Femtosecond to Microsecond Excited State Dynamics of a Novel Zinc Phthalocyanine Using Transient Absorption Spectroscopy

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The photo physics of a novel Zinc Phthalocyanine: ImZnPc [3,9,17,23-tetraakis(4-(1-hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)-8H,9H-Zinc(II) phthalocyanine; C140H114N16Zn] has been investigated using transient absorption spectroscopy (TAS) with femtosecond to nanosecond laser pulses. Over the years ZnPc has showed potential application in the field of photodynamic therapy (PDT).\textsuperscript{1-3} In PDT, a photosensitizer (PS) is administered in a tissue which undergoes photochemical reaction when activated by visible light and generates cytotoxic species in the presence of oxygen.\textsuperscript{4-8} An ideal PS has: (i) strong absorption peak in the spectral region 650–800 nm, (ii) long lived triplet state leading to good production of cytotoxic species upon irradiation and (iii) low dark toxicity for minimal side-effects.\textsuperscript{9} Phthalocyanines (Pc) are second generation photosensitizers (PS) which suffices all the above criteria making them potential candidate for PDT treatment.\textsuperscript{10} These conditions can be further optimized by tailoring the Pc moiety with appropriate peripheral substituents and central metal ion. Our molecule, ImZnPc has zinc as the central metal attached to the Pc moiety with phenanthro[9,10-d]imidazole group attached to all the four pyrrolic branches via phenyl bridge. As a result, ImZnPc has better solubility in a number of organic solvents over ZnPc with strong absorption around 700 nm. The molecule also showed efficient intersystem crossing (ISC) from singlet to triplet state with long triplet lifetime in microseconds.

\textbf{EXPERIMENTAL DETAILS:}

0.5 mM solution of ImZnPc [C\textsubscript{140}H\textsubscript{114}N\textsubscript{16}Zn] in dichloromethane (DCM) was prepared for all experiments. Cary 100 UV–vis spectrophotometer (Varian) was used to record the absorption studies. Fluorolog-3 spectrofluorometer (Spex model, JobinYvon) was used to record the steady-state fluorescence spectra at the excitation wavelength ($\lambda_{ex}$) = 400 nm. Fluorescence lifetimes were recorded using a time–correlated single-photon counting (TCSPC) spectrometer -5000, IBH. The transient absorption studies (TAS) were carried out with 70 fs, 1 kHz rep. rate pulses and 8 ns, 20 Hz rep. rate pulses. For the fs-TAS experiment, excitation (pump) wavelength was achieved with second harmonic (400 nm) of the laser pulse with a BIBO crystal whereas the probe pulse is a white light continuum (WLC, 440-820 nm). The cuvette length used was 0.1 cm with pump energy~200 nJ. For ns-TAS, the solution was excited (pump) by the third harmonic (355 nm) of the laser and probed with WLC. A perpendicular configuration was chosen for the excitation of the sample. Quartz cuvette with a path length of 1 cm was used. A spectrometer from Applied Photophysics (model LKS.60) was used for detection. Data fitting was done using multiexponential decay equation:

$$\Delta A(\lambda, t) = A_0 + A_1(\lambda)e^{\frac{t}{\tau_1}} + \cdots + A_n(\lambda)e^{\frac{t}{\tau_n}}$$

Difference absorbance, $\Delta A(\lambda, t)$: $A_{\text{pump on}}- A_{\text{pump off}}$ for a particular wavelength $\lambda$ at delay time $t$; $\tau_{1-\text{me}}$ fitted lifetimes.
RESULTS AND DISCUSSION:

Figure 1 (a) Molecular structure. (b) Absorption and emission spectra. (c) fs-TAS spectra. (d) fs-TAS kinetics at TA maxima 540 nm and GSB minima at 650 nm. (e) ns-TAS spectra. (f) ns-TAS kinetics at TA maxima 480 nm.

ImZnPc [molecular structure figure 1 (a)] red shifts the absorption band with Q-band peaks at 648 nm and 704 nm and a broad Soret (B) band peak at 349 nm. On exciting the molecule at B band, we obtained emission peak at 704 nm which suffices the rule of mirror symmetry showing fluorescence lifetimes of 2.78 ns [Figure 1(b)]. The excited state dynamics studies with 70 fs pulses, recorded for 0–2 ns delay showed a broad transient absorption (TA) signal [ΔA>0, figure 1(c)] being overlapped with the ground state bleach, GSB [ΔA<0] signal. This is typical to Pcs showing TA contribution due to singlet-singlet and singlet-triplet transitions. The molecule rapidly relaxes from higher excited state (Sn2) to lower excited state (S1) but the blue shift in the GSB signal show that it doesn’t completely relax back to its ground state (S0) over 2 ns. This might indicate to intersystem crossing (ISC) of ImZnPc from S1 to T1 state. The kinetics at TA maxima 540 nm and GSB minima at 650 nm showed two lifetimes in the range: 9.3–13.3 ps (τ1, S2→S1*) and 577.2–478.5 ps (τ2, S1→T1/S0*). For the triplet dynamics, the TA peak due to triplet transition, Tn→T1 was found to be at 480 nm and fitted data revealed one triplet lifetime: τT as 1.4 µs [Figure 1(e, f)].

CONCLUSION:

The photophysics of a phenanthro [9,10-d] imidazole substituted zinc phthalocyanine, ImZnPc, was studied for its potential application in photodynamic therapy (PDT). Studies have shown that ImZnPc has strong absorption peaks between 600 nm–800 nm with fluorescence lifetime of 2.78 ns (at 704 nm). Upon excitation in the B-band, the molecule reaches singlet excited state S2 which relaxes to vibrationally hot S1 state within ~13 ps. Following vibrational relaxation of S1 state, some of the molecule goes to the triplet state (T1) via excited state charge transfer (~250 ps) while some relaxes non-radiatively to the ground state S0. The triplet state species absorbs energy to further excite them to higher triplet state whose lifetime is long lived ~1.4 µs. The above studies indicate ImZnPc as a good photosensitizer for PDT.
REFERENCES:


