

Ultrafast nonlinear optical properties and excited-state dynamics of Soret-band excited D- π -D porphyrins

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ARTICLE INFO

Keywords:

Porphyrins
Ultrafast dynamics
Two-photon absorption
Z-scan
Degenerate four-wave mixing

ABSTRACT

Herein, we report results from our studies on the ultrafast nonlinear optical (NLO) properties and excited-state dynamics in three different porphyrin molecules designed in D- π -D fashion (phenothiazine-porphyrin-phenothiazine) and with two different central metal ions [Zn(II) and Cu(II)]. We have performed extensive target analysis of the femtosecond transient absorption data obtained conveying the true excited state/species spectra of each process with respective lifetimes along with microscopic rate constants of each excited state. The obtained life time values were in the range of 250–500 fs, 20–142 ps, 1.5–6.2 ns and 0.1–1.23 μ s and have been associated from relaxation with the S_n , Hot S_1 (to S_1), S_1 , and T_1 states. Furthermore, the third-order nonlinear (NLO) coefficients [two-photon absorption (TPA) and nonlinear refractive index (n_2)] of CPPHT and ZPPHT exhibited superior values compared to HPPHT recorded with $\sim$ 50 fs, 1 kHz repetition rate pulses at a wavelength of 800 nm. The magnitude of the TPA coefficients of these molecules was compared with some of the recently reported porphyrin moieties and were found to be superior. The time-resolved degenerate four-wave mixing (DFWM) measurements confirmed a large magnitude and an ultrafast response of the $\chi^{(3)}$ in these molecules suggesting potential photonic and all-optical switching applications.

1. Introduction

Porphyrins and phthalocyanines are organic molecules possessing incredible chemical and thermal stabilities [1–3]. Alteration of the macrocyclic structure of porphyrins can significantly affect their chemical, physical, optical, and optoelectronic properties [3–6]. As a consequence, several research groups have been aiming to apply porphyrins in artificial photodevices such as photonic devices [7], molecular switches [8], and dye-sensitized solar cells (DSCs) for solar energy conversion [5,9,10]. Metalloporphyrins (MPs) have gained attention due to their functional universality, stability, and ease of chemical modification [9]. MPs have been used as versatile substrates in various light-driven chemical reactions [11,12], enabling the inter/intramolecular energy redistribution [13]. MPs have also been demonstrated as a promising material for the conversion of solar energy into electric energy in SCs [14]. Moreover, π -conjugated 2D organic

molecules (e.g., phthalocyanines, porphyrins) demonstrated superior nonlinear optical (NLO) properties compared to other organic materials [15,16]. The optical properties of porphyrin molecules can be modulated simply by varying the central metal ion or the surrounding environment [17,18]. There exists great flexibility in modulating physicochemical attributes by synthetic substitutions on planar π -conjugated porphyrin ring and central metal ion, which can be incorporated into donor-acceptor assemblies. In general, donor- π -acceptor porphyrin systems possess good light-harvesting properties for solar cells and also have higher thermal stability and favorable electrical properties [13, 19]. By changing the donor- π -acceptor design as sensitizers for DSSC applications to the donor- π -donor approach, porphyrins can be potential candidates as hole-transporting materials for optoelectronic applications [20]. The electron transfer dynamics is essential in many processes and has been a great research area relevant to solar energy conversion, information storage, catalysis and NLO processes. Therefore,

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understanding the molecular level dynamics in an ultrafast time scale is important for fundamental science and applications of such molecules. Apart from this, the NLO properties of porphyrins have been studied extensively for their tremendous applications in many fields such as optical limiting, optical switching, storage, imaging etc., arising mainly from the delocalized π -electron system. Incorporation of the metal ion into the porphyrin system helps the generation of a large number of delocalized π -electrons. Generally, organic molecules with electron donor and acceptor groups, which are connected to a large π -electron conjugation, demonstrate strong third-order NLO properties. The MPs offer a large change in ground and excited state dipole moments in response to a given electric field intensity, which is the fundamental reason behind the observed strong optical nonlinearities [6,18,21]. However, the applications of porphyrins are mostly associated with electronic transitions taking place in a broad spectral range, primarily from the Q-band transitions. Hence, it is crucial to study the excited state dynamics of porphyrins [22–25]. Particularly, the excited-state absorption (ESA) such as excited singlet or triplet absorption properties are the object of several investigations due to their importance in photonics applications such as all-optical switching and optical limiting [26,27]. It is also important to understand the excited state dynamics in porphyrin moieties because the nonlinear transmission properties of these molecules depend on the excited state energy transfer processes. Various time-resolved spectroscopic techniques such as time-resolved fluorescence by frequency upconversion and transient absorption (TA) are generally used to investigate the excited state dynamics and motion of vibrational wave packets in real-time. Herein, we report the results from the transient absorption studies and third-order NLO measurements of three phenothiazine-porphyrin-phenothiazine derivatives (D- π -D) porphyrin molecules [28] namely.

- 3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine) [henceforth referred to as **HPPHT**]
- 3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine)-Cu [henceforth referred to as **CPPHT**] and
- 3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine)-Zn(II) [henceforth referred to as **ZPPHT**].

Further, the conjugation effect on the third-order NLO properties is also discussed. The excited-state lifetimes accomplished through transient absorption studies have been investigated in detail. Furthermore, the mechanisms of third-order NLO absorption and refraction effects are also investigated. The superior NLO coefficients (TPA coefficients and cross-sections, n_2) along with the fast response times obtained for these molecules suggest their usage in potential photonic applications such as optical limiting, bio-imaging, and all-optical signal processing.

2. Results and discussions

2.1. UV-visible absorption and emission measurements

Fig. 1 shows the schematic for the synthesis of the porphyrins investigated in the present study. The steady-state absorption spectrum of three porphyrin molecules HPPHT, CPPHT, and ZPPHT in DMF are shown in Fig. 2. The intense peak at 458 nm, called the Soret (S_2) band, is due to $a_2(\pi)/b_1(\pi^*)$ electronic transition. ZPPHT illustrates a sharp Soret absorption with a redshift compared to CPPHT and HPPHT at 463 nm, probably due low energy gap between highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO) [28]. The absorption peaks in the spectral region above 550 nm are due to $a_2(\pi)/b_2(\pi^*)$ electronic transitions, assigned to the first excited state (S_1) having two bands. The peaks at 703 and 617 nm are due to the origins of two non-degenerate electronic transitions (Q_x and Q_y) of the free base porphyrin. The steady-state emission spectra of porphyrin molecules dissolved in DMF solvent were recorded at 450 nm excitation. The strongest emission was observed from HPPHT and which demonstrated a smaller Stokes shift from the Q-band absorption edge. The photophysical parameters of the investigated molecules obtained from steady state measurements are summarized in Table 1. Further detailed discussion on the photophysical parameters of HPPHT and ZPPHT has been reported in our earlier work [28].

