Strong two-photon absorption properties and ultrafast pump-probe studies of novel porphyrin derivatives

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A B S T R A C T

Herein we report strong two-photon absorption (2PA) properties and ultrafast pump-probe dynamics of five novel porphyrin derivatives. The investigated molecules were β-octamethoxyporphyrin (H_2OMP), its Zn(II)-derivative (ZnOMP) and 3,8,13,18-tetrachloro-2,7,12,17-tetramethoxyporphyrin (H_2TCTMP), and its Zn(II)- and Ni(II)-derivatives i.e. ZnTCTMP and NiTCTMP respectively. NLO coefficients were obtained from the Z-scan measurements using ~2 ps pulses at 800 nm. Open aperture data confirmed 2PA whereas closed aperture data indicated positive nonlinearity. 2PA cross-sections in the range of 10^3–10^4 GM were recorded. Femtosecond pump-probe results at 600 nm of above compounds demonstrated triple exponential decay pattern indicating three lifetimes arising from high lying excited states.

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1. Introduction

Porphyrins are unique in nature because of its biological importance and have rich photophysical properties arise from their 18π-electron conjugated aromatic system. Also, properties of this macrocycle can be easily manipulated via substituting its peripheral meso- and/or β-positions [1]. Thus porphyrin research not only limited to fascinated synthetic interest but also to various other discipline like physics, biology, engineering, materials and theoretical studies. In the last two decades several porphyrins/porphyrin derivatives, inclusive of a few from our own research group, have been designed and synthesized to study their utility as nonlinear optical (NLO) material [2–27] using ns, ps, and fs pulses. Porphyrin based oligomers, in association with other chromophores and polymers derived from porphyrins demonstrate interesting nonlinear optical behavior and hence hold great promise as second and third order NLO materials, as broadband optical limiters, in optical switching, and in two-photon photodynamic therapy (PDT) [2–7]. Drouet et al. [19] recently reported new Zn(II) tetraphenylporphyrin derivatives functionalized with electron-rich d^6-transition metal alkynyl complexes at periphery. They retrieved strong 2PA cross-sections (σ_2) of 10^3–10^4 GM for their molecules. Wang et al. [20] using nanosecond (ns) and picosecond (ps) pulses investigated a novel porphyrin derivative bearing one D-π-A-π-D pyrimidine

chromophore at the periphery. They demonstrated that appropriate coupling of the chromophore to a porphyrin moiety with reverse saturable absorption was an efficient way for preparing molecules with superior nonlinearities. Senge's group has investigated several push–pull types of porphyrins [10–13] using ns laser pulses. Drobizhev et al. [22] studied double stranded conjugated porphyrin arrays and reported 10^3–10^4 GM cross-sections. Collini et al. [23] reported strong 2PA cross-section of ~4000 GM measured by Z-scan technique for a push–pull A-π-D Zn(II) porphyrin complex di-substituted in the meso position with strong donor and acceptor moieties. Dogan et al. [9] studied nonlinear absorption behavior in 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrins with different central metal ions (Zn^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+}) using open aperture Z-scan technique with 65 ps/4 ns excitation.

