum ether/ pyridine (2:1)	(0.1, 5.3)	5.045	9.627	_d	_d	_d

^a λ_{max} measured in benzene.

^b λ_{max} measured in chloroform.

 λ_{max}^{c} λ_{max} measured in toluene.

^d Not determined.

respective OBTMPc solution (absorbance ~0.5) containing the singlet oxygen quencher, 1,3-diphenylisobenzofuran(DPBF), was irradiated in the Q-band region using the photo-irradiation set-up described above. Singlet oxygen quantum yields (ϕ_{Δ}) for the complexes were calculated according to Eq. (11):

$$\phi_{\Delta} = \phi_{\Delta}^{\rm Std} \frac{R \cdot I_{\rm abs}^{\rm Std}}{R^{\rm Std} \cdot I_{\rm abs}} \tag{11}$$

 $\phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard ZnPc ($\phi_{\Delta}^{\text{Std}}$ = 0.67 in DMSO (cited in Ref. [32])); *R* and *R*^{Std} are the DPBF photobleaching rates in the presence of OBTMPc and standard respectively; *I*_{abs} and *I*_{abs}^{Std} are the rates of light absorption by the OBTMPc and ZnPc, standard respectively. DPBF concentrations were calculated using log ε = 4.36 at 417 nm in DMSO. The light intensity used for ϕ_{Δ} determinations was found to be 1.14×10^{16} photons

s⁻¹ cm⁻². Photodegradation quantum yields were determined using Eq. (12),

$$\phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I \cdot S \cdot t} \tag{12}$$

 C_0 and C_t are OBTMPc concentrations before and after irradiation respectively, *V* is the reaction volume, N_A the Avogadro's constant, *S* the irradiated cell area and *t* the irradiation time. *I* is the overlap integral between the radiation source and OBTMPc absorption. The light intensity of 5.02×10^{16} photons s⁻¹ cm⁻² was employed for the photodegradation studies of the complexes.

3.4. The concept of the red shift index (R_sI). Case study: OBTZnPc and unsubstituted ZnPc in different solvents

The red (bathochromic) shift of an organic dye is the shift of the absorption spectrum to longer wavelengths due to a substitution



Fig. 7. (a) 3D correlation multiparameter plot: polarisation red shift ($\Delta\lambda$), solvent donor (DN) and *F*(OBTZnPc), (b) 3D correlation multiparameter plot: polarisation red shift ($\Delta\lambda$), red shift index (R_sI) and solvent donor number (DN), (c) 3D correlation multiparameter plot: Q-band (λ_{max} of OBTZnPc, red shift index, R_sI and refractive index, n and (d) linear dependence string plot function of the solvent parameters: $\Delta\lambda(F)$, $\lambda_{max}(n)$ and $\lambda_{max}(R_sI)$.

or solvent effect. We defined the red shift of a substituted MPc in Eq. (2) to be the difference between the Q-band in solution and the Q-band in the vapour phase. The red shift index, R_s , may therefore be defined as the fraction of the red shift of the substituted dye (OBTZnPc) to the Q-band (λ_{max}) of the unsubstituted dye [ZnPc] in the vapour phase multiplied by a scaling factor, N_{dye} .

$$(R_{\rm s}I) = \frac{\Delta \lambda^{\rm sample}_{\rm solution} \times N_{\rm dye}}{\lambda_{\rm max}^{\rm (vapour) reference}}$$
(13a)

$$N_{dye} = \frac{10 \left(\lambda_{max(solution)}^{sample} - \lambda_{max(vapour)}^{reference} \right)}{\lambda_{max(vapour)}^{reference}} = 10 \left(\frac{\lambda_{max(solution)}^{sample}}{\lambda_{max(vapour)}^{reference}} - 1 \right)$$
(13b)

 $\lambda_{\max(vapour)}^{\text{reference}}$ is the unsubstituted dye in the vapour phase. The red shift index is a modified formula from Freed et al. [35]. N_{dye} is the scaling factor of the dye when dissolved in the solvent with the highest polarity index value. The scaling factor is measured from three parameters, namely: the red shift of the substituted dye

 $(\Delta \lambda_{\text{solution}}^{\text{sample}} \text{ in Eq. (2)})$, $\lambda_{\max(vapour)}^{\text{reference}}$ of the unsubstituted dye, and the solvent choice that has the highest solvent polarity index value (PI).