2.2. Transient absorption studies

The excited state properties of the synthesized molecules were investigated using fs TAS experiments using 400 nm as the pump for photoexcitation of the Soret band and the probing in the spectral region of 480 nm–780 nm. Fig. 3 shows the transient absorption (TA) spectra of HPPHT, CPPHT, and ZPPHT dissolved in DMF solvent (concentration of

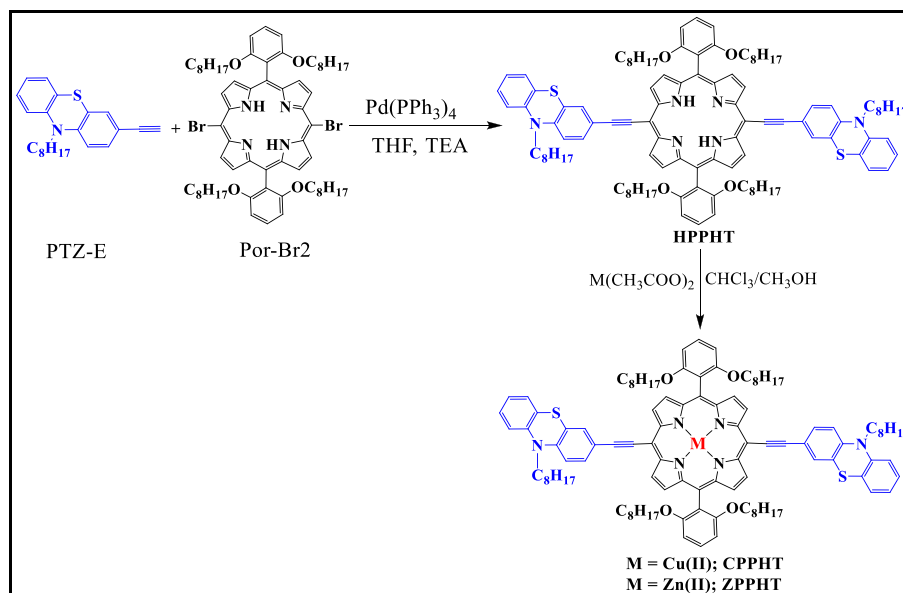


Fig. 1. Synthetic scheme of porphyrin systems investigated in the present study.

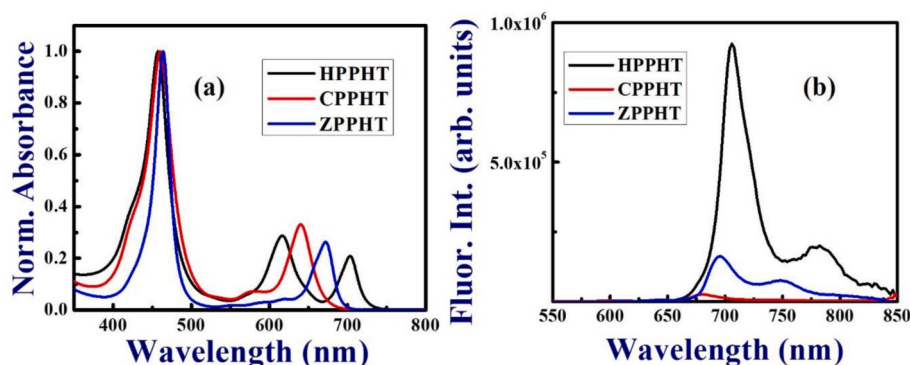


Figure 2. (a) absorption and (b) emission spectra of studied porphyrin molecules in DMF. CPPHT depicted a weak emission compared to the other two molecules.

Table 1

Summary of the steady state absorption and emission peaks of three porphyrins measured in DMF (ϵ is the extinction coefficient).

Sample	Absorption (nm) [ϵ M ⁻¹ cm ⁻¹]		Emission (nm)	Radiative Lifetimes (ns)
	Soret band	Q-band		
HPPHT	458 [491500]	617 [132500] 703 [88000]	705, 781	6.2 [28]
CPPHT	458 [343100]	640 [107011]	678	1.5 [unpublished]
ZPPHT	463 [452450]	673 [104292]	695, 748	1.8 [28]

80 μ M) at increasing probe delays varying from 100 fs to 2 ns. From the absorption data (Fig. 2) it is evident the porphyrin molecules have strong Soret band absorption at $\sim$ 458 nm possessing strong molar extinction coefficients than for other wavelengths of the spectra. Due to the limitation of the probe spectral range the lower spectral region of GSB from S_2 could not be recorded. The obtained TA spectra of CPPHT and ZPPHT revealed two distinct regions i) photo-induced absorption (PIA) in the spectral range of 480–605 nm and $>$ 670 nm ii) ground state bleach (GSB_{Q-band}) from 605 to 650 nm overlapped with stimulated emission (SE). The contribution of SE for the molecules was observed at 705 nm, 680 nm and 695 nm for HPPHT, CPPHT, and ZPPHT, respectively. The PIA of ZPPHT with a maximum near 520 nm illustrated a long-lived TA signal, which might be due to the long lifetime of the triplet state. Similarly, for other molecules of CPPHT and HPPHT, the PIA maximum was at 510 nm and decays were faster compared to ZPPHT. Among these, the free-base porphyrin HPPHT exhibited a faster decay time ($<$ 1 ns).

The obtained TA spectra exhibited different time evolutions at different spectral regions due to the several processes taking place after the photoexcitation such as ground state bleaching (GSB), excited-state absorption (ESA), and stimulated emission (SE). The In depth analysis of the femtosecond transient absorption spectra is obtained by performing the global and target analysis based on compartmental model [29] as shown in figure (4), using Surface Explorer (Ultrafast systems) and Glotaran [30].

First the TA spectra were globally fitted using a parallel and sequential model, which yielded decay associated difference spectra (DADS) and evolution associated decay spectra (EADS). Both DADS and EADS provides information on the evolution of difference spectra with different microscopic rate constants. The obtained time constants from parallel and sequential model were used to estimate the species associated difference spectra (SADS) in the target analysis (combination of parallel and sequential model), which contains all the possible branching routes with specific rate constants i.e. decay of compartments and transfer of population between compartments. Fig. 5 represents the

kinetics at different probe wavelengths of the TA spectra of ZPPHT after photoexcitation. The scattered points represent the experimental data while the solid lines are theoretical fits obtained from target analysis. The representative wavelengths are chosen at different portions of the TA spectra corresponding to ground state bleach and photo induced absorption process. The obtained time constants are summarized in Table 2.

