EXCITED TRIPLET STATE ENERGY OF PHTHALOCYANINES: INVESTIGATION OF THE EFFECT OF CENTRAL METAL

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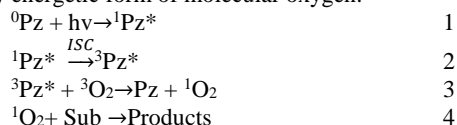*Corresponding author: bogunbayo@unilag.edu.ng

Abstract: The investigation of the effects of presence of central metal on the excited triplet state energy of octakis(pentylthio)-derivatisedphthalocyanines (**α-H₂Pc**, **β-H₂Pc**, **α-PdPc** and **β-PdPc**) is presented. Though all the molecules show high triplet quantum yield, the lack of correlation between triplet quantum yield and singlet oxygen quantum yield for the metal-free phthalocyanines (Pcs) is found to be a result of low triplet state energy of the phthalocyanines (< 94.00 KJ/mol). The palladated Pcs show high triplet state energy (> 94.00 KJ/mol) resulting in high singlet oxygen quantum yield.

**Keywords:** Triplet state, singlet state, energy, phthalocyanines, central metal

Introduction

Photo-oxidation reactions have been used for the decontamination of organic pollutants in natural waters (Machado *et al.*, 2003). Direct and photosensitized reactions are the two major types of photochemical reactions that have been deployed in photo-assisted chemical changes. While the former is applicable where the direct absorptions of photons are possible and can produce the desired product(s), the latter is used where direct absorption of the photons of the required wavelength is either impossible or produces different products. This is the case when the substrate molecule is transparent at the required wavelength. When it is impossible for the substrate molecule to directly absorb the photon of the energy required to initiate the reaction, energy transfer by induction is a plausible alternative. This is photosensitization. A molecule that absorbs at the desired wavelength is excited and this molecule transfers the energy to the substrate molecule, which uses the energy for its own excitation. This mode of excitation has been used for many reactions of which photosensitized oxidation reaction is a prominent example.

In photosensitized oxidation reactions, direct photons are absorbed by photosensitizer molecules (eqn 1), which go from its singlet ground state (^0Pz) to its triplet excited state ($^3Pz^*$) through its singlet excited state $^1Pz^*$ (eqn 2). This in turn transfers the energy to ground state molecular oxygen ($^3O_2$) (eqn 3). The triplet ground state molecular oxygen absorbs the energy for its excitation to its singlet excited state ($^1O_2$), a very energetic form of molecular oxygen.

$$^0Pz + h\nu \rightarrow {}^1Pz^* \qquad 1$$
$$^1Pz^* \xrightarrow{ISC} {}^3Pz^* \qquad 2$$
$$^3Pz^* + {}^3O_2 \rightarrow Pz + {}^1O_2 \qquad 3$$
$$^1O_2 + Sub \rightarrow Products \qquad 4$$

More often this energetic singlet oxygen either attack the substrate to form the oxidation product (eqn 4) in a type II reaction but a type I reaction pathway where the triplet state photosensitizer radical directly react with the substrate (eqn 5) are also infrequently encountered as a pathway. The efficacy of energy transfer from sensitizers to ground state molecular oxygen upon which the success of this photo-driven reaction lies depends on the triplet quantum yield, triplet state lifetime and triplet state energy of the sensitizer.

$$^3Pz^* + Sub \rightarrow Products \qquad 5$$
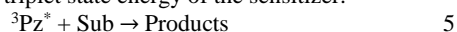
A lot of research efforts have been directed towards investigation of these factors in phthalocyanines, a versatile molecular dye that has been investigated as photosensitizers (Iliev, 2002; Marais *et al.*, 2007; Ogunbayo and Nyokong, 2010; Ozoemena *et al.*, 2001; Pepe *et al.*, 2005; Xiong *et al.*, 2005). However, these efforts have been concentrated on the first two factors. Triplet state energy, which is also as crucial, if not more crucial, than the first two has, to the best of our knowledge, not undergone systematic investigation vis-à-vis factors that may affects its magnitude. Its value must reach the threshold of 94 KJ/mol required to excite ground state molecular oxygen for effective performance.