The basis of design in most of these systems for better NLO response is to have suitable donor and acceptor functionalities at the periphery of aromatic porphyrin ring or extended multi-porphyrinic systems. In this regard, monomeric porphyrin units were also studied as either reference for designing more accomplished systems or as standalone systems to gain understanding about their NLO response. The presence of multiple donor and acceptor functional groups at the porphyrin periphery is achieved either through direct link or through phenyl bridge or a combination of both. Furthermore, it is well known that direct linkage of functional groups at the porphyrin periphery imparts a greater influence on the electronic properties of macrocyclic ring. In this regard, β-octa substituted porphyrins which could be synthesized quite conveniently, could possibly, emerge as attractive target systems. However, porphyrins
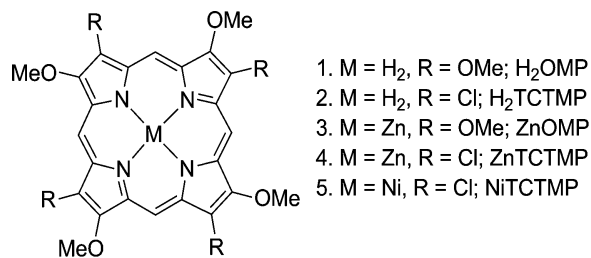
with other than alkyl group at β-position are quite uncommon [28–33] and β-substituted pyrrole containing both electron donating and electron withdrawing groups are rare [34–38]. Toward this, our recently reported symmetrical type I 3,8,13,18-tetrachloro-2,7,12,17-tetramethoxyporphyrin (H$_2$TCTMP) appears a very promising candidate [39,40]. In particular, the uniqueness of this molecule arises from the presence of orderly arrangement of pyrrole molecules in a cyclic fashion, where each pyrrole moiety is endowed with an electron donating methoxy- and an electron withdrawing chloro-group on its adjacent β-positions. Furthermore introduction of a metal ion in the core of porphyrin modifies the absorption/emission and NLO properties. Such novel molecules are essential in identifying potential contenders with strong nonlinearities and ultrafast electronic response for device applications in the fields of photonics and solar cells, respectively. Many of the earlier studies focused either on NLO properties or excited state dynamics. In this Letter, we present results from both NLO and pump-probe studies of H$_2$TCTMP and its Zn(II)-and Ni(II)-derivatives, i.e. ZnTCTMP and NiTCTMP, respectively. We have also investigated the NLO properties of analogous β-octamethoxyporphyrin (H$_2$OMP) and its Zn(II)-derivative (ZnOMP). The data obtained from such studies will help in designing superior molecules of interest.

2. Experimental details

The synthesis and characterization of all porphyrins and their Ni(II) and Zn(II) complexes were recently reported by us [39–41]. Z-scan measurements [42–47] were performed using ~2 ps [FW(1/e^2)M], 800 nm pulses with a repetition rate of 1 kHz delivered by an amplified Ti:sapphire system (Legend, Coherent). The amplifier was seeded with pulses of duration ~15 fs (~50–60 nm, FWHM) from a tunable laser oscillator (Micra, Coherent). The transform limited nature of amplified pulses was confirmed from the product of bandwidth and pulse duration measurements performed using external auto-correlation experiments. A quartz cuvette (1-mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist (2ω_0) at focal plane was estimated to be 60 ± 4 μm (FW(1/e^2)M) with a corresponding Rayleigh range (Z_R) of 3.5 ± 0.4 mm ensuring the validity of thin sample approximation. The Z-scan was performed over a distance of 10 Z_R on a high-resolution linear translation stage (Newport ILS250PP) by recording the sample transmittance. A LABVIEW program was designed and used for automating the data acquisition of the Z-scan experiments. Typical energies in the range of 1–5 μJ, corresponding to peak intensities in the range of 70–200 GW/cm^2, were used for all the experiments. The closed aperture scans were performed at peak intensities <50 GW/cm^2 to avoid contribution from higher order nonlinearities. For degenerate pump probe measurements the amplified pulses (~40 fs) pumped an OPA (TOPAS-C; Light Conversion) delivering 600 nm pulses with duration of ~70 fs. The pump to probe intensity ratio was ensured to be >10:1. The probe beam was delayed using an optical delay line and the change in probe transmittance was monitored using the combination of a sensitive silicon photodiode and lock-in amplifier (Signal Recovery 7265). The pump pulses were chopped at a frequency of 109 Hz which was the reference for the lock-in amplifier. The samples were placed in a 5-mm quartz cuvette to achieve better signal-to-noise ratio. Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba JobinYvon IBH). PicoBrite diode laser source was used as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector. The pulse repetition rate of the laser source was 10 MHz. The width of the instrument response
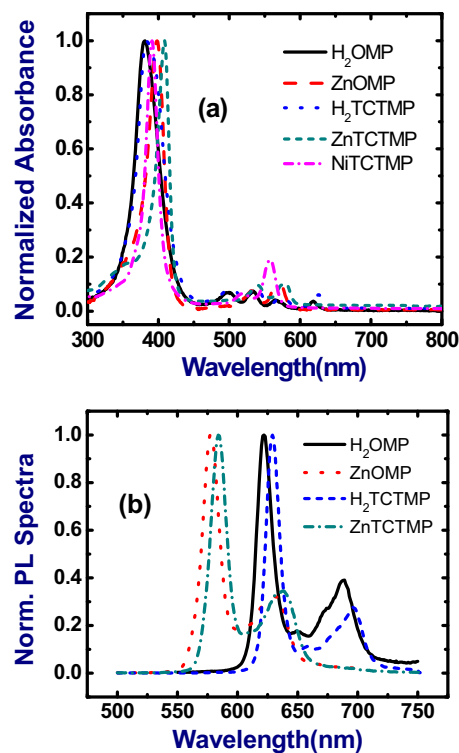
function, which was limited by the FWHM of the exciting pulse, was ~55 ps. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time resolved emission decay profiles were collected at steady state emission spectrum maxima. Decay curves were analyzed by non-linear least-squares iteration procedure using IBH DAS6 (version 2.2) decay analysis software. The quality of the fit was assessed by inspection of the χ^2 values and the distribution of the residuals.

