Estimation of Fluorescence Lifetimes of Zinc Phthalocyanine in various Organic Solvents – A Semi-Empirical Approach

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Abstract

The effect of solvents on the ground state electronic absorption spectra and fluorescence properties of zinc phthalocyanine is presented. Q-band positions vary between 668 nm (in tetrahydrofuran) and 677 nm (in 1-chloronaphthalene), and is found to be solvent refractive index-dependent. The fluorescence quantum yields, fluorescence lifetimes and Stern–Volmer's quenching constant for fluorescence quenching by benzoquinone are all solvent viscosity-dependent, with the most viscous solvent exhibiting the highest values. The Stern–Volmer's quenching constant, together with the calculated bimolecular quenching constant were used in the determination of fluorescence lifetime. This work presents a semi-empirical approach for the determination of fluorescence lifetime of a fluorophore, which is its main objective. The fluorescence lifetime of zinc phthalocyanine ranges between 2.89 nm in tetrahydrofuran and 5.06 nm in 1-chloronaphthalene.

Keywords: fluorescence lifetime, fluorescence quenching, solvent effects, viscosity, zinc phthalocyanine

Introduction

Phthalocyanines have chromophores of commercial importance. They are closely related structurally to haem and chlorophyll, however, there is no evidence that phthalocyanines occur in nature. Metal-free phthalocyanine (Pc) is an intensely blue–green coloured aromatic macrocycle used in dyeing (McKeown, 1998; Kadish *et al*., 2003). Like the porphyrins, the Pc macrocycle can play host to over 70 different metal ions in its central cavity, giving rise to the corresponding metallophthalocyanine (MPc). Pc and MPc derivatives function as active components in various visible light-driven processes.

In this respect, they find applications in photoredox reactions, photooxidations in solution (Wöhrle *et al*., 1988), photochemical and photovoltaic cells (Wöhrle & Meissner, 1991). The use of Pcs and MPcs in oncology, particularly photodynamic therapy (PDT), is worth stressing (Rosenthal, 1991; Spikes, 1990). For this purpose, transition metal Pcs are not applicable and so attention is focused on Pcs containing non-transition metal centres.

Figure 1: Structure of Zinc phthalocyanine (ZnPc)

Zinc phthalocyanine (ZnPc, Figure 1) finds uses in industry (catalysts, photoconductors) and biomedical (PDT) (Ogunsipe *et al*., 2003). ZnPc may be used to photooxidise cyclohexane (Sehlotho & Nyokong, 2004). A study also reports the functionalization of polymer membranes with ZnPc (Goethals *et al.*, 2014). MPcs exhibit very intense absorption in the red region of the visible spectrum.

A molecule, which is photochemically promoted to an excited state, is capable of undergoing various physical and chemical processes, depending on its lifetime in the excited state. Notable among the post-absorption processes are fluorescence, intersystem crossing and internal conversion. Fluorescence is the only radiative process of the aforementioned and it is directly related to the excited state lifetime. As a result, the estimation of the excited state lifetime (fluorescence) of MPcs becomes a focus in the study of their photophysics and photochemistry.

The excitation energy in molecules is lost in form of fluorescence. However, it is possible to "trap" this energy by adding a compound that interacts with the excited chromophores, thus quenching fluorescence. This way, the excitation energy, which would have been lost as fluorescence, is therefore intercepted and channelled to other uses.

In this work, the spectral and fluorescence characteristics of ZnPc are examined in different solvents. Additionally, ZnPc florescence quenching using benzoquinone is also investigated and the quenching data is exploited in the estimation of the fluorescence lifetimes of ZnPc in different solvents.

Materials and Methods

Zinc phthalocyanine (ZnPc) was synthesised according to Literature (Tomoda *et al.*, 1983). Tetrahydrofuran (THF), dichloromethane, toluene, benzene, chloroform, dimethylsulphoxide (DMSO) and *N,N′*-dimethylformamide (DMF) were obtained from SAARCHEM while pyridine, benzonitrile and 1-chlorophthalene were obtained from Fluka. Chlorophyll-*a* and benzoquinone were purchased from Sigma–Aldrich and used as received.

UV–Vis absorption spectra were recorded on a Varian 500 UV/Visible/NIR spectrophotometer and fluorescence spectra were obtained from a Varian Eclipse spectrofluorometer.

Fluorescence Quantum Yields

Fluorescence quantum yields (Φ_F), were determined by the comparative method (Fery–Forgues and Lavabre, 1999; Maree *et al.*, 2002; Equation 1), using chlorophyll-*a* in ether (Φ_F = 0.32; Montalban *et al.*, 1999), as the reference.

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F_x \,.\, A_{Std} \,.\, n_x^2}{F_{Std} \,.\, A \,.\, n_{Std}^2} \qquad (1)$$

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 absorbance values of the sample and standard, respectively, and n_x and n_{Std} are the refractive indices of the solvents used for sample and standard, respectively. Both the sample and reference were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 nm and 0.05 nm.

Fluorescence Quenching by Benzoquinone

Fluorescence quenching experiments on ZnPc in different solvents were carried out by the addition of varying concentrations of benzoquinone (BQ) to a fixed concentration of ZnPc, and the concentrations of BQ in the resulting mixtures were 0, 0.002 M, 0.004 M, 0.006 M, 0.008 M, 0.010 M and 0.012 M. The fluorescence spectra of ZnPc at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation (2):

$$\frac{I_0}{I} = 1 + K_{SV}[\mathrm{BQ}] \qquad (2)$$

where I_0 and I are the fluorescence intensities of ZnPc in the absence and presence of BQ, respectively, [BQ]; the concentration of the BQ, and K_{SV}, the Stern–Volmer constant, which is the product of the bimolecular quenching constant (k_Q) and the fluorescence lifetime τ_F (Equation 3):

$$K_{SV} = k_Q.\tau_F \qquad (3)$$

The ratios $\frac{I_o}{I}$ were calculated and plotted against [BQ] according to (2), and K_{SV} was determined from the slope.

The bimolecular rate constant for diffusion-controlled reactions (k_D) is related to the apparent bimolecular quenching constant (k_Q) by Equation 4 (Lakowikz, 1999).

$$k_Q = f k_D \qquad (4)$$

where *f* is the quenching efficiency.

The bimolecular rate constant (k_D) can be obtained from the Einsten–Smoluchowski relationship (5):

$$k_D = \frac{4\pi\, N_A(D_{ZnPc} + D_{BQ})(r_{ZnPc} + r_{BQ})}{1000} \qquad (5)$$

where N_A is the Avogadro's number, D_{ZnPc} and D_{BQ}; the diffusion coefficients of the fluorophore and quencher, respectively, whereas r_{ZnPc} and r_{BQ} are the molecular radii of ZnPc and BQ, respectively.

The diffusion coefficient D is given by the Stokes' equation (6).

$$D = \frac{kT}{6\pi\eta r} \qquad (6)$$

where *k* is the Boltzman constant, T; the absolute temperature, η; the solvent's viscosity and r; the ZnPc or BQ radius.

The Literature value of r_{ZnPc} is 7.5 Å (Theisen *et al.*, 2015). r_{BQ} is assumed to be equal to the molecule's Onsager cavity radius (a), which is obtained from molecular volume, as given by Suppan's equation:

$$a = \sqrt[3]{\frac{3M}{4\pi\rho N}} \qquad (7)$$

where M is the molecular weight of BQ (108.10 g mol^{-1}) and ρ; its density (1.32 g cm^{-3}) and N; the Avogadro's number.

k_Q values may be determined from Equation 4 using the calculated k_D value, provided that *f* is known. From the values of k_Q, the values of τ_F can then be calculated using Equation 3.