The TA spectra was collected up to 2 ns delay and, consequently, the T_0 spectra cannot be estimated precisely from this data. Therefore, the lowest excited state (S_1) lifetime is fixed with time constant obtained from time-correlated single photon counting (TCSPC) measurements [28] and T_0 lifetime was fixed in the range of 1–2 μ s. Under these assumptions the spectral data fitted well and the rate constants obtained are summarized in Table 2. The goodness of the fits is shown in Fig. 5 [for the data of other two molecules please see supporting information Figures S6–S7]. The estimated species associated difference spectra of ZPPHT and respective population time profiles are shown in Fig. 6. The first SADS1 spectra is attributed to the S_n state, with life time of 250 fs, 330 fs, and 500 fs for HPPHT, CPPHT and ZPPHT, respectively. This time corresponds to the internal conversion from S_n states (population transfer) to S_1 hot state. The lifetime $\tau_2 = 142$ ps, 20 ps, and 50 ps are associated with the vibrational relaxation from S_1 hot to thermally relaxed S_1 state with corresponding SADS2 spectra as shown in Fig. 6 [please see the target analysis figures for HPPHT and CPPHT in supporting information files S6–S7]. The life time $\tau_3 = 6.2$ ns, 1.5 ns, and 1.8 ns is assigned to the radiative relaxation from S_1 state to the S_0 state as well as intersystem crossing to the lowest triplet state T_0 with SADS3 spectra. Finally, the SADS4 spectra and lifetime $\tau_4 = 1.01$ μ s, 0.1 μ s, and 1.23 μ s can be recognized to T_0 state with excited state absorption peak at 505 nm. The microscopic rate constants pertaining to each state are summarized in Table 2. Fig. 6 illustrates the depopulation of excited state (S_n) SADS1 spectra happening through two different channels: first 20% of the population decayed through radiative process to ground state with 2.5 ps (k_1)⁻¹ time constant, second, remaining population of SADS1 goes to S_1 hot state through internal conversion with a time constant of 625 fs (k_2)⁻¹. Here k_1 , k_2 are corresponding rate constants of kinetics with $\tau_1 = 1/(k_1 + k_2)$ ⁻¹ and its value was 500 fs. From SADS2 90% of the population is decayed in nonradiative pathway from S_1 hot state to thermally relaxed S_1 state through vibrational relaxation with time constant of 500 ps (k_3)⁻¹ and remaining population decayed through radiative pathway from S_1 hot state to ground state with time constant of 55.5 ps (k_4)⁻¹. The lifetime of S_1 hot state was determined to be 50 ps from $\tau_2 = 1/(k_3 + k_4)$ ⁻¹. Next, 30% of the population of SADS3 decayed by radiative process to ground state with time constant of 6 ns (k_6)⁻¹, the life time of SADS3 was constrained to be the value obtained from TCSPC of 1.8 ns from $\tau_3 = 1/(k_5 + k_6)$ ⁻¹ and remaining population undergoes ISC to lowest triplet state T_0 with time constant of 2.57 ns (k_5)⁻¹. Finally, SADS4 very slowly decayed to ground state from T_0 , with time constant arbitrarily set to 1.26 μ s from $\tau_4 = 1/k_7$ ⁻¹ due to

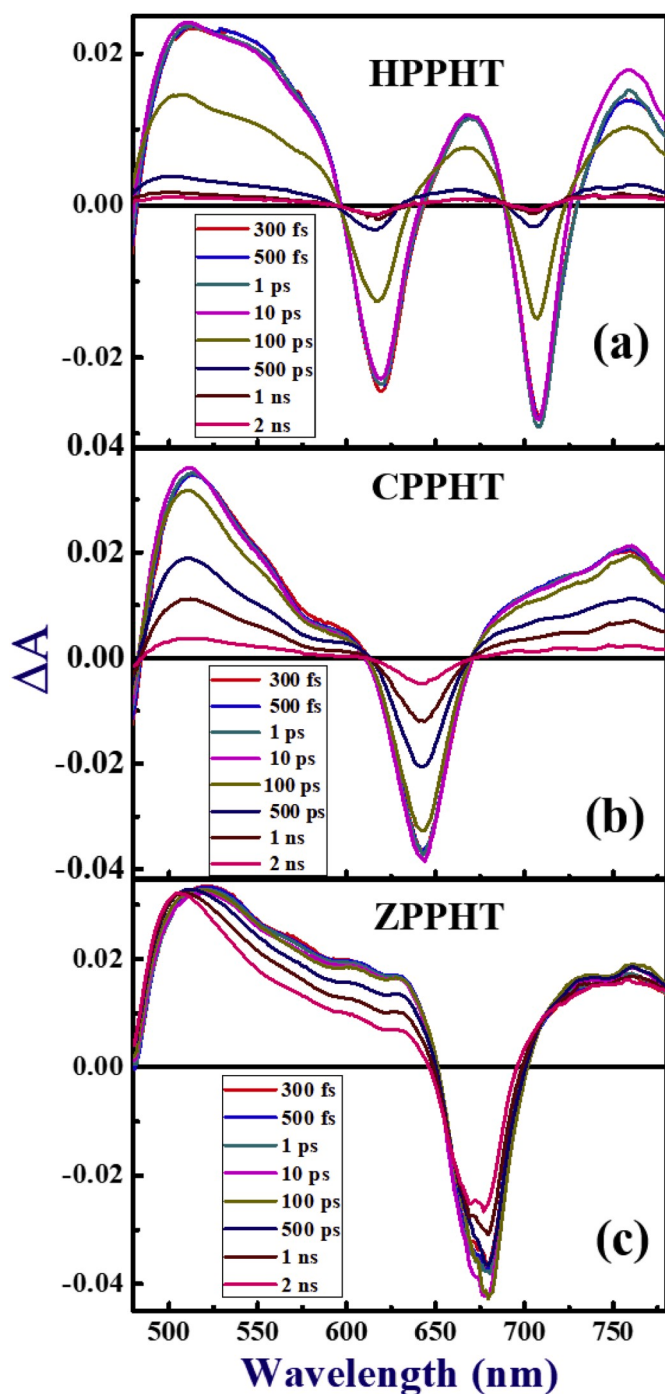


Figure 3. fs-TAS spectra of three different porphyrins in solution phase at different delay times at 400 nm photoexcitation for (a) HPPHT (b) CPPHT and (c) ZPPHT.

the limitation in detection window of our setup. Similar values of these parameters were obtained for other two porphyrin molecules HPPHT and CPPHT listed in Table 2 [please see Figures S6–S7 of the supporting information file]. Fig. 7 shows the TA spectra at 300 fs and 2 ns probe delay with excellent agreement with global analysis fitting.