The red shift index can be applied to any type of organic dye, provided the Q-band shows a monomer peak in the absorption spectrum. It is a useful parameter for estimating, in empirical terms, the coordinating power of a solvent in the presence of a dye, irrespective of the state of the dye (charged or neutral). The linear plots of the polarisation red shift and the Q-band (λ_{max}) vs. the red shift index of OBTZnPc and ZnPc (Fig. 5a and b) are given below:

$$\Delta \lambda = 5.4295 R_{\rm s} I - 4.3971$$
 with $R^2 = 0.9875$ (OBTZnPc) (14a)

$$\Delta \lambda = 1.2139R_{\rm s}I - 0.13943 \text{ with } R^2 = 1 \text{ (ZnPc)}$$
(14b)

$$\lambda_{\max} = 5.3517 R_s I + 656.49 \text{ with } R^2 = 1 \text{ (OB1ZnPc)}$$
(14c)

$$\lambda_{\max} = 1.2139 R_s I + 659.87 \text{ with } R^2 = 1 \text{ (ZnPc)}$$
 (14d)

Fig. 6a–i shows the chart variation of the data in Table 2. In DMF, except for (py)ZnPc, the four other complexes represented show red shift indices that are almost the same. In THF, only ZnPc shows a low red shift index compared to the other two complexes represented. Surprisingly in pyridine, the red shift index of ZnPc



Fig. 7 (continued)

represents the highest value. Also good red shift values are represented for the other complexes in the same solvent. The red shift indices of the various complexes in pyridine may be due to the high coordinating activity of pyridine, which is a function of its solvent donor, DN (33.1). This may also explain why the red shift indices for OBTZnPc in the mixed solvents remain exceptionally high except for Fig. 6i, where the red shift index of ZnPc in PET/Py is low (which may be due to low coordinating activity in the mixture). The red shift index shows a strong correlation with the following solvent parameters represented in Table 1: the refractive index, n_D and the solvent donor, DN. The red shift index increases as these two parameters increase (n_D and DN). The red shift indices of the complexes represented show good empirical scale, since the index values are in agreement with the refractive indices of single and mixed solvents. There is no clear correlation between the red shift index with the following parameters: the polarity index of solvent. PI and the dipole moment, μ in Table 1. Fig. 7a–c shows the solvation pattern of OBTZnPc. The pattern illustrates six parametric values used in the study of solvent effects of OBTZnPc, namely: the Q-band (λ_{max}), the polarisation red shift ($\Delta\lambda$), F(OBTZnPc), the solvent donor number (DN), the red shift index (R_{sl}) and the refractive index, $n(n_D)$. The linear dependence functions of these parameters were further confirmed using the string plot shown in Fig. 7d.

3.5. Explanation of the photophysical and photochemical parameters

The excitation spectra of the three complexes OBTMPc represent mirror images of their emission spectra. Fig. 8a and b also shows that the complexes absorbing light in the ground state are the same complexes that are being excited. This confirms that the absorbing species is also the fluorescing species. In general, all the parameters in Table 3 show strong correlations that can be summarised using the Jablonski energy level diagram (not shown as a figure legend). Following the absorption of light at the excitation wavelength of these complexes, electrons are promoted from the ground state to the singlet state by the absorption of photon I_{ab} . The excited state complexes (¹M^{*}) fluoresce by emitting photons, with decreasing ϕ_F efficiency as follows: OBTAlPcO-H > OBTSnPcCl₂ \approx OBTZnPc. Fluorescence quantum yield values are usually expected to be higher for MPcs with lighter atoms and lower for MPcs with heavier atoms, where intersystem



Fig. 8. (a) Normalized fluorescence excitation (blue curve) and emission spectra (red curve) of OBTZnPc in DMSO. Excitation wavelength at 645 nm and (b) normalized ground state absorption (black curve) and excitation (blue curve) spectra of ZnPc(SR)₈ in DMSO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table	3

Photophysical	and photochemica	parameters	obtained	in DMSO

Complex	$\lambda_Q (nm)$	$\lambda_F(\mathbf{nm})$	$\Delta_{stokes(nm)}^{a}$	$\tau_T(\mu s)$	$\phi_{F\pm(0.03)}$	ϕ_T	$\phi_{IC}^{\mathbf{b}}$	ISC ^c ratio, χ	$\phi_d imes 10^5$	ϕ_{Δ}	n_p^{d}	S_{Δ}^{e}
OBTZnPc	710	719	9	630	0.13	0.53	0.34	4.08	0.03	0.43	$\begin{array}{c} 4\times10^5\\ 8\times10^5\\ 5\times10^4 \end{array}$	0.81
OBTAlPcOH	699	707	8	810	0.31	0.40	0.29	1.29	0.04	0.36		0.90
OBTSnPcCl ₂	703	717	14	610	0.15	0.47	0.38	3.13	0.33	0.35		0.74

The photophysical and photochemical properties were all measured in DMSO at the average LT (laboratory temperature = 20 °C).

^a Δ_{stokes} is the stokes shift and values calculated using $\Delta_{\text{stokes}} = \lambda_F - \lambda_Q$.

^b ϕ_{IC} is the internal conversion. Values calculated using Eq. (10), $\phi_{IC} = 1 - (\phi_F + \phi_T)$.

^c ISC ratio $\chi = \phi_T / \phi_F$.

^d n_p is the photon yields per molecule. Values calculated using a rough estimation $n_p = \phi_F / \phi_d$.

^e S_{Δ} is the fraction of triplet state quenched by triplet state oxygen. Values calculated using $S_{\Delta} = \phi_{\Delta}/\phi_T$.



Fig. 9. Triplet decay curve of OBTAIPCOH in DMSO. Exponential fit was obtained with OriginPro 7.5 software.

crossing (ISC) of heavier atoms is expected to cause a decrease in fluorescence quantum yield [36].

The complexes can lose energy in three different ways: (i) through internal conversion to move to the ground state (ϕ_{IC}), with decreasing vields as follows: OBTSnPcCl₂ > OBTZnPc > OBTAlPcOH: a direct correlation with the Stokes shift values are also compared. From Table 3, the larger the Stokes shift, the greater the internal conversion yield; meaning that more of the electronic energy of the excited singlet state is lost through internal conversion to the ground state in OBTSnPcCl₂ when compared to the two other (OB-TAIPcOH and OBTZnPc). (ii) Through intersystem crossing, ISC moving to the triplet state, with decreasing yields of ϕ_T as follows: $OBTZnPc > OBTSnPcCl_2 > OBTAlPcOH$, which is the direct inverse of ϕ_{F} . These trends observed in quantum yields of fluorescence and triplet are due to the heavy atom effect. The effect is caused by the spin-orbit coupling of atoms of higher atomic number, which causes a reduction in fluorescence quantum yield and increases the probability of such compounds undergoing successful intersystem crossing from the singlet state to the triplet state. The presence of axial OH in complex 5 and axial Cl in complex 6 could in addition facilitate radiationless decay to the ground state, and hence a subsequent drop in the fluorescence quantum yield as shown for the corresponding values obtained in OBTAIPcOH and OBTSnPcCl₂ in Table 3. Again from Table 3, the intersystem crossing ratio is directly proportional to the triplet quantum yield and inversely proportional to the fluorescence quantum yield.