Results and Discussion

UV–Visible and Fluorescence Spectra

The ground state electronic absorption spectrum of ZnPc is shown in Figure 2. The assignment of the ground state electronic absorption bands in MPcs is done qualitatively on the basis of the Gouterman's model (McHugh *et al.*, 1972). The Q and B (Soret) bands both arise from π–π* transitions and can be explained in terms of linear combination of transitions from a_{1u} and a_{2u} HOMO orbitals to the doubly degenerate e_g (LUMO) orbital. The UV–Vis spectrum of a metallophthalocyanine typically has a Q band near 670 nm with extinction coefficient greater than 10^5 L mol^{-1} cm^{-1}, accompanied by a series of vibrational bands. It has been evidenced (Nyokong *et al.*, 1987a; 1987b) that the Soret of MPcs is a superimposition of two bands B_1 and B_2 in the 350 nm expanse, especially in the absence of strong axial ligands (Ogunsipe and Nyokong, 2004).

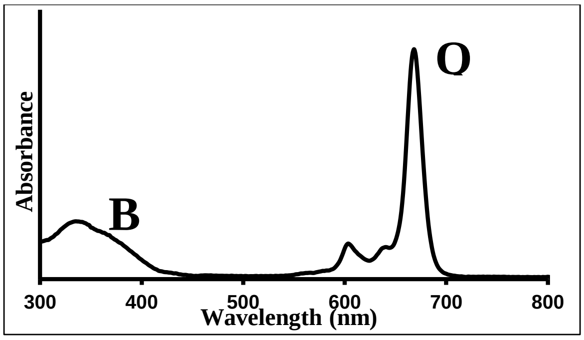

Figure 2: Ground state electronic absorption spectrum of zinc phthalocyanine (ZnPc) in DMF

A tricky situation is observed in the optical spectra of MPcs due to the presence of non-bonding electrons on the azomethine nitrogens of the macrocycle. The n orbitals are proximal in energy to the π orbitals (HOMO) and consequently, the π*←n transition is expected to be coupled with π*←π transition. Huang and co-workers (1981; 1982) proposed that the band around 605 nm in the optical spectra of MPcs could have a partial contribution from the π*←n transition. This was supported by the clear observance of the 605 nm band in the spectra of oxidised and reduced MPc ions, in which case the normal π*←π (Q and Q_{vib}) transition probabilities are drastically weakened around the 605 nm and 670 nm regions (Stillman *et al.*, 1993) but the 605 nm band does not change.

Figure 3 shows the UV–Vis spectra of ZnPc in four solvents. The dependence of Q-band position on solvent refractive index is well documented in Literature (Ogunsipe *et al.,* 2003; Ogunsipe & Nyokong, 2011). Table 1 shows that Q-band maxima of ZnPc increase with solvent refractive index.

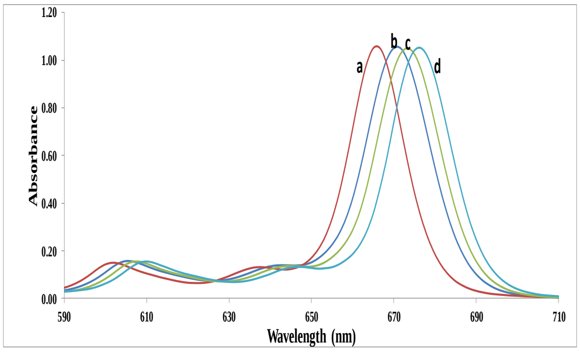

Figure 3: UV–Vis absorption spectra of ZnPc in five solvents: THF (a), DMSO (b), pyridine (c) and 1-chloronaphthalene (d). [ZnPc] ~ 4 x10^{-6} M

In Figure 4, there is a good linear correlation between the Q-band position and solvent refractive index. The departure from perfect linearity demonstrates that a combination of solvent parameter could be necessary to explain solvatochromism in MPc complexes. However, there is no clear correlation between the Q-band position and other solvent parameters like aromaticity, polarity, coordinating power, viscosity, dielectric constant, donor number and acceptor number, which further substantiates the assertion that no single solvent parameter can be used to elucidate phenomenon of solvatochromism. Figure 5 shows the absorption and fluorescence emission spectra of ZnPc in DMF. Stokes' shifts in the respective solvents range between 4 nm and 8 nm, which is usual of MPc complexes (Table 1).