From Table 2 data it is evident that the ZPPHT and HPPHT porphyrin molecules revealed longer relaxation times significantly compared to the CPPHT. This could be attributed to either a greater triplet quantum yield through intersystem crossing or reduction in the radiative lifetime in the case of ZPPHT due to the incorporation of Zinc in HPPHT [28]. The obtained rate constants are consistent with the literature [23–25],

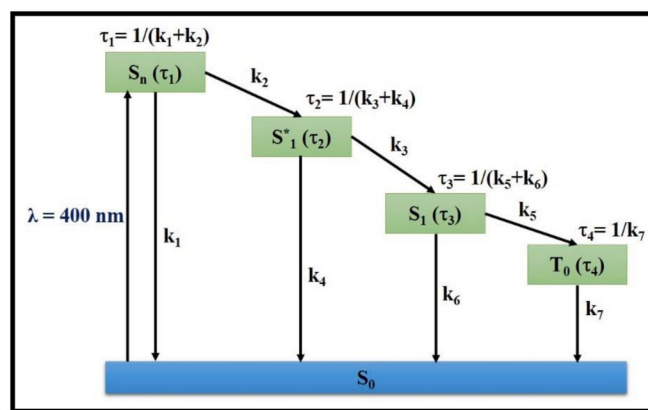


Fig. 4. Schematic of the target model used to fit TA spectra of synthesized porphyrins after 400 nm photoexcitation.

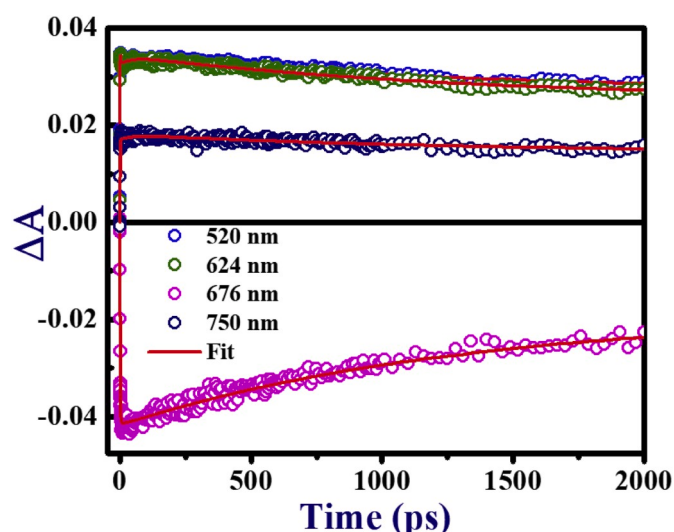


Fig. 5. Kinetics of ZPPHT molecule at selected probe wavelengths after target analysis. Open symbols represent data points from experiments while the solid lines represent theoretical fits.

thus representing the usefulness and reliability of the analysis scheme for synthesized new porphyrin moieties.

2.3. Z-scan data and analysis

The NLO properties of synthesized porphyrins were deliberated using the Z-scan technique with an input intensity of $\sim 160 \text{ GW/cm}^2$. The open aperture (OA) Z-scan curves confirmed the presence of reverse saturable absorption (RSA) behavior as illustrated in Fig. 8. The origin of RSA can be due to the excited state absorption or two-photon absorption. The obtained OA curves were fitted using a standard two-photon absorption equation [31] and the obtained NLO parameters are listed in Table 3. Metal doped porphyrins depict strong NLO coefficients and this enhancement depends on several factors such as the central metal ion, intramolecular charge transfer and expanded π -conjugated system of these molecules. Closed aperture (CA) Z-scan transmission curves confirmed the self-focusing behavior had positive refractive index $n_2 > 0$. The CA data were fitted to a standard equation [31]. The magnitude of the NLO coefficients obtained from our molecules is compared with a few of the recently reported molecules [18,32–40]. Terazima et al. [18] reported an n_2 value of $10^{-15} \text{ cm}^2/\text{W}$ from porphyrin oligomers with picosecond laser pulse excitation at 800 nm, the n_2 values were found to increasing linearly with number of porphyrin units and the meso

Table 2

Summary of the kinetic parameters of three porphyrin molecules obtained from global and target analysis of fs-TA data (τ_3 value is obtained from TCSPC measurements [28]). The error in the obtained rate constants is <1%.

Lifetime and decay parameters	HPPHT	CPPHT	ZPPHT	Microscopic rate constants		
				HPPHT	CPPHT	ZPPHT
$\tau_1 = 1/(k_1 + k_2)$	333 fs	250 fs	500 fs	$k_1 = (1.66 \text{ ps})^{-1}$ $k_2 = (416 \text{ fs})^{-1}$	$k_1 = (1.25 \text{ ps})^{-1}$ $k_2 = (312 \text{ fs})^{-1}$	$k_1 = (2.5 \text{ ps})^{-1}$ $k_2 = (625 \text{ fs})^{-1}$
$\tau_2 = 1/(k_3 + k_4)$	142 ps	20 ps	50 ps	$k_3 = (1.42 \text{ ns})^{-1}$ $k_4 = (158 \text{ ps})^{-1}$	$k_3 = (25 \text{ ps})^{-1}$ $k_4 = (200 \text{ ps})^{-1}$	$k_3 = (500 \text{ ps})^{-1}$ $k_4 = (55.5 \text{ ps})^{-1}$
$\tau_3 = 1/(k_5 + k_6)$	6.2 ns	1.5 ns	1.8 ns	$k_5 = (8.9 \text{ ns})^{-1}$ $k_6 = (20.8 \text{ ns})^{-1}$	$k_5 = (2.16 \text{ ns})^{-1}$ $k_6 = (5.05 \text{ ns})^{-1}$	$k_5 = (2.57 \text{ ns})^{-1}$ $k_6 = (6 \text{ ns})^{-1}$
$\tau_4 = 1/(k_7)$	1.01 μ s	0.1 μ s	1.23 μ s	$k_7 = (1.01 \text{ } \mu\text{s})^{-1}$	$k_7 = (0.1 \text{ } \mu\text{s})^{-1}$	$k_7 = (1.23 \text{ } \mu\text{s})^{-1}$

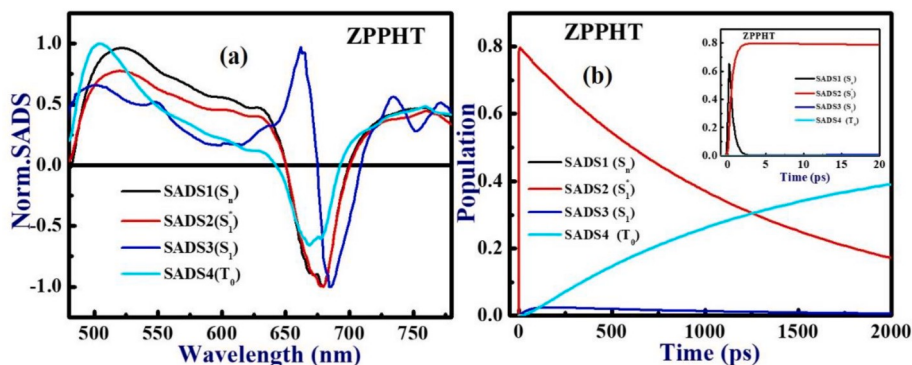


Fig. 6. (a) Estimated species associated spectra and (b) population decay profiles of respective species/states of ZPPHT. The inset shows the enlarged view of population profiles up to 20 ps. At 400 nm photoexcitation.

