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Third-order nonlinear optical response and ultrafast dynamics of tetraoxa[22]porphyrin(2.1.2.1)s⁺

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Ultrafast dynamics and third-order nonlinear optical studies of tetraoxa[22]porphyrin(2.1.2.1)s are reported using single beam Z-scan technique with femtosecond (fs) and nanosecond (ns) pulses at respective near-IR and visible wavelengths. Excited State absorption mediated reverse saturable absorption was observed at 527 nm while two photon absorption was observed at 800 nm. High nonlinear refractive index coefficient (γ) and nonlinear absorption coefficient (β) values and the fast response times were attributed to the availability of polarizable π -electrons of the cyclic conjugated aromatic porphyrin framework. Our proposed mechanism of third-order nonlinearity were verified by ultrafast transient absorption spectroscopy. With the observed fast electronic nonlinearities the studied molecules are potential candidates for use as optical limiters.

1 Introduction

Extensive efforts have been continually invested to design π conjugated chemical entities for use in photodynamic therapy (PDT),¹ organic photovoltaics, optical communication, data processing, organic semiconductors etc.² Among these, nonlinear optical (NLO) materials with large and fast secondorder and/or third-order NLO responses are efficient candidates for the optical switches, optical rectification, optical power-limiting and future advanced photonic applications.³ Conceptually, NLO materials with fast intersystem crossing (ISC) and long triplet lifetimes are most suited for the biomedical PDT.⁴ Excited-state absorption (ESA) and electronic polarization are known mechanisms for producing large and fast NLO responses in such molecules. Materials exhibiting reverse saturable absorption (RSA)⁵ are of particular interest since these have direct applications in optical switching devices, and typically exhibit a large ratio of absorption cross-section between excited and ground states, which highlight their potential of large nonlinear attenuation in spite of low linear absorption. In addition, because optical energy is generally absorbed and converted to heat, RSA materials are well suited for use in fast optical systems and sensor protection.⁶ The overall picture of observed nonlinearities in these porphyrins can be solely described by population redistribution among the accessible energy states of the compounds under the wavelengths used for studying nonlinear processes, which gives rise to absorptive nonlinearities (change in absorption) as well as refractive

nonlinearities (change in refractive index). The complete characterization of the nonlinear optical response of a compound undertakes measurements of both absorptive and refractive nonlinearities. These parameters, which characterize nonlinear properties of materials are generally measured by Zscan⁷⁻⁹ technique (S1-S3 and Fig. S1 ESI⁺). In this technique a sample of material either solid or liquid is scanned from one side of the focus (negative Z) to other side of the focus (positive Z) along the propagation path (Z) of a tightly focused Gaussian laser beam where apertured (Close aperture Z-scan) and non-apertured (full beam transmittance) (Open aperture Z-scan) transmittance of the sample is measured as a function of sample position with respect to the focus. For a third-order nonlinear process closed aperture (CA) Z-scan technique gives sign and magnitude of nonlinear refractive index γ , which is related to the real part of the third-order nonlinear susceptibility $\chi(3)$ and Open aperture (OA) Z-scan measurements.

Porphyrin chemistry has witnessed tremendous expansion by way of modification of core as well as macrocyclic size.¹ Structure-dependent photo-physical properties¹¹ of porphyrins as well as their linear arrays¹² linked through a conjugated bridge and self-assembled architects namely porphyrin tapes, wires etc.¹³ have also been rationalized. Thus, porphyrins are ideal candidates for varied types of applications owing to the flexibility in structure modification, stability, aromaticity and the attendant interesting properties. Previous studies on porphyrins¹⁴ have shown RSA at ~532 nm, however, reports on nonlinear refraction of porphyrins in addition to RSA at ~527 nm are rare. On the other hand, porphyrins show off-resonant third-order nonlinearity and two-photon absorption (TPA) at ~800 nm. In the case of tetrathia[22]porphyrin(2.1.2.1)s and their tetraoxa analogues, we have demonstrated additional structure dependent p-channel charge transport in thin film as well as single crystal organic field-effect transistor (OFET) devices.¹⁵ More recently, excited state cross-sections of 5,16-