This effort was inspired by our previous work where there was no correlation between high triplet quantum yield and lifetime on one hand and singlet oxygen quantum yield on the other (Ogunbayo and Nyokong, 2010). This suggested the need for a systematic investigation of those parameters such as presence of central metals and substituents position on the magnitude of the energy of the triplet state.

This work investigated the effect of position of substitution and metallation of metal-freeoctakis(pentylthio)phthalocyanines on the triplet state energy and S_1-T_1 energy gap and its effect on the previously reported incidental photophysical parameters. We report thephysicochemical behavior of α-octakis(pentylthio)-derivatised H₂Pc whose synthesis has previously been reported (Ogunbayo and Nyokong, 2009). The previously unreported photochemical properties are needed to fully interpret the energy states data. The synthesis and photochemical properties of the three other molecules namely: β-octakis(pentylthio)-derivatised H₂Pc, α-octakis(pentylthio)-derivatised PdPc and β-octakis(pentylthio)-derivatised PdPc have been reported before (Ogunbayo and Nyokong, 2010; Ogunbayo and Nyokong, 2009).

Experimental

Materials and equipment

1-Chloronaphthalene (1-CNL) was purchased from Sigma-Aldrich. α-octakis(pentylthio)-derivatised H₂Pc(**α-H₂Pc**) β-octakis(pentylthio)-derivatised H₂Pc(**β-H₂Pc**), α-octakis(pentylthio)-derivatisedPdPc(**α-PdPc**) and β-octakis(pentylthio)-derivatisedPdPc(**β-PdPc**) (**Fig. 1**) were synthesized and characterized, as reported in literature (Ogunbayo and Nyokong, 2009; Ogunbayo and Nyokong, 2010).
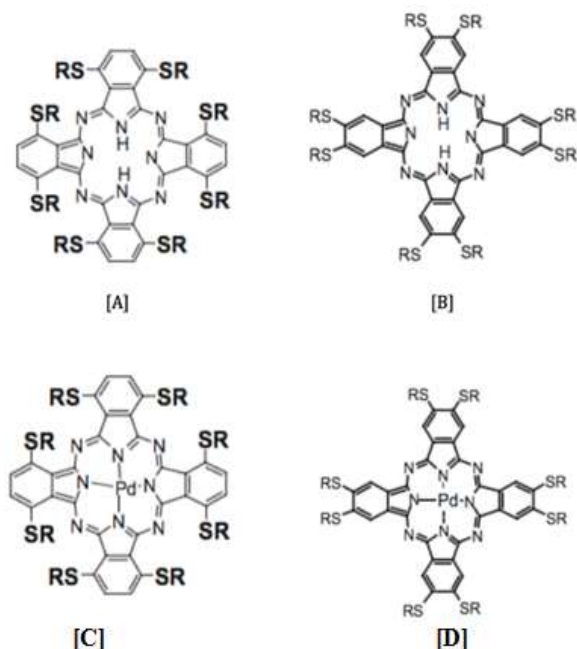
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Fig. 1: Shaibu Phthalocyanines: (A) α-H₂Pc, (B) β-H₂Pc (C) α-PdPc (D) β-PdPc [R=C₅H₁₁]

Equipment

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system. Triplet state energies were determined through the determination of triplet state quenching by molecular oxygen at different oxygen concentration. Triplet lifetime was determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