3. Results and discussion

The structures of molecules investigated in this study are presented in Figure 1. The UV–visible spectral data for compounds H$_2$OMP, ZnOMP, H$_2$TCTMP, ZnTCTMP and NiTCTMP are presented in Figure 2a [40]. Freebase porphyrin H$_2$OMP and H$_2$TCTMP displayed strong near-UV Soret absorption bands at 381 nm and 383 nm, respectively, accompanied with four weaker Q-bands in the visible region, whereas the corresponding Zn(II)-complexes of H$_2$OMP and H$_2$TCTMP and NiTCTMP derivatives possessed strong Soret absorption bands at 403 nm, 409 nm and 391 nm, respectively, with two characteristic weaker Q-bands in the visible

Figure 1. Structures of the β-substituted porphyrins used in present study.

1. M = H$_2$, R = OMe; H$_2$OMP
2. M = H$_2$, R = Cl; H$_2$TCTMP
3. M = Zn, R = OMe; ZnOMP
4. M = Zn, R = Cl; ZnTCTMP
5. M = Ni, R = Cl; NiTCTMP

Figure 2. (a) UV–vis spectra of the studied porphyrins (in chloroform) demonstrating strong absorbance near 400 nm. (b) Emission spectra of H$_2$OMP, ZnOMP, H$_2$TCTMP, ZnTCTMP in chloroform. NiTCTMP did not show any detectable fluorescence.
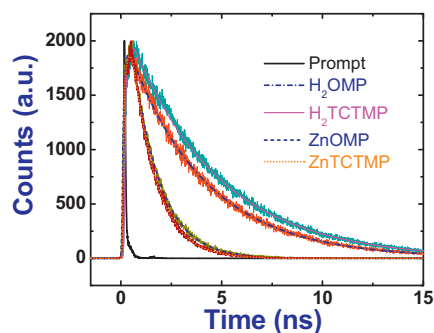
Figure 3. Fluorescence decay profile of H_2OMP, H_2TCTMP and their Zn(II) derivatives in chloroform.