Fluorescence Quenching by Benzoquinone (BQ)

Figure 6 demonstrates the fluorescence quenching of

Table 1: Spectral and fluorescence data for ZnPc in various solvents

Solvent	n	λ_Q (Abs) /nm (Log ε)	λ_Q (Ems) /nm	$\Delta\lambda_{Stokes}$ /nm	E_S /eV	Φ_F
Tetrahydrofuran (THF)	1.406	668 (5.48)	672	4	1.848	0.23
Dichloromethane*	1.424	671 (5.27)	679	8	1.829	0.08
***n*-Butylamine**	1.405	669 (5.46)	674	5	1.843	0.12
***N,N'*-Dimethylformamide (DMF)**	1.430	670 (5.37)	675	5	1.840	0.17
Chloroform*	1.446	673 (5.29)	680	7	1.826	0.07
Dimethylsulphoxide (DMSO)	1.479	672 (5.38)	679	7	1.829	0.20
Toluene*	1.497	672 (5.32)	676	4	1.837	0.07
Benzene*	1.501	672 (5.33)	676	4	1.837	0.06
Pyridine	1.509	674 (5.42)	681	7	1.824	0.20
Benzonitrile	1.528	674 (5.40)	681	7	1.824	0.13
1-Chlorophthalene	1.633	677 (5.24)	685	8	1.813	0.08

*one drop of pyridine added to effect dissolution

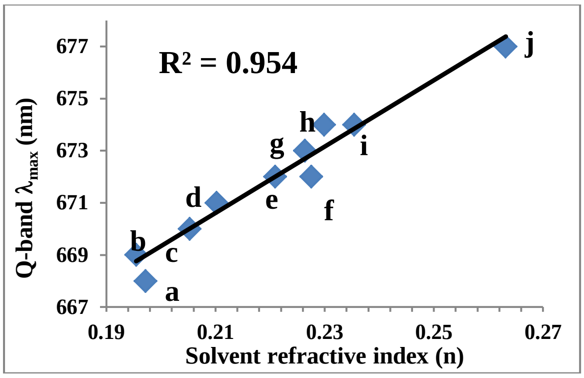

Figure 4: Variation of ZnPc Q-band maxima with solvent refractive index: (a) THF, (b) *n*-butylamine, (c) DMF, (d) dichloromethane, (e) DMSO, (f) benzene, (g) toluene, (h) pyridine, (i) benzonitrile and (j) 1-chloronaphthalene

ZnPc by BQ, in toluene. A plot of I_0/I versus [BQ] (Equation 2) gave a straight line (Figure 6 inset), which implies an exclusively dynamic quenching. In addition, there was no modification to the ZnPc absorption spectrum in the presence of BQ, ruling out the existence of static quenching. The operational quenching mechanism therefore involves a diffusion-controlled collisional interaction between ZnPc and the BQ molecules; and under this situation, *f*, the quenching efficiency (*cf*. Equation 4) is assumed to be ≅ 1. Diffusion coefficients of ZnPc (D_{ZnPc}) and BQ (D_{BQ}) (Table 2), in the various solvents were calculated using Equation 6 and these were in turn used to calculate the diffusion-controlled bimolecular rate constant (k_d) for the quenching of ZnPc by BQ. The Stern–Volmer quenching constant (K_{SV}, Table 2), determined as the slope of the plot in Figure 6 (inset), ranged between 13.2 M^{-1} (in 1-chlorophthalene) and 47.5 M^{-1} (in tetrahydrofuran).