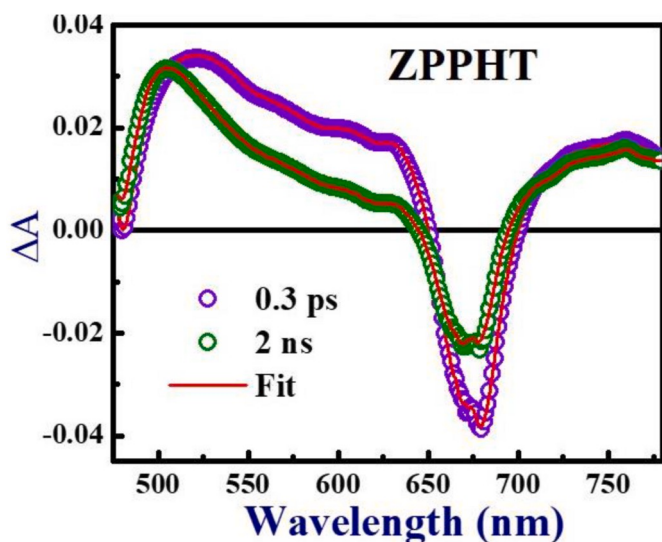


Fig. 7. Fs-TAS spectra of ZPPHT at 0.3 ps and 2 ns probe delay with global analysis. Solid lines are theoretical fits while the open symbols are the experimental data (400 nm photoexcitation).

substitution of porphyrin units exhibited enhanced two-photon absorption values ($2.1\text{--}7 \times 10^{-11} \text{ cm}^2/\text{W}$). Ahn et al. [37] investigated the two-photon absorption from the expanded porphyrin arrays by altering the dihedral angle and they report 2 PA cross-section values $\sigma^{(2)}$ of 10^3 GM with fs laser pulse excitation at 240 kHz repetition rate, and they have found larger 2 PA and longer excited state absorption from the aromatic hexaphyrin compared to Antiaromatic hexaphyrin due to the extended aromaticity. Recently, an increase/decrease of the excited state lifetime and extension of π -electron conjugation have been linked to increased 2 PA cross-section values in different porphyrin moieties are

reported [32,33]. Ogawa et al. [39] observed strong 2 PA from the butadiyne-linked bisporphyrin system by designing donor/acceptor molecules connected to a π -conjugation symmetrically or asymmetrically and they have found an increased $\sigma^{(2)}$ with a magnitude of $\sim 3.7\text{--}76 \times 10^2 \text{ GM}$ with fs laser pulse excitation at a wavelength of 817 nm. Similar studies were performed by Odom et al. [40], wherein they observed the strong electronic coupling between (D-A-D) bisporphyrin motifs enhancing the 2 PA values ($\sim 6.9\text{--}9.7 \times 10^3 \text{ GM}$) measured with 140 fs from 700 to 1600 nm, arising from the several transitions due to large number of low-lying excited states. Sheng et al. [41] have reported D- π -A structures (A_3B type porphyrins) with asymmetric porphyrins possessing large 2 PA cross-section values (compared to symmetric analogues) of $6.1 \times 10^5 \text{ GM}$ which was attributed to the intramolecular energy transfer (from excited pyrene to the porphyrin molecule and was confirmed from fluorescence data). Mikhaylov et al. [42] also reported a large 2 PA cross-section values ($\sim 10^5 \text{ GM}$) from self-assembled butadiyne Zn-porphyrin nanostructures due to the efficient π -conjugation arising from axial oriented π -orbitals. However, these were obtained with nanostructures wherein confinement effects are prominent. Hisaki et al. [43] reported a large 2 PA cross-section values of 9620 GM from doubly β -to- β butadiyne-bridged diporphyrins arising from the rigid planar structure. Yoon et al. [44] have observed strong PA property correlation from hexaporphyrin molecules with larger number of π -electrons and rectangular rigid structures possessing increased polarizability along the molecular direction, and they have reported 2 PA cross-section values of 2600–3100 GM with fs pulse excitation. In the present case we observed 820–5400 GM, which are significantly higher.

However, several factors were found to influence the 2 PA values of porphyrin macrocycles such as conjugated π -electron delocalization, the symmetry of the system, length of the π -conjugation and directionality playing a central role in the obtained enhanced 2 PA values [41–46]. From the obtained NLO coefficients metal doped porphyrin moieties exhibited stronger 2 PA cross-section values than free-base porphyrin (HPPHT), possibly because of the substantial excited state population as seen from the TA Spectra. It has earlier been proved that porphyrins with

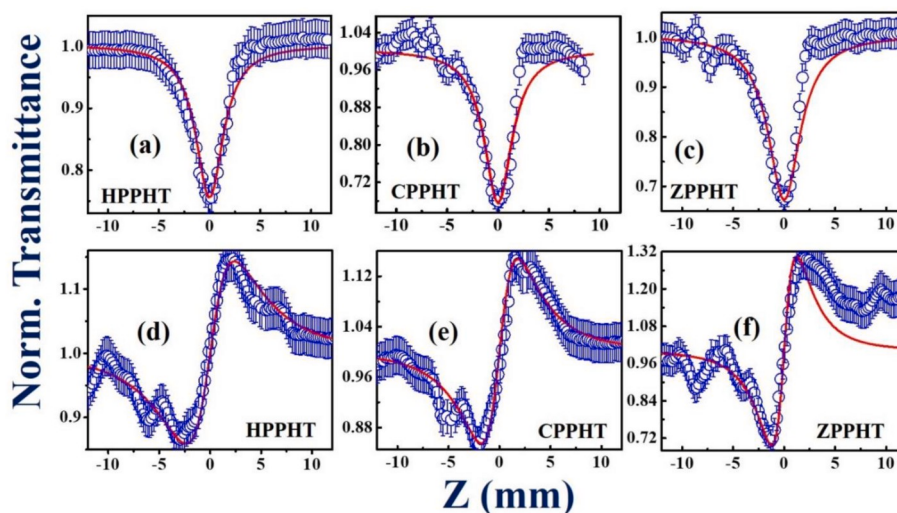


Figure 8. (a)-(c) Open aperture Z-scan data (d)-(f) closed aperture Z-scan data of HPPHT, CPPHT, ZPPHT, respectively, recorded at 800 nm with fs pulses and 1 kHz repetition rate. Open symbols represent the experimental data and the solid lines are theoretical fits.

Table 3

Summary of the NLO coefficients of porphyrins investigated in the present study and obtained using the Z-scan technique at 800 nm.

Sample	β $\times 10^{-13}$ (m/W)	n_2 $\times 10^{-19}$ (m ² /W)	$\sigma^{(2)}$ $\times 10^3$ (GM)	$\chi^{(R)}$ $\times 10^{-21}$ (m ² /V ²)	$\chi^{(I)}$ $\times 10^{-22}$ (m ² /V ²)	$\chi^{(3)}$ $\times 10^{-21}$ (m ² /V ²)	$\chi^{(3)}$ $\times 10^{-13}$ (esu)
HPPHT	1.0 ± 0.02	5.8 ± 0.11	0.82 ± 0.016	6.3 ± 0.12	0.7 ± 0.014	6.3 ± 0.03	4.5 ± 0.022
CPPHT	6.5 ± 0.13	6.0 ± 0.12	5.4 ± 0.1	5.7 ± 0.11	4.0 ± 0.08	5.7 ± 0.028	4.1 ± 0.020
ZPPHT	4.4 ± 0.09	13 ± 0.65	3.6 ± 0.07	120 ± 6	2.6 ± 0.05	12 ± 0.022	8.8 ± 0.044

different central metals demonstrated superior nonlinearity compared to free-base porphyrins. The obtained TPA cross-section values in the present case are found to be on par or superior compared to some of the recently reported porphyrin molecules (Table 4). Therefore, we believe that these molecules find applications in optical limiting and TPA-based imaging. The error bars in the obtained NLO coefficients is capped at $\pm 2-5\%$ predominantly due to errors in the estimation of peak intensities and input laser fluctuations.

The DFWM experiments were performed at 800 nm using five different input energies (the same concentrations used for Z-scan measurements were utilized for the DFWM measurements). Fig. 9 (a) data illustrates the cubic dependency of the DFWM signal confirming the third-order NLO process. Carbon tetrachloride (CCl₄) solvent was used as a reference with $\chi^{(3)} = 4.4 \times 10^{-14}$ esu and the $\chi^{(3)}$ of molecules was calculated following the standard procedure [31]. The obtained NLO coefficients from the DFWM studies and Z-scan studies matched in the orders of magnitude. The obtained $\chi^{(3)}$ values are significantly higher

Table 4

Summary of 2 PA cross-section values from recent works on different porphyrin molecules. DFWM Data and Analysis.

Compound	Laser parameters	β (cm/GW)	$\sigma^{(2)}$ (GM)	Solvent	Ref.
Butadiyne-Linked Bisporphyrin (5D)	0.7–1.6 μ m, 140 fs, 1 kHz	–	7600	CHCl ₃	40
A ₃ B type porphyrin 1	800 nm, 170 fs, 1 kHz	0.148	610000	CHCl ₃	41
(cP12).(TS) ₂ (DABCO)12 (nanostructures)	900–1600 nm, 100 fs, 1 kHz	–	173000	Toluene	42
2Zn	800 nm, 130 fs, 5 kHz	–	9620	Toluene	43
[26], [28] hexaphyrins	1200 nm, 130 fs, 5 kHz	–	2600–3100	Toluene	44
Bis(Porphyrin)-dimer 3	710 nm, 140 fs, 80 MHz	–	1000000	DCM	45
PtTBP(CO ₂ Bu) ₈	810 nm, 150 fs, 80 MHz	–	800	DMA	46
Monozinc bisporphyrin 7D	887 nm, 120 fs, 1 kHz	–	7600	CHCl ₃	47
H ₂ TTP	780 nm, 150 fs, 1 kHz	–	25	Toluene	48
NiTCTMP	800 nm, 2 ps, 1 kHz	0.0052	53690	Chloroform	49
DPP-ZnP-ZnP-DPP	910 nm, 120 fs, 80 MHz	–	21500	DCM	50
DPP-ZnP porphyrin	900 nm, 100 fs, 80 MHz	–	4000	DCM	51
meso-meso, β - β , β - β triply linked porphyrin tape (4)	2.3 μ m, 130 fs, 5 kHz	–	41200	Toluene	52
(OMe) ₂ TPC	Nanosecond, 1064 nm	–	67.6	CS ₂	53
H ₂ TPYRP,	800 nm,	–	42600	Chloroform	54
H ₂ TPHEP	170 fs, 1 kHz	–	13600		
5,16-Di-(4-bromophenyl)-tetraoxa [22]porphyrin(2.1.2.1)	800 nm,	–	29	DCM	55
	50 fs, 1 kHz				
D- π -D porphyrins	800 nm,		820		Present work
	50 fs, 1 kHz		5400		
			3600		

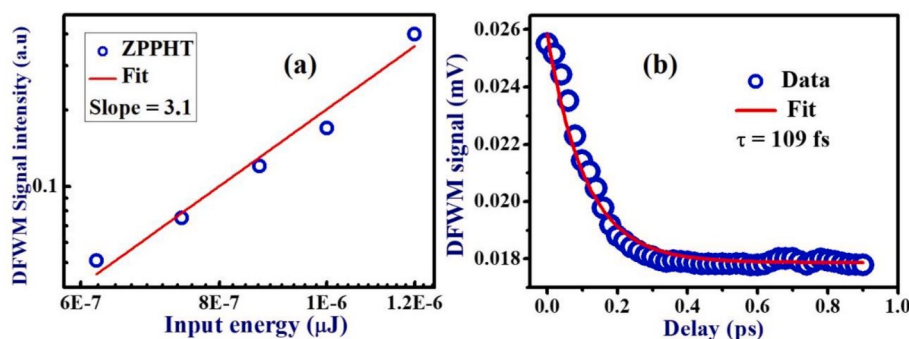


Fig. 9. (a) Cubic dependency of the DFWM signal. a.u. stands for arbitrary units. (b) time-resolved DFWM signal profile of ZPPHT.

compared to the free-base porphyrin molecule. Many research groups have investigated the NLO properties of different porphyrins, their nanostructures and related moieties with sub-picosecond pulses [32,33,56–63]. The exponential decay of the time-resolved DFWM signal (fitted to an exponential decay) confirms the origin of nonlinearity, which is mainly due to pure electronic contribution, as shown in Fig. 9b. The nonlinear refractive index was calculated from the following equation n_2 (cm^2/W) = $(\frac{0.0395}{n_0^2}) \chi^{(3)}$ esu. Metal doped porphyrin molecules depicted higher n_2 values compared to freebase porphyrin HPPHT (Table 5). The DFWM data of the other two porphyrin molecules are shown in Figure S8 of the supporting file.