spectral region. The presence of metal ion (such as Zn and Ni) in the center of porphyrin molecule led to two weak absorption bands. The porphyrins H_2OMP, ZnOMP, H_2TCTMP and ZnTCTMP emit in the red regions with emission maxima at 622, 578, 629 and 584 nm, respectively. The emission spectra of all the above porphyrin are presented in Figure 2b [40]. Except for Ni(II)-derivative all other porphyrins demonstrated emission with two prominent peaks near 575 and 630 nm for ZnOMP and ZnTCTMP, respectively. These are blue shifted when compared to the freebase porphyrins, i.e. H_2OMP and H_2TCTMP, which displayed two peaks near 625 and 680 nm, typical of a porphyrin molecule. NiTCTMP did not exhibit any detectable florescence. Between the two emission bands, the one at higher energy appeared more intense, a trend in tune with that of other β-substituted porphyrins. The fluorescence lifetime data of H_2OMP, H_2TCTMP, and their Zn(II) derivatives are tabulated in Table 1, whereas their life time decay profiles are depicted in Figure 3. Freebase porphyrins H_2OMP and H_2TCTMP both demonstrated shorter lifetimes of 3.77 and 4.54 ns, respectively, compared to its octaethyl analog [48]. Whereas, Zn(II) complexes of H_2OMP and H_2TCTMP exhibited dual lifetimes, however, relatively shorter compared to their freebase analogs. The reduced singlet life time of these molecules may be attributed to efficient deactivation by oxygen and/or chloro groups present at the periphery.
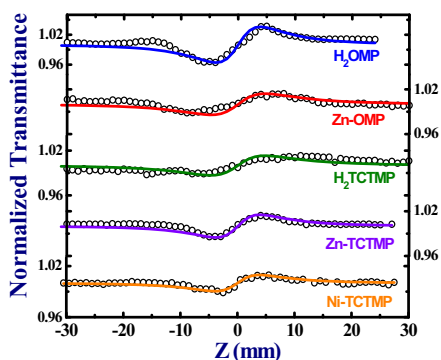
The NLO coefficients (β) and cross-sections (σ_2) were extracted from the open aperture data presented in Figure 4 while n_2 was calculated from the closed aperture data presented in Figure 5 using the Sheik–Bahae formulation [49]. Table 1 depicts the n_2 values of the molecules investigated indicating a positive non-linearity (magnitude of $\sim 10^{-16}$ cm^2/W). Two photon absorption (2PA) coefficients were obtained from experimental data and the magnitudes were $\sim 10^{-11}$ cm/W. 2PA cross-sections (σ_2) were also
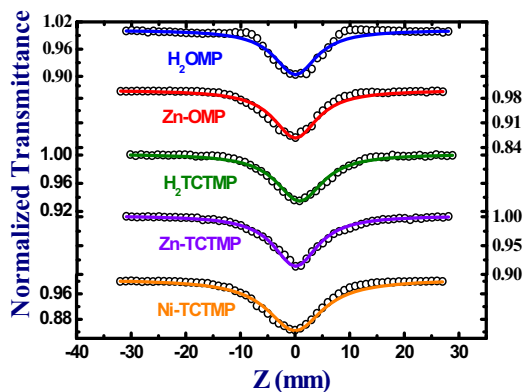
Figure 4. Open aperture data of (a) H_2OMP (b) Zn-OMP (c) H_2TCTMP (d) Zn-TCTMP and (e) Ni-TCTMP. The data were recorded at 800 nm in chloroform with a peak intensity of ~ 100–200 GW/cm^2. For clarity the tick labels for two samples are indicated on right axes.

Table 1
Summary of NLO coefficients, cross-sections, fluorescence lifetimes and various non-radiative lifetimes of various porphyrin derivatives studied using ~ 2 ps, 1 kHz pulses.

| Sample	n_2 (cm^2/W) $\times 10^{-16}$	β (cm/W) $\times 10^{-11}$	σ_{2PA} (GM)	$Re\|\chi^{(3)}\|$ (esu) $\times 10^{-14}$	$Im\|\chi^{(3)}\|$ (esu) $\times 10^{-14}$	$\|\chi^{(3)}\|$ (esu) $\times 10^{-14}$	$\|\chi^{(3)}\|$ (m^2/V^2) $\times 10^{-22}$	Fluorescence lifetime (τ_f) (ns)	Lifetime 1 (τ_1) (ps)	Lifetime 2 (τ_2) (ps)	Lifetime 3 (τ_3) (ps)
H_2OMP	2.90	2.85	1960	1.52	0.95	1.80	2.50	3.77	0.6	6.0	250
ZnOMP	1.20	4.20	4000	0.63	1.40	1.52	2.10	0.17, 1.32	0.3	22.0	480
H_2TCTMP	1.10	1.85	6440	0.57	0.61	0.85	1.20	4.54	0.6	8.0	430
ZnTCTMP	1.25	2.50	14740	0.65	0.83	1.06	1.50	0.17, 1.18	–	–	–
NiTCTMP	0.80	5.20	53690	0.41	1.74	1.80	2.50	–	–	–	–

Figure 5. Closed aperture data of H_2OMP, Zn-OMP, H_2TCTMP, Zn-TCTMP, and Ni-TCTMP. The data were recorded at 800 nm in chloroform with a peak intensity of <50 GW/cm^2. For clarity the tick labels for two samples are indicated on right axes.

Figure 6. Pump-probe data (wriggly line) and the theoretical fits (dotted lines) of H_2OMP, H_2TCTMP, ZnOMP recorded at 600 nm in chloroform.

estimated from 2PA coefficients and the magnitudes were in the range of 10^3–10^4 GM. The complete summary of NLO coefficients and cross-sections along with third order NLO susceptibilities are presented in Table 1. The effect of introduction of electron withdrawing chloro-groups to an electron rich porphyrin core, hence a donor–acceptor characteristic to the resultant macrocycles, could be clearly perceived in these porphyrins, with large enhancement in σ_2 values in case of H_2TCTMP and its metallo-derivatives (containing four electron donating methoxy and four electron withdrawing chloro- groups), as compared to H_2OMP and its metallo-derivatives (containing only eight electron donating methoxy groups). The largest σ_2 value was obtained for NiTCTMP ($\sim5 \times 10^4$ GM). Interestingly, Zn-TCTMP and NiTCTMP molecules demonstrated strong 2PA coefficients and cross-sections compared to H_2TCTMP which, probably, could be attributed to the effect of central metal ion [6]. H_2OMP and ZnOMP molecules exhibited nearly twice the nonlinear absorption when compared to H_2TCTMP and ZnTCTMP molecules. However, the n_2 value of H_2OMP was stronger compared to H_2TCTMP molecules and metal derivative of H_2OMP, i.e. ZnOMP. The closed aperture scans were performed with peak intensities <50 GW/cm^2 where we expect minimal contribution from nonlinear absorption and higher order nonlinearities. The NLO coefficients presented here are expected to encompass predominant contributions from electronic motion since the studies were performed with ~2 ps pulses. However, detailed studies with using techniques such as degenerate four wave mixing have to be performed to separate contribution from other kind of nonlinearities such as molecular orientation [50]. The solvent contribution was negligible and was confirmed through open aperture data of solvent alone. In one of our earlier studies [39] we had investigated the fs (~40 fs) NLO properties of some representative molecules and recorded n_2 values of $\sim10^{-17}$ cm^2/W and β values of 10^{-13} cm/W (solvent contribution was minimal). These n_2 values truly represent the electronic nonlinearity.

Figure 6 depicts the pump-probe data of H_2OMP, ZnOMP, and H_2TCTMP obtained at 600 nm using ~70 fs pulses. The data was fitted using the equation given below containing triple exponentials [46,47].