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diaryltetrathia[22]porphyrin(2.1.2.1) were measured using open aperture Z-scan technique at 527 nm using laser of 100 ns pulse-width at low repetition rates of 250 Hz and at very low average powers.¹⁶ In continuation of our interest in this area of investigation, we herein provide an elaborate NIO characterization response of of 5.16diaryltetraoxa[22]porphyrin(2.1.2.1)s using Z-scan technique in nanosecond (ns) and femtosecond (fs) regimes at the respective wavelengths of 527 nm and 800 nm. These porphyrins possess unique third-order nonlinear optical behaviour with wide spectral range as they show both ESA and TPA in the same solvent but at different wavelengths and pulse widths and therefore are future potential candidates for widespread application in the field of nonlinear optical materials.

2 Experimental Section

2.1 Materials and Methods

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Dimethylformamide (DMF), 1,2-dichloroethane, TiCl₄, pyridine and dichloromethane (DCM) were purchased locally, dried and distilled prior to use. POCl₃ was distilled at constant b.p. prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone (benzophenone ketyl). Anhydrous DCM was stored over fused CaCl₂ and distilled before use. Zinc dust was activated prior to use using standard (2M HCl and subsequent water washing and oven drying) methods. 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) and hydrazine hydrate were purchased from Sigma-Aldrich, and were used as received.

¹H NMR spectra were recorded on 500 MHz AVANCE III Bruker spectrometer equipped with a 5 mm double channel solution state probe using DMS0- d_6 and CDCl₃ as solvent and tetramethylsilane (TMS) as an internal standard. The high resolution mass spectra (HRMS) were recorded on Bruker MICROTOF II spectrometer. Electrochemical studies were carried out on CHI 660C Electrochemical Workstation with a conventional three-electrode configuration consisting of platinum working electrode (2 mm diameter), counter electrode and Ag/AgCl as reference electrode. The experiments were carried out on 10⁻⁴ M solutions of samples in DCM containing 0.1 м tetrabutylammoniumhexafluorophosphate (TBAPF₆) as supporting electrolyte at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for 30 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate of 100 mVs⁻¹. All theoretical studies were performed with Gaussian 09 software.¹⁷

For Z scan study at 527 nm, a frequency doubled Q-switched Nd:YVO₄ laser (Evolution 15, Coherent Inc.) was used as ns laser source operating at 250 Hz with a central wavelength of 527 nm with perfect Gaussian shaped 100 ns pulse width. A 20 cm lens was used to focus the beam into the quartz cuvette containing sample solutions mounted on a steeper motor driven stage of 0.1 μ m resolution and controlled by LabView software interfaced with GPIB through a GHz fast oscilloscope

linked to a PC. The schematic of the experimental setup is shown in Fig. S1, ESI⁺, and the experimental setup was standardized with $CS_2^{18,19}$ for 800 nm, while for 527 nm, the setup was standardized using reported compounds.¹⁶ Whole set of experiments were performed at 295 K. Time resolved fluorescence anisotropy and intensity decays were collected using a commercial TCSPC setup (LifeSpec-II, Edinburgh Instruments, UK). All samples were excited at 405 nm and the full width at half maxima of the instrument response function is about 110 picosecond (ps). For lifetime measurements, peak counts of 8000 were collected with the emission polarizer oriented at magic angle polarization and decays were collected at 480 nm. For fs studies a mode locked Ti:sapphire fs oscillator and a Ti:sapphire amplifier (Spitfire Pro XP, Spectra-Physics) pumped by a 20-W Q-switched Nd:YLF laser (Empower, Spectra-Physics) was used. The output from the amplifier generates 50-fs pulses, centered at 800 nm, with a 1kHz repetition rate and of ~4 mJ energy per pulse. Fs transient absorption measurements were performed in a commercially available spectrometer (Femto-Frame-II, IB Photonics). The beam from the amplifier output was split by means of a beam splitter into two with the major part being used to generate the pump pulses. Frequency doubling was done through a βbarium borate (BBO) crystal. A small portion of the fundamental light was allowed to pass through a computercontrolled motorized delay stage and was used to generate a white-light continuum with a spectral range of 450-770 nm by focusing it onto a sapphire crystal, which acts as probe and the other half at 400 nm used as excitation pulse acts as pump. All measurements were performed with pump energy of $\sim 1 \mu$ J, with pump polarization set at magic angle (54.7°) with respect to the probe beam. The probe was delayed in time w.r.t to the pump pulse with the help of optical delay line providing a maximum delay of 1.8 ns. The probe beam after passing through the sample cell was focused onto a 200-µm fiber optic cable, which was dispersed by means of a polychromator into a CCD camera.