The obtained NLO parameters are similar or higher in magnitude than some of the recently reported metalloporphyrin molecules. Recently, Narendran et al. [36] have reported the $\chi^{(3)}$ values with a magnitude of 10^{-12} esu from *Meso*-tetrakis porphyrin complexes obtained with ns pulses. Rao et al. [34] reported a $\chi^{(3)}$ value of 10^{-9} esu from benzoporphyrins with ps laser pulses at 532 nm. Venugopal Rao et al. [35] reported $\chi^{(3)}$ values of $\sim 10^{-12}$ esu from tetraphenyl porphyrins obtained with a ps pulses at 532 nm. Kumar et al. [56] extensively studied alkyl phthalocyanines using DFWM experiments with 100 fs pulses and have reported the highest $\chi^{(3)}$ of 4.31×10^{-14} esu. Biswas et al. reported DFWM measurements with 70 fs pulses for quinoxalines molecules with highest $\chi^{(3)}$ values of 4.35×10^{-14} esu [64]. Furthermore, on comparison of the obtained nonlinearities with similar molecules (such as phthalocyanines) Bhattacharya et al. [65,66] have reported $\chi^{(3)}$ values for carbazole and triphenyl imidazole induced phthalocyanine moieties with magnitudes of $\sim 10^{-15}$ – 10^{-14} esu, measured using the fs Z-scan technique at 800 nm. Therefore, we firmly believe that the investigated porphyrin molecules from the present study, having demonstrated strong $\chi^{(3)}$ values and ultrafast response time, can find applications in all-optical switching and optical limiting.

3. Conclusions

In this work, a thorough photophysical investigation and the ultrafast NLO studies of three novel porphyrins (HPPHT, CPPHT, and ZPPHT) have been performed. Femtosecond transient absorption spectroscopic studies elucidated the evolution of excited state photo-processes various photophysical processes. By performing a thorough global and target analysis of the TAS data, helps to estimated different rate constants for various photophysical processes such as IC from S_n – S_1 (k_2) hot found to

be in the range of ~ 250 – 500 fs and vibrational cooling from S_1 hot - S_1 (k_3) state happens in the range of ~ 20 – 142 ps. From S_1 the population relaxed to ground state upon radiative process as well as lowest triplet state T_0 with nanosecond time scale. The NLO properties of synthesized porphyrins were investigated using the fs Z-scan and DFWM experimental techniques. The obtained NLO coefficients were found to be stronger in the case of the ZPPHT molecule when compared to the other two molecules. The two-photon absorption cross-sections were found to be in the range of 820–5400 GM, significantly superior to some of the recently reported organic moieties. We firmly believe that these molecules have the potential for various optoelectronics and photonics applications.

4. Experimental details

4.1. Synthesis

Both the starting materials 3-ethynyl-10-octyl-10H-phenothiazine (PTZ-E) and 5,15-bis(2,6-bis(octyloxy)phenyl)-10,20-dibromoporphyrin (Por-Br2) were synthesized as per methods reported in the literature [28]. Free-base derivative (HPPHT) was obtained by Sonogashira coupling between PTZ-E and Por-Br2 using Pd catalyst, and the corresponding metallo-derivatives were obtained by metal insertion into the porphyrin cavity. All three porphyrins were characterized by elemental analysis, ^1H NMR and MALDI-MS techniques and the obtained data confirmed the proposed molecular structures (See experimental section and Figures S1–S5).

Synthesis: 3-ethynyl-10-octyl-10H-phenothiazine (PTZ-E) and 5,15-bis(2,6-bis(octyloxy)phenyl)-10,20-dibromoporphyrin (Por-Br2) were synthesized as per the methods reported in literature.²⁸

Synthesis of 3,3'-(10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl)bis(10-octyl-10H-phenothiazine) [HPPHT]: We have adopted slightly modified procedure than reported in the literature. Por-Br2 (0.500 g, 0.42 mmol) was dissolved in a mixture of 10 ml triethylamine (TEA) and 10 ml of dry tetrahydrofuran (THF) under an inert atmosphere. The resulting solution was purged with N_2 gas for ~ 15 min followed by the addition of CuI (0.020 g), and Tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$] (0.10 g), which were heated to 60°C . Subsequently, 3-ethyl-10-octyl-10H-phenothiazine (PtZ-E) (0.42 g, 1.25 mmol) was dissolved in 3 ml of THF and added slowly with the help of a syringe, and a spontaneous colour change (brown to green) was observed. The progress of the reaction was monitored by TLC until all the starting materials were consumed. Later the reaction mixture was bring down to room temperature (RT) and the solvent was removed by rotary evaporation. Then the obtained crude material was dissolved in DCM, filtered and dried over anhydrous Na_2SO_4 . The solvent removed and obtained solid was subjected to silicagel column chromatography Hexane: DCM (3:1 v/v) and recrystallized with methanol/DCM yielded 81% as reddish-green powder. Anal. Calcd. For $\text{C}_{108}\text{H}_{132}\text{N}_6\text{O}_4\text{S}_2$ (1641.98): C, 78.98; H, 8.10; N, 5.12. Found; C,

Table 5

Summary of the NLO coefficients obtained from the DFWM technique measured at 800 nm with ~ 70 fs pulses.

Molecule	$\chi^{(3)}$ (esu)	n_2 (cm^2/W)
HPPHT	5.13×10^{-14}	1.00×10^{-15}
CPPHT	6.87×10^{-14}	1.33×10^{-15}
ZPPHT	7.69×10^{-14}	1.49×10^{-15}

79.03; H, 8.19; N, 5.13. MALDI-TOF: m/z [M]⁺calcd. For C₁₀₈H₁₃₂N₆O₄S₂, 1641.98; found, 1641.97. ¹H NMR (400 MHz, CDCl₃) δ 9.50 (d, J = 4.6 Hz, 4H), 8.72 (d, J = 4.3 Hz, 4H), 7.76–7.67 (m, 6H), 7.20–7.18 (m, 4H), 7.00–6.91 (m, 10H), 3.94 (t, J = 7.0 Hz, 4H), 3.82 (t, J = 6.2 Hz, 8H), 1.55 (s, 16H), 1.24 (s, 12H), 1.02–0.95 (m, 10H), 0.89 (s, 10H), 0.80 (dt, J = 14.7, 7.3 Hz, 10H), 0.62 (dt, J = 14.0, 7.0 Hz, 10H), 0.54 (s, 8H), 0.50 (dd, J = 14.6, 7.4 Hz, 16H), –1.82 (s, 2H).

