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ARTICLE

Nonlinear absorption in tetrathia[22]porphyrin(2.1.2.1)s: Visualizing strong reverse saturable absorption at non resonant excitation

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The nonlinear optical absorption properties of three *meso*-substituted aromatic, neutral tetrathia[22]porphyrin(2.1.2.1) compounds were investigated using open aperture Z-scan technique at 527 nm with a pulse width of 100 ns in dichloromethane. The response obtained were accounted by invoking reverse saturable absorption arising due to strong excited state absorption. Both ground and excited state absorption cross sections are reported, which follow the same trend as the respective structural parameters.

Introduction

Nonlinear optical¹⁻⁵ materials have drawn considerable attention owing to the promising applications in the field of photonics,^{6,7} nanophotonics⁸ and optoelectronics⁹ such as optical signal processing, broad band optical communications, integrated optics, optical computing and optical limiting, etc. Nonlinear optical effects such as reverse saturable absorption (RSA) and two photon absorption¹⁰ (TPA) constitute key mechanisms of the latter. Optical power limiters are valuable devices as these cut down the risk of exposure to high energy light radiations including lasers in scientific, commercial and military establishments. RSA results when the absorption cross-section from the excited state is larger than the ground state absorption cross-section. Consequently, it also leads to lower light transmission at higher intensity/energy. The phenomenon of RSA has been observed in a number of material classes including organic and organometallic compounds, which include semiconductors, dyes, phthalocyanines and porphyrins.¹¹⁻¹⁴

Porphyrins enjoy unprecedented status of promising materials owing to the richness of the structural variability^{15,16} and the attended photophysical¹⁷ and photochemical properties¹⁸, such as, large nonlinearities, fast response time, broad-band spectral response and the flexibility in their synthesis and structural diversification and processing into device components. There has been intense effort to search for new nonlinear optical (NLO) materials¹⁹ capable of strong nonlinear absorption for applications in fluorescence microscopy, photodynamic therapy, two photon excitation,^{20,21} 3D

microfabrication,²² sensor protection,²³ optical data storage and optical limiting.²⁴ Improvement of the optical properties that determine nonlinear absorption efficiency (molecular second hyperpolarizability, γ , and excited state absorption cross-section, σ) have been achieved through modifications of the π -electron network of the porphyrin macrocycle by way of macrocyclic ring expansion,^{25,26} alteration of the macrocyclic periphery by appending peripheral substituents for enlargement of the conjugation^{27,28} and/or covalent or noncovalent assembling.^{29,30} In this context, expanded porphyrins³¹ and core modified porphyrins³² constituted efficacious NLO active materials with large excited state absorption cross-sections leading to RSA. This has been attributed, in part, to the expanded π -conjugation pathway and the consequent large number of π -electrons as well as increased number of pyrrole rings in the former.

The synthesis of tetrathia[22]porphyrin(2.1.2.1) was first reported by Cava et.al.^{33,34} almost two decades back until we reported synthesis of a variety of *meso*-elaborated derivatives.³⁵⁻⁴¹ Likewise, several tetraoxa analogues have also been synthesized and have demonstrated great potential for structure dependent p-channel charge transport in thin film as well as single crystal organic field-effect transistor (OFET) devices.^{36,39} Owing to the interesting features, these represent arguably ideal candidates for optical limiting study, which has remained elusive on this class of porphyrins. In this paper, we report excited state cross-sections of 5,16-diaryltetrathia[22]porphyrin(2.1.2.1) **1-3** 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.

Results and discussion

Porphyrins **1-3** are neutral,³⁵⁻⁴¹ thermally stable and planar members (Figure 1) with identical molecular dimensions and extensive π -electron conjugation and exhibit aromatic (22 π)