Photochemical study of α-H₂Pc was performed using General Electric Quartz line lamp (300W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. For singlet oxygen determination the irradiation was carried out with a tungsten lamp (100W, 30V) perpendicular to the direction of measurement. A water filter and an interference filter (of a wavelength close to the wavelength absorption maximum of the sensitizer) were placed in the light beam path of the tungsten lamp. The light intensity was measured with a power meter. The decay of DPBF absorption at 421 nm was detected after each cycle. An interference filter (Intor, appropriate wavelength with a band width of 40 nm) was additionally placed in the light path before the sample. UV/Vis and fluorescence spectra were recorded on a Varian Cary 500 UV/Vis/NIR and Varian Eclipse spectrophotometer, respectively,
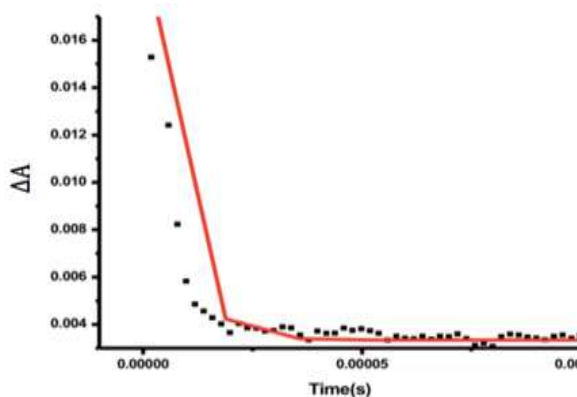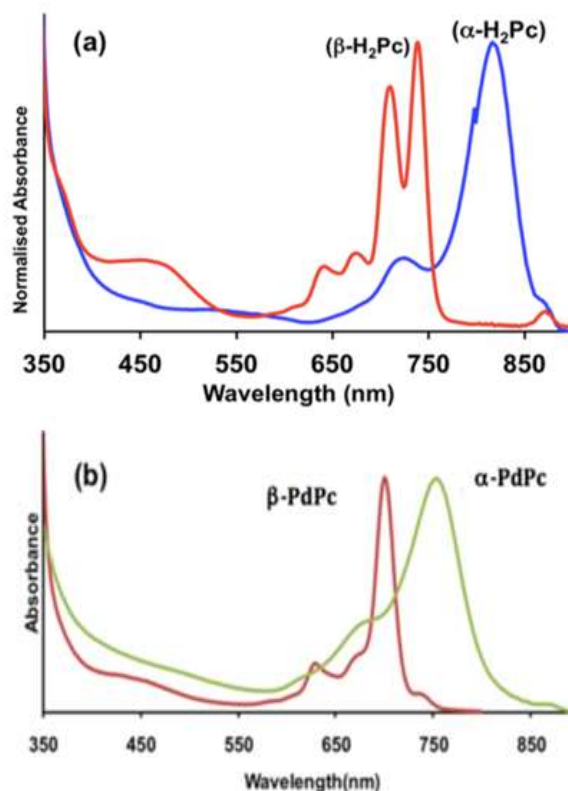

Fig. 2: Triplet decay curve for α-H₂Pc in 1-CNP

Fig. 3: Electronic absorption spectra of (a) α-H₂Pc and β-H₂Pc 1-CNP (b) α-PdPc and β-PdPc 1-CNP. Concentration ~ 1 x 10⁻⁵M

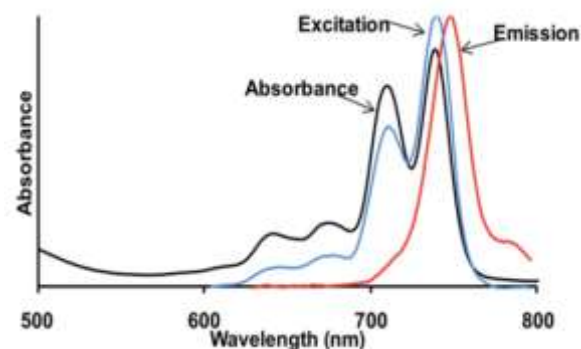**Fig. 4: Estimation of Excited Singlet state Energy: Absorption, Emission and excitation spectra of β-H₂Pc, excitation wavelength =615 nm in 1-CNP**

Singlet oxygen quantum yields

The singlet oxygen quantum yield ($\mathbf{\Phi_\Delta}$) determination of α-H₂Pc was carried out using solutions containing DPBF (90 μM) and the Pc (absorbance ~ 0.2 at the irradiation wavelength). A solution of α-H₂Pc (2 ml) was filled in a quartz cell (1 x 1 cm) and saturated with oxygen. The cell was set into a UV-Vis spectrometer. The irradiation was done using set-up described above. The absorbance measured was corrected by the absorbance of sensitizer at the respective detection wavelength.