Another way in which these complexes may lose energy is (iii) through intermolecular processes via excited state quenching. In Table 3, S_{Δ} represents one such physical parameter, and this is a fraction of the triplet state quenched by triplet state oxygen, with decreasing energy transfer efficiency as follows: OBTAIPCO-H > OBTZnPc > OBTSnPcCl_2. The triplet lifetime values listed in Table 3 are long enough for a variety of quenching processes to

compete with phosphorescence [37], with OBTAIPcOH, exhibiting the highest lifetime. Fig. 9 shows the triplet decay curve of OBTAIPcOH in DMSO. Also from Table 3, there is a strong correlation between the following parameters: τ_T , S_Δ and np (photon yields per molecule). The three parameters indicate that the higher the photon yields per molecule of the complex, the higher the energy transfer efficiency and the higher the triplet lifetime. Singlet oxygen is most commonly produced by photosensitisation from the triplet state of molecules. Consequently, the singlet oxygen quantum yield (ϕ_Δ) should depend on the triplet quantum yield. Also from Table 3, the presence of axial ligands in OBTAIPcOH and OBTSnPcCl₂ may have also contributed to their low singlet oxygen yields. This has also been reported in this review [37].

The degradation of the molecules under irradiation is used to study the photostability of the molecules, which is especially important for those molecules intended for use as photocatalysts. Table 3 shows the photodegradation yields (ϕ_d) of complexes investigated. These values are generally lower than reported for most MPcs, which further shows that thioether substituents impart a reasonable degree of photostability to the OBTMPc complexes. Fig. 10a shows the kinetic studies of OBTAIPcOH in air, oxygen, DABCO (a singlet oxygen scavenger), deuterated DMSO and nitrogen. A similar study was carried out with OBTZnPc and OBTSnPcCl₂. A faster rate is observed in oxygen than in nitrogen, air or deuterated DMSO, meaning that oxygen may be involved in the photodegradation, but not just as singlet oxygen, since the complex is highly photostable in deuterated DMSO. However when DABCO was employed, the spectral changes shown in Fig. 10b were observed, which might be attributed to the phototransformation of OBTAIPCOH, accompanied by a shift in band positions (Q and B bands) to a highly photostable complex. Similar studies on OBTZnPc and OBTAlPcOH indicate the lowering of the Q-band positions without the accompanied phototransformation observed for OBTAIPcOH in DABCO. The observed trends of these complexes in DABCO suggest that radical mechanisms may play a major role in the degradation of OBTZnPc and OBTSnPcCl₂, and that this mechanism play a less important role in OBTAlPcOH.

4. Conclusion

Solvent effects on the ground state absorption and physicochemical parameters of OBTMPc with central metal ions of Zn^{2+} , Al^{3+} and Sn^{4+} are not well understood. The inclusion of a thioether derivative (SR, where R is CH₂Ph) in the phthalocyanine moiety resulted in OBTZnPc exhibiting excellent spectral properties, as monomeric peaks were observed in single and mixed solvents. These complexes also showed a high photon yield per molecule (n_P), very low photodegradation yield (ϕ_d), and high photosensitisation-efficiency (S_Δ), which suggests they should be further investigated for light-driven applications such as photosensitisers, photocatalysts and as advanced optical materials.



Fig. 10. (a) Kinetic studies of OBTAIPcOH in DMSO in the presence of (i) oxygen, (ii) nitrogen, (iii) DABCO and (iv) AIPc(SR)₈OH in deuterated DMSO. Excitation wavelength ~699 nm. (b) Electronic absorption spectral changes observed during the photolysis of AIPc(SR)₈OH in DMSO containing DABCO. AIPc(SR)₈OH ~1.3 × 10⁻⁶ mol dm⁻³. Excitation wavelength ~699 nm.

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