2.2 Synthesis

The new member **5** substituted with *p*-BrC₆H₄ group at 5- and 16-positions of tetraoxa[22]porphyrin(2.1.2.1)s, was obtained as purple leaflets (from DCM/toluene) through DDQ oxidation of the precursor 5,16-dihydrotetraoxa[22]porphyrin(2.1.2.1) **3** (R = *p*-BrC₆H₄) obtained via McMurry coupling of 4bromophenyl-di(5- formylfuran-2-yl)methane **2** obtained via Vilsmeier-Haack formylation of 4-bromophenyl-di(furan-2yl)methane **1**. The dehydrogenation of **3** (R = *p*-BrC₆H₄) by DDQ occurred in toluene to give insoluble black complexes, which were reduced by hydrazine to crystalline **5**. All compounds/precursors involved in the synthesis of **5** were characterised using standard spectroscopic techniques (Fig. S2–S12, ESI⁺). Porphyrins **4** and **6** were synthesized as reported by us earlier.^{15a}

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Scheme 1 Synthetic scheme for 5 and structures of 8 and 9.

4-Bromophenyl-di(furan-2-yl)methane 1. To a mixture of 4bromobenzaldehyde (0.5 g, 2.7 mmol) and furan (0.4 g, 5.9 mmol), amberlyst 15 (0.5 g) was added. The mixture was stirred for 2 h at room temperature and then diluted with, DCM (100 ml). The catalyst was filtered and the solvent removed by distillation under reduced pressure. The residue was purified by column chromatograph (petroleum ether as eluent) to obtain 1 (0.36 g, 44%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.41 (d, *J* = 9 Hz, 2H), 7.33 (s, 2H), 7.09 (d, *J* = 9 Hz, 2H), 6.28 (s, 2H), 6.01 (s, 1H), 5.39 (s,1H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 153.0, 142.7, 137.4, 130.8, 128.8, 110.6, 106.9, 44.7, 21.4. HRMS: *m/z* calcd for C₁₅H₁₁O₂Br 303.1506, found 326.2462 (M⁺+23).

4-Bromophenyl-di(5-formylfuran-2-yl)methane 2. POCl₃ (0.94 g, 6.1 mmol) was added slowly to N,N'-dimethylformamide (0.48 g, 6.6 mmol) maintained below 20°C, using ice cooled water and under a nitrogen atmosphere. To this solution, 4bromophenyl-di(furan-2-yl)methane (0.5 g, 1.65 mmol) dissolved in dry 1,2-dichloroethane (30 ml) was added with vigorous stirring over 20 minutes, maintaining the temperature below 20°C. The mixture was left at r.t. for 3 h, refluxed (110 °C) for 1 h, cooled and added to a aqueous solution (15 % w/v) of sodium acetate. The mixture was refluxed for 15 minutes, cooled and extracted thoroughly with ethyl acetate (3 x 30 ml). The combined ethyl acetate extract was washed with saturated aqueous sodium bicarbonate solution and then with water. The extract was dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (60-120 mesh) and the dialdehyde 2 was isolated as thick oil (0.21 g, 35%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 9.49

(s, 2H), 7.41 (d, J = 9 Hz, 2H), 7.06-7.13 (m, 4H), 6.26 (s, 2H), 5.50 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 178.4, 155.2, 151.0, 137.4, 132.5, 130.0, 123.2, 121.5, 44.5.HRMS: m/z calcd for C₁₇H₁₁O₄Br 359.1708,found 359.2576 (M⁺).