$$\frac{\Delta T(t)}{T} = y_0 + A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2} + A_3 e^{-(t-t_0)/\tau_3}$$

where $\Delta T(t)$ is the time dependent change in probe transmission. We attempted fitting the data using two exponentials [47] but the fits were poor, especially at the initial time scales (<30 ps). The three lifetimes obtained (τ_1, τ_2, and τ_3) are summarized in Table 1. Before assigning the lifetimes observed from our pump-probe data we thoroughly investigated the literature on similar porphyrins and their dynamics.
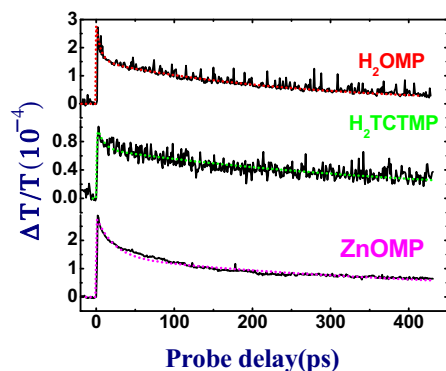
Ha-Thi et al. [7] studied ultrafast dynamics of copper tetra-phenylporphyrin (CuTPP), copper octaethylporphyrin (CuOEP), and the free base tetraphenylporphyrin (H_2TPP) in the gas phase. The first two molecules exhibited a sequential four-step decay ending on a slow evolution in the nanosecond range $2S_2 \rightarrow {}^2CT \rightarrow {}^2T \rightarrow {}^2$ground state. For the free-base case, the first ultrafast time constant of ~110 fs was attributed to an extremely rapid S_2–S_1 internal conversion. Okhrimenko [51] measured a slow component with lifetime of ~690 ps in a Ni(II)–porphyrin derivative, which was independent of probe wavelength. This process was established to be an electronic deactivation from the metal $d_{x^2-y^2}$ excited state to its d_{z^2} ground state. Three lifetimes were observed in the studies of Ni(II)TPPF, Ni(II)TNPP, and Ni(II)TPrF$_7$P [52–54]. The fastest lifetime (<1.2 ps) was assigned to $(\pi\pi^*) \rightarrow (\mathbf{d},\mathbf{d})$ transition while the intermediate lifetime (of few ps) was assigned to vibrational relaxation within the (d,d) states and the longest lifetime of 450–690 ps was assigned to the $(\mathbf{d},\mathbf{d}) \rightarrow$ ground state transition. In the present case we do not expect participation of any 'd' states since there are no unfilled 'd' orbitals in our systems. In the case of NiTCTMP we can possibly expect such states but the pump-probe data of this molecule has not been presented here. Furthermore, there is also no possibility of any charge transfer (CT) states existing in our molecules. Dogan et al. [9] investigated the pump-probe dynamics of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin with different central metal ions (Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}) using 532 nm excitation and observed three components in the data. They attributed the observed three lifetimes to $(S_2 \rightarrow S_1)$, $(S_1 \rightarrow ISC)$, $(T_1 \rightarrow S_0)$ transitions for filled '**d**' shell metal and free base porphyrins, on the other hand those were attributed to $(S_2 \rightarrow S_1)$, $(S_1 \rightarrow \mathbf{d})$, $(\mathbf{d} \rightarrow S_0)$ for unfilled '**d**' shell metal porphyrins. Yoon et al. [55] investigated several highly symmetric expanded porphyrins and observed singlet excited state lifetime varying from 0.7 ps to 560 ps. Zewail's group [56,57] studied ultrafast dynamics in free base/Zn tetraphenyl porphyrins and from the detailed transient absorption data they have assigned the lifetimes of (a) 100–200 fs for intramolecular vibrational energy redistribution (b) 1.4 ps for vibrational redistribution caused by elastic collision with solvent molecules and (c) 10–20 ps for thermal equilibration by energy exchange with solvent. Howe and Zhang [58] studied two phthalocyanine molecules and observed two lifetimes (10 ps and 370/460 ps) which they assign to internal conversion from S_2 to S_1 (possibly including vibrational relaxation within S_1) and S_1 to S_0 non-radiative transitions.