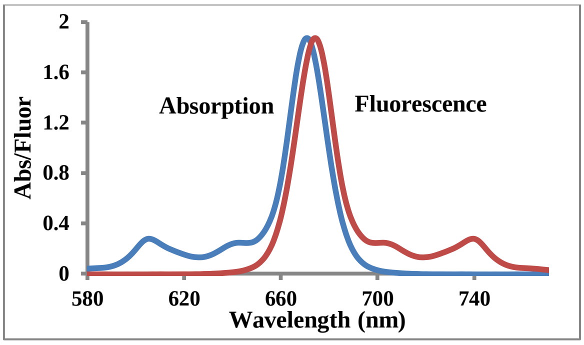

Figure 5: Corrected UV–Vis absorption and fluorescence emission spectra of ZnPc in DMF

As observed before by Ogunsipe *et al.*, (2008) and Natarajan (1984), the Stern–Volmer quenching constant (K_{SV}) decreases as the solvent viscosity is increased (Table 2). In a viscous solvent like 1-chlorophthalene, collision between the fluorophore and quencher is impeded, thereby limiting the frequency of collision. From this observation, a phenomenological relation is proposed for the variation of K_{SV} with solvent viscosity, as given in Figure 7 (Equation 8):

$$\text{Log } K_{SV} = k + \text{Log } \eta \tag{8}$$

The channel of quenching of ZnPc by BQ cannot be energy transfer (ET), since this process is endothermal. In BQ, the lower excited states $^1(n,\pi^*)$ and $^3(n,\pi^*)$ have energies 2.6 eV (Losev *et al.*, 1999) and 2.17 eV (Bunce and Hadley, 1975), respectively, while the energy of the excited singlet state of ZnPc is ~ 1.8 eV (Table 1). The most probable quenching channel is bimolecular photoinduced electron transfer (BPET) from the excited singlet state of ZnPc to BQ. It is, therefore, proposed that ZnPc quenching by BQ occurred via an ion-radical pair intermediate (Idowu *et al.*, 2007). However, the influence of solvent polarity on K_{SV} values is insignificant; it therefore follows that the ion-radical pair intermediate must be really metastable.

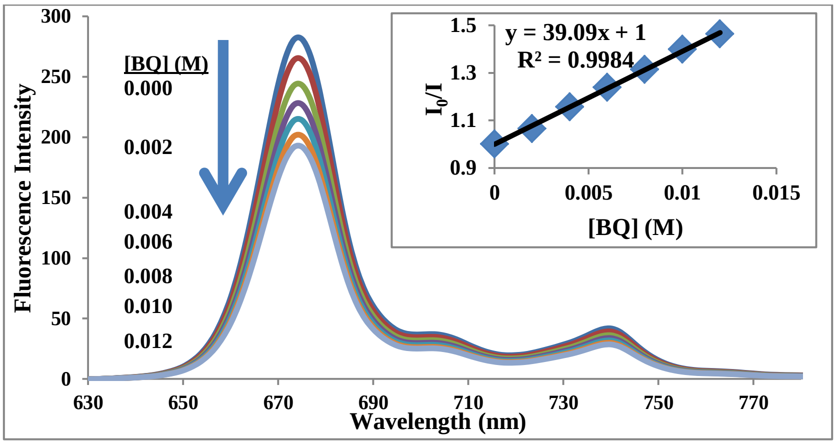

Figure 6: Fluorescence quenching of ZnPc in DMF by benzoquinone (BQ). Inset: Stern–Volmer plot for the process

Table 2: Data for ZnPc fluorescence quenching by benzoquinone in various solvents

Solvent	$10^4.\eta$ /kg m^{-1}	D_{ZnPc} /10^{-10} m^2 s^{-1}	D_{BQ} /10^{-10} m^2 s^{-1}	k_d /10^{10} M^{-1} s^{-1}	K_{SV} /M^{-1}	τ_F /ns	Φ_F
Tetrahydrofuran (THF)	4.60	6.05	14.2	1.64	47.4	2.89	0.23
Chloroform	5.42	5.36	12.6	1.45	46.1	3.17	0.07
Benzene	6.52	4.46	10.4	1.21	44.4	3.67	0.06
***N,N'*-Dimethylformamide (DMF)**	7.80	3.72	8.73	1.01	39.1	3.87	0.17
Benzonitrile	12.7	2.29	5.36	0.62	26.8	4.32	0.13
DMSO	19.9	1.46	3.42	0.40	18.3	4.61	0.20
1-Chlorophthalene	30.2	0.96	2.25	0.26	13.2	5.06	0.08

Fluorescence Lifetimes and Quantum Yields

Fluorescence lifetimes (τ_F) and quantum yields (Φ_F) of ZnPc in the various solvents are listed in Table 2. For τ_F, the values increase with solvent viscosity (Table 2). In a highly viscous solvent, translational and rotational motions in the ZnPc molecules are reduced through viscous damping by the solvent (Georghiou & Gerke, 1999). The result is a lowering of the excited singlet state decay rate constant. In a low-viscosity solvent, however, free rotational diffusions of the ZnPc result in a high rate of internal conversion. By using a pheomenological power law:

$$\tau_F = C.\eta^{\alpha}$$

where α is a measure of viscous damping by the solvent, C; a constant proportional to the activation barrier term and η; the solvent viscosity, an α value of 0.30 was obtained (Figure 8). It has been reported that the fluorescence lifetimes of some cyanine dyes follow a 1/3 power dependence of solvent viscosity (Taylor *et al.*, 1980).

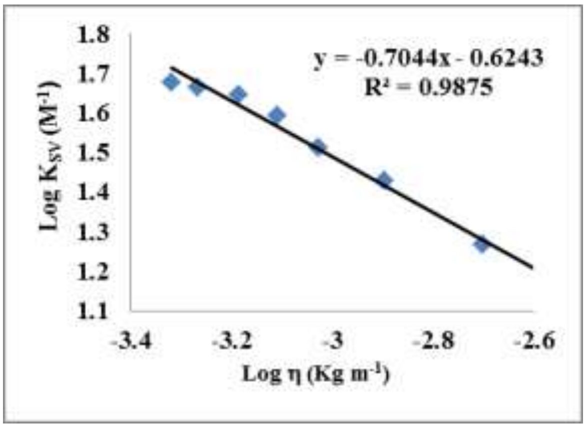

Figure 7: Dependence of Stern–Volmer′s quenching constant on solvent′s viscosity

The increase in ZnPc's Φ_F values with solvent viscosity is not well-pronounced, for example, THF is the least viscous of the solvents used yet the highest Φ_F value was recorded in this solvent. Also, Φ_F value in 1-chloronapthalene is considerably lower than what is expected on the basis of the solvent's viscosity. These observations suggest that the consideration of solvent viscosity alone is insufficient to explain the observed trend in the variation of Φ_F values.

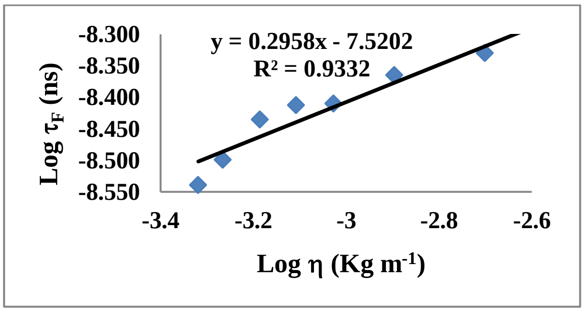

Figure 8: Dependence of ZnPc's fluorescence lifetime on solvent viscosity

Conclusion

In conclusion, this work has explored the effects of solvent viscosity on the spectral and fluorescence properties of zinc phthalocyanine (ZnPc). Photophysical parameters, such as fluorescence quantum yield and lifetime, show higher values in the more viscous solvents like DMSO and 1-chloronaphthalene. Fluorescence quenching of ZnPc by benzoquinone in the various solvents was studied, and a phenomenological relation was proposed for the variation of Stern Volmer's constant (K_{SV}) with solvent viscosity. Fluorescence lifetimes were determined from the experimental values of K_{SV}, apparent bimolecular quenching constants (k_Q) and the solvent viscosity-dependent bimolecular rate constant (k_D) for the quenching process.

Acknowledgement

Thanks to Professor Tebello Nyokong of Rhodes University for the use of her laboratory.

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