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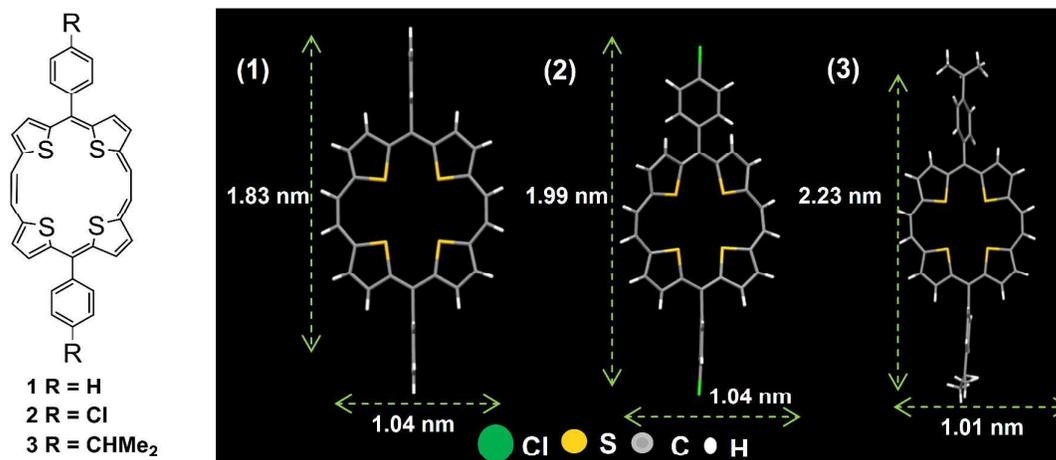


Fig. 1 Molecular structures and Density Functional Theory calculated (Gaussian09, B3LYP/6-311G) molecular dimensions of 1-3.

character according to Huckel's rule. The peripheral aromaticity is evidenced by ¹H NMR spectral features supported by the existence of diatropic ring currents in these molecules as seen from the considerable downfield chemical shifts of the β_{CH} (Δδ = 3.75-3.82 ppm) and ethene protons (Δδ = 4.46-4.60 ppm, Table 1) as well as a large negative NICS(1)⁴²⁻⁴⁴ values in the range 13.11-13.67 ppm, calculated at the centre of the π-conjugated circuit. Bond length alteration values (Table 1) further supports aromaticity of these compounds. The UV-visible absorption spectroscopic data (Figure 2A) is consistent with fully aromatic porphyrins and is characterized by Soret and Q-type bands.

Measurement of excited state cross-section for porphyrins **1-3** was performed in dichloromethane with 527 nm laser pulses of 100 ns width at repetition rate of 250 Hz. Sample solutions (1 mM, CH₂Cl₂) of **1-3** were taken in a 1 mm quartz cuvette and scanned along the direction of propagation of the laser on a motorized stage that was computer controlled through general purpose interface bus (GPIB) using LabView© programming. The open-aperture Z-scan setup was calibrated using *trans*-stilbene (1 mM, CH₂Cl₂). Comparing absorption spectra of **1-3** before and after Z-scan experiments suggested no photo-degradation, which also confirmed stability of these compounds to measurement conditions. Compounds **1-3** were almost transparent at 527 nm (Figure 2A). Thus, the nonlinear optical measurements were performed with non-resonant excitation. The solvent itself did not show any RSA under the experimental conditions. The excited state absorption cross section σ_{ex}, were calculated by assuming that these systems can be modelled by a simple five-level system (Figure 3). In this model, molecules are optically excited to the first singlet excited state from the ground state and thereafter they either relax directly to the ground state or to a low lying triplet state. Finally, assuming that intersystem crossing (ISC) is very fast compared to the pulse width (100 ns), the low lying triplet state is depleted due to excited state absorption.

The transmitted intensity in Z-scan can be written as:⁴⁵

$$T = \frac{\ln\left(1 + \frac{q_0}{1+x^2}\right)}{\left(\frac{q_0}{1+x^2}\right)}$$

We have: $q_0 = (\sigma_{ex}\alpha FL_{eff})/2hv$, $x = Z/Z_0$, where Z_0 is the Rayleigh range, F is the fluence of the laser at the focus i.e., at $Z = 0$, and $L_{eff} = (1 - e^{-\alpha l})/\alpha$; where l is the sample thickness. The experimental data were fitted to the above equation, which yielded the excited state cross sections (σ_{ex}). The ground state absorption cross section, σ_{gr} values were calculated from the linear absorption coefficient, $\alpha = \sigma_{gr}N_A C$, where N_A is Avogadro's number and C being the concentration of the analyte used in mol cm⁻³ and the value comes out to be 3.32 X 10⁻¹⁹ cm², 3.01 X 10⁻¹⁹ cm² and 3.18 X 10⁻¹⁹ cm², respectively, for **1**, **2** and **3**. In molecules exhibiting strong RSA in the visible region, which includes metallo-porphyrins⁴⁶, azulenes⁴⁷, and metallo-phthalocyanines,^{48,49} the typical cross section ratios σ_{ex}/σ_{gr} are between 10 and 100 and in some extreme cases in the region of 200.⁵⁰ However, in the present work, we report very high cross-section ratio (σ_{ex}/σ_{gr}) as 250, 498 & 197 for compounds **1**, **2** and **3**, respectively, at 527 nm.