Figure 7 shows a typical energy level diagram considering the various absorption peaks for the molecules investigated. We propose the following mechanisms of de-excitation and based on that the observed three different lifetimes can possibly be assigned to specific processes. The shortest lifetime (τ_1) of 300–600 fs could be attributed to the internal conversion (IC) from S_2 states to the
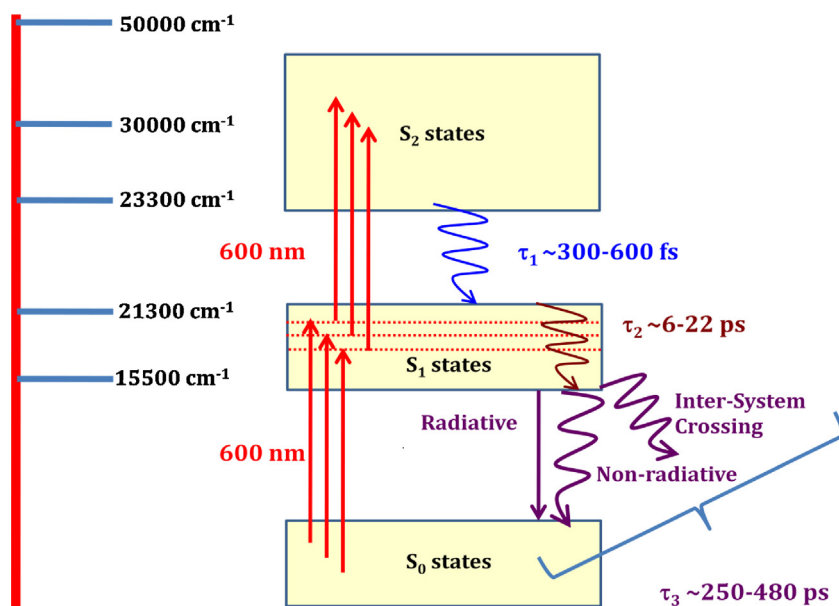
Figure 7. Simplified energy level diagram explaining the observed pump-probe dynamics using possible de-excitation mechanisms.

highest lying S_1 states. The shorter lifetime (τ_2) could, possibly, be attributed to vibrational relaxation within the S_1 states manifold. The longest lifetime, probably, has strong component from the non-radiative relaxation from S_1 states to the ground state. The other two plausible contributions to τ_3 [58] are (a) from the radiative lifetime (S_1 to S_0) and (b) intersystem crossing (S_1 to T_1). However, magnitude of the former can be considered to be negligible since the fluorescence quantum yields of these molecules are typically <6% [40] while the intersystem crossing component, though occur on similar time scales or shorter, cannot be quantified from the present studies. Moreover, it was reported in similar molecules that in the absence of interaction between porphyrin macrocycle π orbitals and metal ion 'd' orbitals intersystem crossing rates will typically be in the ns time scales [9]. Furthermore, there could be a longer component (of few ns) in the pump-probe data since the bleaching has not recovered fully (Figure 6) and this possibly could reflect the radiative lifetime. Due to limitations in our delay stage we could not record the signal beyond 600 ps. However, detailed transient absorption data (using white light probe) is essential to exactly identify the origin of the observed three lifetimes. The important point we try to convey is that these molecules possess fast lifetimes and can be tailored with structural modifications, which is essential to arrive at potentially device capable molecules. The lifetimes observed in the present studies are similar to the ones measured in porphycenes and corroles, recently investigated by our group [45,46].

4. Concluding remarks

In conclusion, we have performed detailed studies for extracting the NLO coefficients and cross-sections for five novel porphyrins. Fluorescence lifetimes measured for these molecules indicated radiative lifetime of ~0.17–4.54 ns. NLO coefficients and cross-sections retrieved from ps Z-scan technique were ~1.85–5.2 × 10⁻¹¹ cm/W and ~2000–54 000 GM, respectively. The magnitudes of nonlinear refractive index were ~0.8–2.9 × 10⁻¹⁶ cm²/W. NLO measurements performed with ~40 fs pulses revealed the electronic contribution to the nonlinearity. Ultrafast decay dynamics were also investigated using fs degenerate pump-probe technique and three lifetimes observed were assigned to different de-excitation mechanisms.

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