5,16-Di-(4-bromo)phenyl-5,16-dihydrotetraoxa[22]porphyrin (2.1.2.1) 3. To a stirring suspension of zinc dust (1.88 g, 28.9 mmol) in 250 ml of THF maintained under nitrogen atmosphere, a solution of 14.4 ml of 1.0 M TiCl₄ (in DCM) was added over 20 minutes. The reaction mixture was refluxed for 1 h, and treated with a solution of dialdehyde 2 (0.52 g, 1.44 mmol) and pyridine (1.74 g, 22 mmol) dissolved in 200 ml of THF. The addition was made using a hypodermic syringe over 40 minutes to the gently refluxing suspension. After refluxing under nitrogen for 18 h, the reaction was carefully quenched with a solution of aqueous K_2CO_3 (10%, 100 ml). The reaction mixture was filtered over celite bed, and the filtrate was concentrated under reduced pressure and the residue extracted with DCM (3 x 100 ml). The combined extract was washed with water (2 x 50 ml) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was chromatographed over silica gel (60-120 mesh) to isolate 5,16-Di-(4-bromo)phenyl-5,16dihydrotetraoxa[22]porphyrin(2.1.2.1) 3 (0.052 g, 11%). M.p. >250°C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.30 (s, 4H), 7.15 (d, J = 9 Hz, 4H), 6.99 (s, 4H), 6.28 (s, 4H), 6.14 (m, 4H), 5.75 (s, 1H). 13 C NMR (75 MHz, CDCl₃, ppm): δ 155.2, 155.1, 139.8, 129.4, 128.1, 119.5, 110.7, 106.8, 44.8, 23.1. HRMS: m/z calcd for $C_{34}H_{22}O_4Br_2$ 654.3440, found 654.1278 (M⁺). 5,16-Di-(4-bromophenyl)-tetraoxa[22]porphyrin(2.1.2.1) 5. To

a solution of 3 (0.16 g, 0.24 mmol) in 5 ml toluene, a solution of DDQ (0.07 g, 0.3 mmol) in 5 ml toluene, was added under nitrogen with stirring. Shortly after mixing the two solutions and gentle reflux (1 h), purple precipitates formed and the reaction mixture was stirred for additional 2h. The purple precipitates were filtered and added in hydrazine hydrate (98%) (14.7 g, 14.3 ml). After boiling for 10 minutes, the solid was filtered, washed with water, and dried. The resulting product was dissolved in DCM and chromatographed on silica gel (60-120 mesh). Evaporation of the purple solution gave0.01 g (6.6%) of shining metallic purple 5. ¹H NMR (500 MHz, DMSO- d_6 , ppm): δ 10.66 (d, J = 15 Hz, 2H), 9.94 (d, J = 15 Hz, 2H), 9.29 (d, J = 15 Hz, 2H), 9.11 (d, J = 5Hz, 2H), 9.01 (d, J = 5 Hz, 2H), 8.35 (d, J = 5 Hz, 2H), 8.05-8.12 (m, 4H), 7.85 (d, J = 5 Hz, 2H), -5.68 (d, J = 15 Hz, 2H). HRMS: m/z calcd for C₃₄H₂₀O₄Br₂ 652.3282, found 653.4559.

3 Results and discussions

Absorption spectra of the three tetraoxa[22]porphyrin(2.1.2.1)s (Fig. 1a and S13, ESI⁺) are characterized by the presence of split (C_2 symmetry) Soret bands (414, 432 nm) and less intense Q-type bands (588, 786 nm) (Table 1), which are red shifted compared to the unsplit higher (D_{4h}) symmetric aromatic (18π) tetraoxaporphyrin dication perchlorate **8** (370 nm) and tetraoxaporphycene dication **9** (perchlorate) (372 nm) counterparts. Porphyrins **4-6** are aromatic as indicated by negative nucleus independent

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chemical shift $(NICS(0))^{20}$ (Table 1) values (Fig. S14-S16, ESI⁺) calculated at the centre of the molecular plane from the energy minimized molecular structures (Fig. S17 and S18, Tables S1-S4, ESI⁺) using Gaussian¹⁷ *ab initio* method at the B3LYP level, using Gauge independent atomic orbital (GIAO) method with 6-311G* basis set. These porphyrins have the same number of π -electrons (22 π) within their shortest

conjugation pathway, therefore there is very minimal shift in the position of Soret and Q-bands, indicating very little, if any, influence of the *meso*-substituents on the π -electrons of the porphyrin ring. Treating 5 with 70% HClO₄ yielded 20π antiaromatic dicationic species 7, the formation of which was corroborated by the disappearance of the Soret band (Fig. 1b) and broadened spectral features as are normally seen in most antiaromatic porphyrinoids.²¹ This is attributed to the facile two electron oxidation of the easily polarizable 5 to 7 as also attested by cyclic voltammogram recorded in DCM (Fig. 1b, inset for 5). Further, upon exciting the Soret band wavelength, 4-6 fluoresce, albeit weakly giving spectra that are mirror images of the absorption spectra (Fig. 1a). However, excitation of the low energy bands did not show any fluorescence. The decay process for 4-6 is slow with a time constant (singlet excited-state lifetimes, Fig. S19, ESI⁺) in the range 336-513 ps (Table 1) in the singlet excited-state $(\pi$ - π *), which also corroborates fine absorption spectral features and fluorescence compared to non-fluorescent antiaromatic porphyrins reported in literature.²²

The TPA cross-section values at 800 nm with 50 fs laser pulses are reported in Table 1. Further, since the π -conjugation pathway of **4-6** is identical, the HOMO (H)-LUMO (L) energies (Table 2) as well as H-L gaps are small and of the same order (Fig. S20-S22, ESI⁺). This also suggested larger molecular



Fig. 1 (a) Steady state absorption (solid) and fluorescence emission (dotted) spectra of 4, 5 and 6 in DCM (b) comparison of the absorption spectra of tetraoxa[22]porphyrin(2.1.2.1) 5 in DCM (i) and antiaromatic 7 (ii) formed in the presence of HClO₄ (70%) [inset: CV of 5].

Table 1.Number of $\pi\text{-electrons}$, steady-state absorption and fluorescence bands, singlet excited-state life times, NICS values and two-photon absorption cross-section σ^2 of 4-6.

N ^a	λ _{abs} (nm)	λ_{fl}	τ_{s}	k _r (s⁻¹) ^d	NICS(0)	$\sigma^{\scriptscriptstyle (2)}$ (GM) $^{ m f}$
	(DCM)	(nm)⁵	(ps) ^c		(ppm) ^e	
4 22	414,432,	563	417	1.63 x 10 ⁹	-14.6	19.4 (±0.3)
	588,786					
5 22	416,432,	566	513	1.50 x 10 ⁹	-12.5	29.0 (±0.4)
	590,786					
6 22	416,432,	567	336	1.52 x 10 ⁹	-14.6	13.0 (±0.3)
	590,786					

^aNumber of π -electrons. ^bFluorescence maximum (excitation wavelength: 410 nm). ^cSinglet excited-state lifetime. ^dDecay constant. ^eNICS(0) values were calculated at the centre of the molecular planes using Gaussian ab initio method at B3LYP level, employing GIAO (Gauge independent atomic orbital) method with 6-311G* basis set. ^fTPA cross-section values at 800 nm in SI units, where 1GM = 10^{-50} cm⁴ s photon⁻¹.

polarizability (Table 2), which is converse of molecular hardness (η) calculated by Koopman's theorem.²³ Thus, the values of the TPA cross-sections (Table 1) are in full agreement with the calculated molecular polarizability (Table 2). The presence of p-BrC₆H₄ substituents at *meso*-positions of **5** seems to render more polarizability (Table S5, ESI⁺) leading to the largest TPA cross-section value (Table 1) among the members of this series of porphyrins.

The open aperture traces were symmetric (Fig. 2) w.r.t the focus and maximum absorption was observed at the focal point. The reduction in transmittance (Fig. 2) for these porphyrins as measured by OA technique is independent of nonlinear refraction and can be used to determine β (Table 2) as nonlinear reflection is ignored. It is observed that the OA traces are symmetric w.r.t focus inferring that absorption is intensity dependent and maximum absorption occurs when the sample is at the focal point of the lens as here the on-axis intensity of the beam is maximum. The normalized OA experimental data obtained for all the three porphyrins 4-6 in DCM was fitted to equation 3 (S1, ESI⁺) and is depicted in Fig. 2. In order to account for the mechanism of nonlinear absorption occurring in 4-6, we have calculated the cross sections of the ground and excited states using fit to equation 7 (S1, ESI⁺) to obtain σ_{ex} . Likewise, σ_{gr} was calculated using equation 9 (S1, ESI⁺) and the values are tabulated in Table 2.

The excited to ground state absorption cross-section ratios (σ_{ex}/σ_g) (Table 2), which is figure of merit for optical limiting property was maximum for **4** having unsubstituted phenyl ring at *meso* position of the porphyrin and **5** bearing *p*-BrC₆H₄ group recorded the minimum value. The cross-section ratio is also indicative of the population of the excited states after ns (100 ns) pulse excitations, which in case of **4** is nearly 750 times greater in excited state, compared to ground state indicating that in this compound the initial build-up of population in the singlet excited state is significantly transferred to triplet states. The observed nonlinear process could be visualized considering a five-level energy state diagram (Fig. S23, ESI⁺).

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Table 2 Energies of the HOMO (H), LUMO (L) orbitals, average polarizability, molecular hardness, excited state and ground state absorption cross-sections, nonlinear absorption and refractive coefficients of 4-6.

	ε _{Η/} ε _L (eV) ^a	$\alpha x 10^{-41}$	η^{c}	σ_{ex} $(m^2)^d$	σ_{g} $(m^{2})^{d}$	$\sigma_{ex}\!/\sigma_{g}$	$\beta \times 10^{-8}$	$\gamma \times 10^{-15}$ (m ² W ⁻¹) ^f
4	-4.49/-2.43	1121.49	1.03	24.9x10 ⁻²¹	3.43x10 ⁻²³	725	2.77 (4.66 x10 ⁻¹⁰)	-5.91 (-4.78)
5	-4.53/-2.52	1141.10	1.00	7.49×10^{-21}	9.96x10 ⁻²³	75	2.90 (7.01 x10 ⁻¹⁰)	-3.80 (-7.92)
6	-4.43/-2.38	1096.48	1.02	7.60×10^{-21}	6.64x10 ⁻²³	114	2.18 (3.97 x10 ⁻¹⁰)	-1.55 (-5.57)

^aHOMO and LUMO energies were determined from optimized (TD-DFT) structures. ^baverage polarizability (Gaussian9). ^cDerived from Koopman's theorem: ($\epsilon_{H^-} \epsilon_L$)/2. ^dexcited and ground state absorption cross-section values recorded at 527 nm; ^{ef}calculated in DCM at 527 nm, the value in parenthesis were determined at 800 nm.

Under ns excitations, intersystem crossing (ISC) is too fast compared to the pulse duration allowing transfer of population to the triplet (T_1) excited state, with minimal contribution from the singlet (S_1) excited state. The higher values of σ_{ex} are thus attributed to RSA due to excited state absorption (ESA) from $T_1 \rightarrow T_n$. The mechanism of RSA in highly conjugated organic chromophores when excited by ns pulses are best described by five-level $\mathsf{model}^{^{24,25,26}}$ whereas excitations with ps and fs pulses are best described by threelevel model.^{27,28} In case of ns excitations significant amount of population is transferred to first excited triplet sate from initially excited singlet state as $k_{\mbox{\scriptsize ISC}}$ (Intersystem Crossing rate)_< τ (pulse width) and thus the triplet state absorption cross section $(T_1 \rightarrow T_n) \sigma_{exc,Triplet}$ contributes to the observed ESA. For ps and fs pulses, which are shorter than the time required to populate triplet states, ESA is mainly due to $S_1 \rightarrow S_n (\sigma_{exc.singlet})$ transition.²⁹ For all the three porphyrins **4-6** the larger values of σ_{ex} as compared to σ_{gr} indicates that with ns pulse excitations nonlinear absorption is mainly due to RSA. Further, RSA in the studied porphyrins is due to ESA and not due to TPA as if the nonlinear absorption was due to TPA then $\boldsymbol{\beta}$ should have remained constant with varying (increasing) the axis fluence. However, the observed decrease of the positive β with increasing axis fluence is proof of ESA assisted RSA^{30,31,32} as shown in Fig. S24 ESI.