The structural and geometric properties and excited state cross section values of **1-3** are given in Table 1. All the three compounds have 22-π electrons in the macrocyclic conjugation pathway, however, the HOMO-LUMO gap is marginally smaller in **2** compared to other congeners, the consequent larger molecular polarizability and hence global softness (as inferred from the inverse of molecular hardness, η)⁵¹ may account for the observed higher excited state cross-section value. In other words, compound **2** with the smallest HOMO-LUMO gap and less molecular hardness (i.e. larger molecular polarizability) has the largest excited state cross-section value at the measured wavelength. The observed trend of cross-section values could also be correlated with the electronic effects of the electron withdrawing (Cl) and electron donating bulky (*iso*-propyl) substituents in **2** and **3**, respectively, compared to their

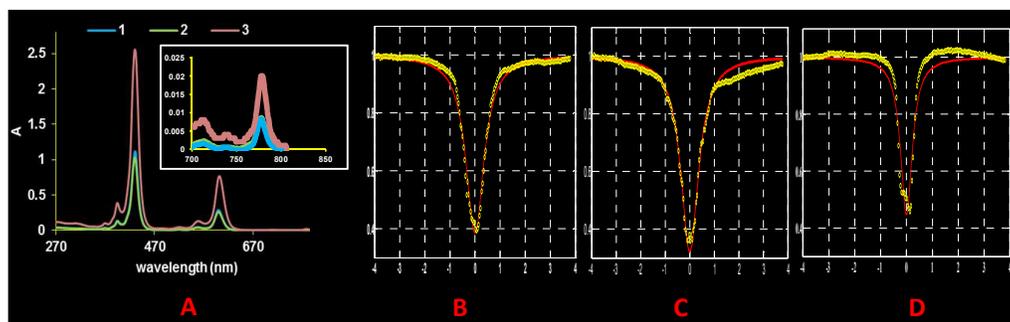


Fig. 2 (A) UV-visible absorption spectra of **1-3** (Inset: 700-850 nm region). (B-D) Open aperture Z-scan traces (Normalized transmittance vs Z (mm)) of **1, 2** and **3**, respectively measured at a 120 ns pulse. The sample concentration is 1.0 mM. The solid lines are the best-fitted curves of the experimental data.

Table 1 Structural properties and excited state cross sections of **1** to **3**.

Compound	N^a	ΔR_x (Å) ^b	ΔR_o (Å) ^c	$\Delta \delta_e$ (ppm) ^d	$\Delta \delta_{\beta CH}$ (ppm) ^e	σ_{ex} (cm ²) ^f	ϵ_H (eV) ^g	ϵ_L (eV) ^g	H-L (eV) ^g	η^h
1	22	0.00	0.00	4.60	3.78	8.32×10^{-17}	-4.86	-2.54	-2.32	1.16
2	22	0.0037	0.00	4.46	3.82	1.50×10^{-16}	-4.89	-2.78	-2.11	1.05
3	22	0.0102	0.00	4.56	3.75	6.27×10^{-17}	-4.86	-2.55	-2.31	1.15

^aThe number of π -electrons in the cyclic conjugated pathway. ^bBond length alternation obtained from single crystal X-ray diffraction analysis.³⁶⁻³⁸ ^cBond length alternation deduced from optimized structures (Gaussian 09: B3LYP/6-311G). ^dDifference between the most upfield ethene signals in 5,16-dihydro tetrathia[22]porphyrin(2.1.2.1) and the most downfield ethene signals in the fully aromatic tetrathia[22]porphyrin(2.1.2.1). ^eDifference between the most upfield β_{CH} signals in 5,16-dihydro tetrathia[22]porphyrin(2.1.2.1) and the most downfield β_{CH} signals in the fully aromatic tetrathia[22]porphyrin(2.1.2.1). ^fExcited state absorption cross-section values were measured at 527 nm. ^gHOMO and LUMO energies were determined from the optimized (TD-DFT) structures. ^hderived from Koopmans theorem: $\eta = (\epsilon_L - \epsilon_H)/2$.

unsubstituted congener **1**. Thus, the electron withdrawing Cl substituents would stabilize the LUMO leading to a reduced band gap as also observed experimentally (Table 1).

Correlation between aromaticity, photophysical properties such as steady-state absorption, excited state life times and excited state cross-section values between set of 22 π aromatic congeners **1-3** has been deduced. The excited state decay profiles of **1-3** indicate the lowest singlet excited state lifetimes of 170, 1500 and 140 ps, respectively (Table 2) and correlate well with the excited state cross-sections values. Surprisingly large (1500 ps) singlet excited state life time of **2** meant slow excited state relaxation i.e. a decelerated internal conversion between S_1 to S_0 states in spite of marginally lower optical band gap (Table 1).

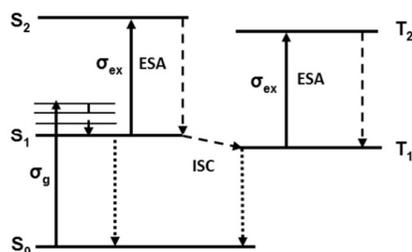


Fig. 3 Proposed energy level diagram with different optical transitions. Excited singlet stage absorption (ESA) process is due to $T_1 \rightarrow T_n$ absorption because of ns pulse width which allows transfer of population from $S_1 \rightarrow T_1$ through ISC thus facilitating the $T_1 \rightarrow T_n$ ESA process (see text for details).

Table 2 Steady-state absorption and fluorescence bands, Stokes shift, and singlet excited state life times of **1-3**.

Compound	λ_{em} (nm) ^{a,b,c}	I_{fl}^d	ΔE_{stokes} (cm ⁻¹) ^e	τ_s (ps) ^f	K_r^g (s ⁻¹)
1	510	38	3647.97	170	5.9×10^9
2	456	296	1325.99	1500	6.6×10^8
3	484	869	2594.65	140	7.1×10^9

^aLowest energy absorption bands were at 430 nm, ^bExcitation wavelength: 430 nm, ^cFluorescence maximum, ^dIntensity of fluorescence emission, ^eStokes shift (i.e. the energy gap between a and c), ^fSinglet excited-state lifetime, ^gDecay constant

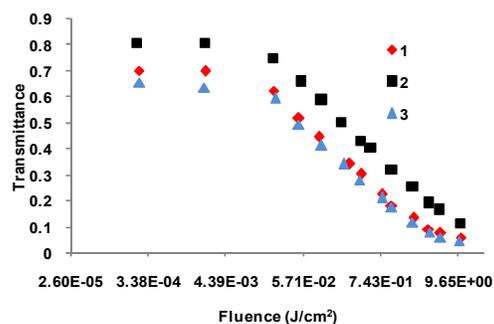


Fig. 4 Normalized transmittance of **1-3** as a function of the laser pulse fluence (527 nm).

The optical limiting potentials of **1-3** are very good (Figure 4) at the measured wavelength (527 nm) using dilute (1 mM) solution to exclude any aggregation of **1-3**. Most importantly, the damage fluence thresholds (i.e., fluence at which the material undergoes irreversible photo-physical changes) are considerably lower. The fluence threshold is found to be 0.310, 0.53 and 0.217 J/cm², respectively for **1-3**, which are quite low compared to the porphyrins and phthalocyanins reported in literature.

Conclusions

In summary, we herein describe reverse saturable absorption (RSA) of neutral, aromatic tetrathia[22]porphyrin(2.1.2.1)s in dichloromethane using open aperture Z-scan technique with 527 nm laser pulses of 100 ns width, which arises due to excited state absorption. The excited state absorption cross-section values of these porphyrins correlate well with the structural properties. Further, the observed RSA response could be due to the π -conjugation as well as large π -electronic interactions between the flat aromatic porphyrins. Given the observed low fluence threshold values, these porphyrin derivatives are possible candidates for optical limiting applications.

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Nonlinear absorption in tetrathia[22]porphyrin(2.1.2.1)s: Visualizing strong reverse saturable absorption at non resonant excitation †

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meso-Substituted neutral, aromatic tetrathia[22]porphyrin(2.1.2.1) represent a new entry in the family of nonlinear optically active porphyrins and show structure dependent reverse saturable absorption. Given the observed low fluence threshold values, these porphyrin derivatives endorse potential application as optical limiters.