The DPBF quantum yield Φ_{DPBF} for each irradiation cycle was calculated using **eqn 6** and the determined exctinction coefficient of DPBF in 1-chloronaphthalene (ε_{CNP}

$$\epsilon_{1-CNP} = 20287 \text{ Ml}^{-1} \text{ cm}^{-1}).$$

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$$\Phi_{DPBF} = \frac{(C_0 - C_t)V_R}{I_{abs}.t} \qquad 6$$

Where: C_0 and C_t are the DPBF concentrations prior to and after irradiation, respectively; V_R is the reaction is the reaction volume; t is the irradiation time per cycle and I_{abs} is defined as **eqn 7**.

$$I_{abs} = \frac{\alpha.A.I}{N_A} \qquad 7$$

Where: $\alpha = 1 - 10^{-A(\lambda)}$; $A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength, A is the irradiated area ($3.142\ cm^2$), I is the intensity of light (10^{15} photons cm^{-2} s^{-1}) and N_A is Avogadro's constant. The singlet oxygen quantum yields Φ_Δ were calculated using **eqn. 8** (Foote, 1979).

$$\frac{1}{\Phi_{DPBF}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi\Delta}.\frac{k_d}{k_a}.\frac{1}{[DPBF]} \qquad 8$$

Where: k_d is the decay constant of singlet oxygen in respective solvent and k_a is the rate constant of the reaction of DPBF with $O_2(^1\Delta_g)$. The value $1/\Phi_\Delta$ is the intercept obtain from the plot of $1/\Phi_{DPBF}$ versus $1/DPBF$. The values of the fraction of the excited triplet state quenched by ground state molecular oxygen (S_Δ) were determined using **eqn 9**:

$$S_\Delta = \frac{\Phi_\Delta}{\Phi_T} \qquad 9$$

This is the efficiency of singlet oxygen generation by the triplet state.

Results and Discussion

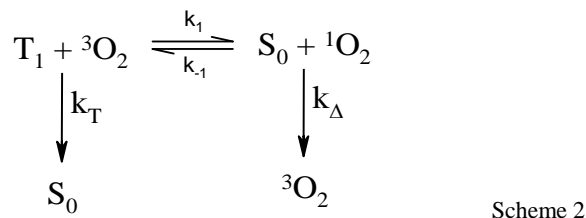### *Triplet quantum yield and lifetime of α-H₂Pc and other Pcs*

The triplet quantum yield (Φ_T) for **α-H₂Pc** is found to be 0.33, so the triplet quantum yields of the molecules deployed in this work range from 0.33 for **α-H₂Pc** to 0.47 for **β-PdPc** (Ogunbayo and Nyokong, 2009; Ogunbayo and Nyokong (2011). As explained in previous work, the higher values for the **α-PdPc** and **β-PdPc** are easily attributed to the presence of palladium metal, leading to enhanced intersystem crossing from heavy atom effect. The triplet lifetime (τ) for **β-H₂Pc** was 62 µs which is longer than for **α-H₂Pc** (55) **(Fig. 2)** and both were higher than what obtained for **α-PdPc** (13 µs) and **β-PdPc** (15 µs), (Table 1) which host palladium in their cavities. The presence of palladium, an open-shell metal, might quench the excited triplet state via intramolecular charge transfer, and subsequently reduce the triplet lifetime. Again, palladium through spin-orbit coupling, imparts some singlet character on the excited triplet state. As a result, the probability of $T_1 \rightarrow S_0$ transition is increased, and the triplet lifetime shortened. The peripherally substituted phthalocyanines have higher yield and lifetime compared to the non-peripherally substituted.

Triplet state quenching by O₂: Triplet and singlet state energy determination

Ground state molecular oxygen is known to quench the excited triplet states of photosensitizers with a high measure of efficiency. The thrust for the quenching is provided by the spin allowed-ness of the triplet sensitizer-triplet oxygen energy transfer. Such quenching reaction results in the formation of singlet oxygen (Scheme 1)

$$T_1 + {}^3O_2 \longrightarrow S_0 + {}^1O_2 \qquad \text{Scheme 1}$$
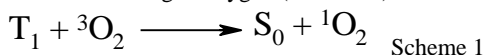
The spontaneous decay of **α-H₂Pc**, **β-H₂Pc**, **α-PdPc** and **β-PdPc** triplet state in the absence of oxygen in 1-CNP followed mono-exponential first order kinetics, and the triplet decay rate constant ($k_T = 1/\tau_T$) varied between $1.6 \times 10^4\ s^{-1}$ (for **β-H₂Pc**) and $7.6 \times 10^4\ s^{-1}$ (for **α-PdPc**) (Table 2). In the presence of oxygen (in air-saturated or oxygen-saturated solutions) however, the observed rate constants ($k_{air} = 1/\tau_{air}$ and $k_{Ox} = 1/\tau_{Ox}$) are much higher, and the kinetics are bi-exponential. In the air-saturated solution the rate constant varied between $1.13 \times 10^5\ s^{-1}$ (for **β-PdPc**) and $3.16 \times 10^5\ s^{-1}$ (for **β-PdPc**) while in oxygen-saturated solution the range was between $2.07 \times 10^5\ s^{-1}$ (for **β-PdPc**) and $3.55 \times 10^5\ s^{-1}$ (for **α-PdPc**) which indicates the establishment of an energy transfer equilibrium (Firey *et al*., 1988; Foley *et al*., 1997) as shown in **Scheme 2**:

$$T_1 + {}^3O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_0 + {}^1O_2$$
$$\downarrow k_T \qquad\qquad\qquad \downarrow k_\Delta$$
$$S_0 \qquad\qquad\qquad {}^3O_2 \qquad\qquad \text{Scheme 2}$$

The mono-exponential decay of oxygen-free photosensitizer solution corroborates the existence of the above energy transfer equilibrium. An in-depth analysis of the triplet quenching by oxygen under the bi-exponential kinetics allows for the determination of the equilibrium constant ($K_Q = k_1/k_{-1}$) and subsequently the Pc triplet state energy (E_T).

K_Q values were determined by varying the concentration of oxygen (triplet quencher) and keeping the Pc triplet concentration constant. For each Pc species, three different solutions, with varying oxygen concentrations: 0 M (argon-saturated solution), 4.8×10^{-4} M (air-saturated solution (Lang, 1992; Solubility Data Series, 1981) and 1.4×10^{-3} M (oxygen-saturated solution (Lang, 1992; Solubility Data Series, 1981) are employed. The K_q may be determined from triplet state absorption measurements using **Eq. 11:**

$$\frac{A_0 - A_{eq}}{A_{eq}} = K_Q \frac{[^3O_2]}{[Pc]} \qquad 11$$

Where: A_0 is the initial triplet state absorbance and A_{eq}, the equilibrium triplet state absorbance extrapolated to t= 0. The values of K_Q can then be used to evaluate triplet state energies (E_T, Table 2) using **Eq. 12** (Firey *et al*., 1988; Foley *et al*., 1997):

$$E_T = RT.ln\ (9K_Q) + E_\Delta \qquad 12$$

Where: E_Δ is the singlet oxygen energy (ca 94 kJ mol^{-1}), and the quotient 9 emanates from the spin-statistical factor.

In Table 2, E_T values for **α-H₂Pc**, **β-H₂Pc**, **α-PdPc** and **β-PdPc** are listed. The values 96.20 and 97.07 kJ mol^{-1} for **α-PdPc** and **β-PdPc,** respectively are higher than E_Δ, hence an efficient energy transfer from these complexes to ground oxygen to form singlet oxygen, is expected. However, the E_T value for **α-H₂Pc** and **β-H₂Pc** (89.55 and 90.0 kJ mol^{-1}, respectively) is below the singlet oxygen energy; hence an inefficient energy transfer to ground state oxygen is expected. The singlet state energy of the molecules were calculated from the spectroscopic data using eqn 13 (Rihter *et al*., 1990);

$$E_s = \frac{1}{2}[E_{max}^{abs} + E_{max}^{Emis}] \qquad 13$$

Where: E_{max}^{abs} is the energy calculated from the maximum wavelength of absorption (Fig. 3) and E_{max}^{Emis} is the energy calculated from the maximum wavelength of emission (Fig. 4). This gives an S_1-T_1 energy gap of 68.15, 71.96, 67.89 and
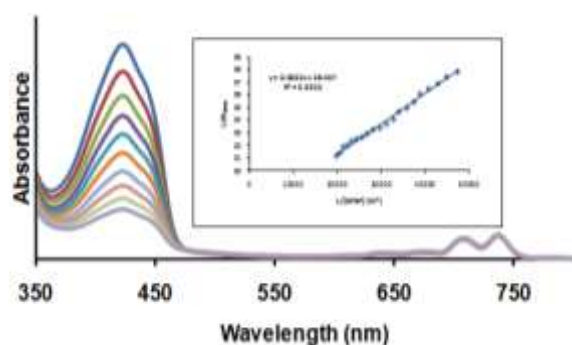
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69.12 kJ mol^{-1} for **α-H₂Pc, β-H₂Pc, α-PdPc** and **β-PdPc,** respectively (Table 2). It was expected that there might be a correlation between triplet quantum yield and S_1-T_1 energy gap of the molecules. The expected correlation does not exist.