Nonlinear refraction in compounds is generally extracted by means of closed aperture (CA) study where a finite aperture is employed before the detector. CA Z-scan alone can yield information both refractive and of absorptive nonlinearities.^{9,33,34} In the present case we have calculated nonlinear absorption coefficient β through both OA and CA techniques at 527 nm & 800 nm for all the three compounds and found that β to be similar as obtained in both OA & CA case. From Fig. 2 we see a peak (pre-focal transmittance maximum) followed by a valley (post focal transmittance minimum) which is a signature of negative nonlinear refractivity that is attributed to negative lensing effect also referred as self-defocusing effect.

The negative value of γ indicates self-defocusing effect and therefore ρ the coupling factor is positive. It is established fact that when the thermal contribution to refractive index is negative i.e. defocusing then the excited state contribution is positive.^{35,36} The current experiments were carried out with 150 ns pulse width after every 4 ms next pulse arrives thus the pulse width is very small as compared to the acoustic transit



Fig. 2 Z-scan traces of 4, 5 and 6 in DCM under closed and open aperture conditions at (i) 527 nm and at (ii) 800 nm.

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time or the rise time of thermal nonlinearity, which is the ratio of acoustic velocity to beam waist. Moreover, in the time interval of 4 ms corresponding to 250 Hz after which next pulse arrives is greater than the thermal relaxation time $(\tau = \omega_0^2 \rho C_v / 4k)$, ρ =density and C_v is specific heat of the medium) hence thermal effects do not come into play.

Under 800 nm Z-scan study, we have observed a valley (dip) in the transmittance curve as obtained in 527 nm but this dip in the transmittance is due to TPA and not ESA, which is proved by the evidence that β is independent of I₀ i.e. β is constant and is independent of the on axis input irradiance I₀. TPA cross section σ_2 in units of GM of a single solute molecule was calculated by using the following relationship:

$$\sigma_2 = rac{\beta h v}{N_A d \times 10^3} \text{cm}^4 \text{s/(molecule × photon)}$$

Where N_A is the Avogadro number, d is the concentration of the sample used, h is Planck's constant, and v is the frequency of the incident laser used. Nonlinear refractive index γ was obtained by fitting the closed aperture Z-scan traces of these porphyrins performed at 527 nm and 800 nm respectively and are shown in (Fig. 2). The positive values of β are a clear indication of RSA, while the negative values (Table 2) of γ indicated self-defocussing effect (coupling factor, positive ρ). From Fig. 2, we find that the peak valley separation follows the expression: Δ Tp-v = 1.72 Z₀, which is valid when there is thirdorder nonlinearity that arises from the electronic property of the molecule. The values of nonlinear refractive coefficient γ in the current work are greater by some 10 order of magnitude compared to organic dyes and porphyrins.³⁷ The values of γ (Table 2) also suggest the contribution of excited state to the refractive nonlinearity and is of electronic origin, as the compounds that show ESA generally exhibit excited state refraction owing to redistribution of population and the consequent change in the absorption behaviour leading to modulation of the refractive index.³⁸

In order to investigate the participation of excited state in the process of ESA mediated RSA and to investigate the excited state dynamics, fs transient absorption measurements were carried out using 400 nm pump and 450 to 750 nm supercontinuum probe, which are represented in Fig. 3 (for **4** and **5**) and in (Fig. S25 ESI⁺) for **6**. All the three porphyrins were excited at 400 nm leading to the population built up of S₂ (π , π *) state corresponding to Soret or B band (S₀ \rightarrow S₂), which

efficiently decays by efficient internal conversion (IC) to S_1 (π,π^*) state and finally to S_0 state.