3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine)-Cu [CPPHT]: 150 mg (0.06 mmol) of HPPHT was dissolved in 30 ml of chloroform. To this, 90 mg (0.45 mmol) of copper acetate (dissolved in 30 ml of methanol) was added. The resultant reaction mixture was refluxed until change in absorption spectra (~2 h) and the solvent was removed to obtain the crude product. By using column chromatography, the crude product was purified with (9:1 v/v) Hexane: THF, and recrystallized from methanol to obtain CPPHT in 87% yield as a green powder. Anal. Calcd. For C₁₀₈H₁₃₀N₆O₄S₂Cu% (1701.89): C, 76.13; H, 7.69; N, 4.93; Found C, 76.10; H, 7.86; N, 4.91. MALDI-TOF: m/z [M]⁺calcd (1701.89): For C₁₀₈H₁₃₀N₆O₄S₂Cu; found, 1702.18.

3,3'-((10,20-bis(2,6-bis(octyloxy)phenyl)porphyrin-5,15-diyl)-bis(ethyne-2,1-diyl))bis(10-octyl-10H-phenothiazine)-Zn(II) [ZPPHT]: We have adopted a similar procedure for CPPHT but one difference is that we have used zinc acetate instead of copper acetate. Yield: 90%. Anal. Calcd. For C₁₀₈H₁₃₀N₆O₄S₂Zn% (1702.89): C, 76.05; H, 7.68; N, 4.93; Found C, 76.10; H, 7.58; N, 4.88. MALDI-TOF: m/z [M]⁺calcd (1702.89): For C₁₀₈H₁₃₀N₆O₄S₂; found, 1702.96. ¹H NMR (400 MHz, CDCl₃) δ 9.62 (d, J = 4.6 Hz, 4H), 8.84 (d, J = 4.6 Hz, 4H), 7.72 (dt, J = 23.1, 8.4 Hz, 6H), 7.19 (t, J = 7.1 Hz, 4H), 7.01–6.91 (m, 10H), 3.94 (t, J = 7.2 Hz, 4H), 3.84 (t, J = 6.4 Hz, 8H), 1.49 (s, 16H), 1.25 (s, 8H), 1.02–0.93 (m, 8H), 0.89 (t, J = 6.9 Hz, 8H), 0.84–0.75 (m, 8H), 0.60 (dt, J = 14.6, 7.1 Hz, 8H), 0.50 (t, J = 7.3 Hz, 26H), 0.46–0.40 (m, 8H).

Highly pure DMF was used to prepare the dilute solutions of 12 μM concentration to avoid the accumulation effects. The steady-state UV–visible absorption and PL-emission measurements were performed using a PerkinElmer spectrophotometer. Femtosecond transient absorption (TAS) measurements were performed using a commercial transient absorption spectrometer (HELIOS) based on a Ti:Sapphire regenerative amplifier (LIBRA, M/s Coherent, USA) delivering 1 kHz repetition rate, ~4 mJ pulses centered at 800 nm wavelength and possessing a duration of ~50 fs. The complete experimental details are described in our earlier works [31,59,60]. In the present work, we have used a second harmonic crystal (β-barium borate, BBO) to generate 400 nm wavelength from first pulses to resonantly excite the Soret band. A small fraction from the amplifier output is focused on the Sapphire plate to generate a stable white-light Continuum (WLC) to probe the pump induced changes. The probe pulses were compressed by using a set of parabolic mirrors and the instrument response was estimated to be ~270 fs from pure CCl₄. A complete description of understanding the signals from the TA measurements can be found elsewhere [67]. The TA spectra for all the samples were recorded from 420 nm to 800 nm up to a time delay of 2 ns and the obtained spectra were cropped (due to the fluctuations in the blue side of the probe pulses) to get 480–800 nm useful data. The input energy of pump pulses was ~0.21 μJ for all the TA measurements. All the TA measurements were performed at room temperature. The third-order NLO properties were measured using the single-beam Z-scan technique at 800 nm.

4.2. Z-scan studies

The solution samples were prepared in DMF at a concentration of 100 μM for NLO measurements. The complete experimental details are summarized in our earlier work [31]. A Ti: Sapphire laser (amplifier) delivering ~50 fs pulses with a repetition rate of 1 kHz was used for the NLO studies. A 1-mm thick quartz cuvette was utilized for holding the sample (liquid). A 15-cm plano-convex lens helped to focus the laser

beam and the sample was translated along the Z-direction. The input beam diameter was ~3.5 mm with a beam waist (ω_0) of 23 μm and the corresponding Rayleigh range being ~2.0 mm. The transmitted signal was collected using a photodiode (Thorlabs) connected to a lock-in amplifier. The data acquisition was performed using a home-made LabVIEW program.

4.3. Degenerate four-wave mixing studies

Degenerate four-wave mixing (DFWM) measurements were performed in a BOXCAR geometry, where the four beams were aligned to the three corners of the box, and the FWM signal was generated at the fourth corner of the box. The experimental configuration can be found in our previous work [31]. The measurements were performed at input energy of 1.2 μJ. A 5-mm quartz cuvette was utilized for these measurements. The fourth signal (DFWM) was collected using a power meter (FieldMax, M/s Coherent, USA) and the time-resolved profiles were recorded using a photodiode and a lock-in amplifier combination. All the instruments were controlled by a LABVIEW program for achieving fast acquisition.

Supporting Information

The following Supporting Information is available

- Figures S1-S5:** ¹H NMR spectra of HPPHT in CDCl₃; MALDI-TOF of the HPPHT; ¹H NMR spectra of ZPPHT in CDCl₃; MALDI-TOF of the ZPPHT; MALDI-TOF of the CPPHT
- Figure S6:** SADS spectra, population decay profiles and global fitting TA spectra of HPPHT.
- Figure S7:** SADS spectra, population decay profiles and global fitting TA spectra of CPPHT.
- Figure S8:** DFWM experimental data and theoretical fits of HPPHT and ZPPHT.

5. Author agreement

All authors have seen and approved the final version of the manuscript being submitted. They article is the authors' original work, hasn't received prior publication and isn't under consideration for publication elsewhere.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Naga Krishnakanth Katturi: Investigation, Formal analysis, Software, Validation, Writing - original draft. **Govind Reddy:** Investigation, Formal analysis, Writing - original draft. **Chinmoy Biswas:** Investigation, Software, Formal analysis, Validation, Writing - original draft. **Sai Santosh Kumar Raavi:** Investigation, Formal analysis, Software, Validation, Resources. **Lingamallu Giribabu:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - review & editing, Supervision. **Venugopal Rao Soma:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Acknowledgments

We thank the DRDO, India, for financial support through the project # ERIP/ER/1501138/M/01/319/D(R&D) dated February 27, 2017. RSSK acknowledges the financial support for the following project numbers BRICS/PilotCall2/IEEE-OSC/2018 (G) and SPARC/

2018–2019/P301/SL. GR and LG acknowledged the financial support from the IICT-RMIT joint research center Ph.D. program (CLP-0102) and the support offered by the Department of K&IM (IICT/Pubs./2019/305).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2020.110041>.

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