Table 1: Photophysical and photochemical properties of the Pcs in 1-CNP

Pcs	Φ_T	τ_T /μs	K_T /10^{-3}s^{-1}	Φ_Δ	S_Δ
α-H₂Pc	0.33	55	18	0.03	<0.1
β-H₂Pc	0.39[5]	62[5]	16	0.04[5]	0.1
α-PdPc	0.42[10]	13[10]	76	0.39[10]	0.79
β-PdPc	0.47[5]	15[5]	66	0.42[5]	0.89

Table 2: Absorption and emission properties and first excited singlet and triplet state energy of the Pcs in CNP

Pcs	λ_{Abs} /nm	λ_{Em} /nm	λ_{Ex} /nm	E_S /kJ mol^{-1}	E_S /kJ mol^{-1}	E_T /kJ mol^{-1}	S_1-T_1 /kJ mol^{-1}
α-H₂Pc	813	708	705	158.25	158.25	89.55	68.15
β-H₂Pc	707,736	745	737	162.00	162.00	90.03	71.96
α-PdPc	757	701	700	164.00	164.00	96.20	67.89
β-PdPc	698	745	738	166.19	166.19	97.07	69.12

Fig. 5: Typical spectrum for the determination of singlet oxygen quantum yields. This determination was for compound β-H₂Pc in CNP. Insert: Stern-Volmer Plot

Dependence of singlet oxygen quantum yield on triplet state energy

Singlet oxygen quantum yield (Φ_Δ) was determined in 1-CNL using DPBF as a chemical quencher (Fig. 5). Many factors could affect the magnitude of Φ_Δ values, and these include: triplet energy, population and lifetime; efficiency of the energy transfer from the Pc triplet excited state to ground state oxygen; and solvent considerations. In the case of this unmetalled Pc there is lack of correlation between its Φ_Δ value of 0.03 and Φ_T value of 0.33 in Table 1, as expected, but its metalled analogue (**α-PdPc**) earlier reported showed a relatively high singlet quantum yield of 0.39, consistent with expectation based on its high triplet state of 0.39 (Ogunbayo and Nyokong, 2011). In another earlier investigation, this same comparative trend was also observed for the peripherally substituted analogues where the high triplet quantum yield of 0.39 **β-H₂Pc** showed a paltry 0.04 singlet oxygen quantum yield while the palladated, **β-PdPc** with a triplet Φ_T value of 0.47 (Table 1) gave a correspondingly high Φ_Δ value of 0.42 (Ogunbayo and Nyokong, 2010). The efficiency of singlet oxygen generation (**S_Δ**) was much higher for the metalled molecules at 0.79 and 0.89 while it is extremely low, almost non-existent, for the metal-free analogue (Table 1). This lack of correlation between triplet quantum yields and singlet oxygen quantum yield for unmetallated phthalocyanines, in spite their high triplet life time, compared to the palladated ones, suggests that, while heavy atoms may be important to the improvement of triplet quantum yield, the presence of metal is desirable because of their impact on the triplet state energy.

Conclusion

We have been able to determine the excited triplet and singlet state energy of both α and β-substituted meta-free and palladium octakis(pentylthio)phthalocyanines. In spite of high triplet quantum yield demonstrated by all the molecules, due to heavy atom effect, the metal-free Pcs still showed low singlet oxygen quantum yield. Though, the presence of metal in the Pc cavity gave rise to a little enhancement in the triplet quantum yield but drastically reduced the triplet lifetime of the molecules. The variation in the singlet oxygen quantum yield between the metallated and the metal-free Pcs was too substantial to be accounted for through this. Triplet state energy were found to be higher for the metallated Pcs with β-substituted having higher energy. It was the proportionate effect of this that was noticed in the trend taken by the singlet oxygen quantum yield. More work is still required to ascertain the reason behind this behavior.

Conflict of Interest

Authors declare that there is no conflict of interest.

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