In analogy to free-base porphyrins, the current porphyrins also have red-shifted Q-band at ~570 to 590 nm and in this Q-band, there is a vibronic side band at the lower wavelength of ~560 nm, which is due to transitions to higher vibrational levels in S_1 . This is unlike the free base porphyrins, where the Q-band splits into a total of four bands due to the presence of NH protons, which thereby breaks the symmetry. In our case, the Q-band only splits into two Q(0,0) and Q(0,1) bands as there is no break in symmetry due to the absence of the labile NH proton. Depletion of the Soret band at ~420 - 425 nm and bleach of Q band at ~580 - 590 nm are all observed as negative signal whereas a strong absorption (excited state absorption) is observed at the two wavelength regions of ~460 - 575 nm and at 625 - 750 nm, respectively, for all the porphyrins studied.

The transient profiles were also acquired for different concentrations (1 µm, 4 µm and 10 µm, data not shown), which showed no distinct concentration dependence, thereby strongly indicating that they were in the monomeric form in DCM solvent and not in the aggregated form. As recently reported for monomeric free base metallated and nonmetallated porphyrins,³⁹ the time evolution of the kinetic traces (Fig. 4) were analyzed by fitting a sum of three exponential time constants convolved with the Gaussian laser pulse shape. But in our case the sharpened ESA spectra is not due to the population build up for (d,d) states as no transition metal is present in the molecule. The fastest time component τ_1 in all the cases varied from 340 fs to 8 ps, which was assigned to the fast population re-equilibration process of vibrational cooling or solvation dynamics since we used the polar DCM solvent in all our experiments.^{40,41} Non-radiative $S_2 \rightarrow S_1$ relaxation, which typically occur in ~1-10 ps⁴² range for free base porphyrins and substituted porphyrins, were of longer duration (τ_2) (slower τ) in the current case. We find this trend is followed at 527 nm for all the porphyrins. Specifically, however, molecules **4** and **6** show a faster τ_2 as compared to molecule 5, which could be attributed to the bromine substitution in 5. The longer time constants τ_3 in case of molecule 4 and 5 are due to equilibrated Q-state bleach (ground state)^{40,43} but is not possible to be measured in molecule 6 within the time window of our experiment (1.8 ns).



Fig. 3 Femtosecond transient absorption spectra of 4 and 5 in DCM. (TA spectra of 6 is given in Fig. S25, ESI)

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Figure 4: Ultrafast dynamics of 4-6 in DCM at 400 nm excitation with IRF of 100 fs.

4 Conclusions

In summary, we have investigated the third order nonlinear absorption and nonlinear refraction of tetraoxa[22]porphyrin(2.1.2.1)s 527 nm and at 800 nm using pulsed lasers with ns and fs pulse widths, respectively employing single beam Z-scan technique. Non- resonant reverse saturation absorption (RSA), mediated by excited state absorption (ESA) in triplet states is the dominant process in these porphyrins upon excitation with 100 ns pulses at 527 nm and was supported by the data obtained from fluorescence life time and transient absorption measurements. The porphyrins depicted higher excited state absorption cross sections compared to ground state absorption cross section at 527 nm. TPA was observed at 800 nm with 50 fs pulses and the TPA cross-section were in the range of 10 to 30 GM. Negative nonlinear refraction indicated self-defocusing phenomena

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(negative lensing effect) which is characterized by pre-focal maxima followed by post focal minima. The refractive nonlinearity measured is of electronic origin and not of thermal origin. The large third-order nonlinearities were attributed to the electron delocalization in the 22π -electron molecular frameworks of these porphyrins. Fs pump supercontinuum probe transient absorption experiments revealed excited state absorptions in two wavelength regions, namely 450 to 570 nm and 620 to 750 nm. The wavelength region 570 nm to 620 nm represented ground state bleaching. This report constitutes a desolate study where nonlinear absorption, refraction as well as TPA are reported for tetraoxa[22]porphyrin(2.1.2.1)s.

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