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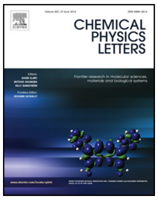

Strong two-photon absorption properties and ultrafast pump-probe studies of novel porphyrin derivatives

Debasis Swain[a], Anup Rana[a,b], Pradeepta K. Panda[a,b], S. Venugopal Rao[a,*]

[a] *Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, India*
[b] *School of Chemistry, University of Hyderabad, Hyderabad 500046, India*

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ABSTRACT

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.

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

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* Corresponding author.
E-mail addresses: svrsp@uohyd.ernet.in, soma_venu@yahoo.com, soma_venu@uohyd.ac.in (S. Venugopal Rao).

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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_2TCTMP) 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_2TCTMP 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_2OMP) 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 ($2\omega_0$) 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 nonlinear 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.

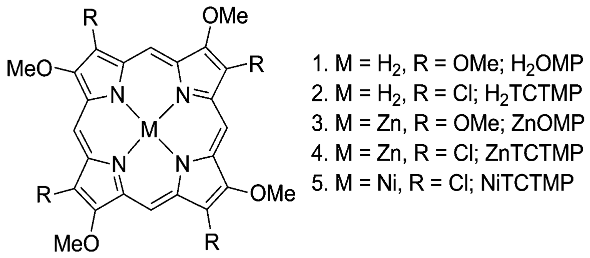

Figure 1. Structures of the β-substituted porphyrins used in present study.

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_2OMP, ZnOMP, H_2TCTMP, ZnTCTMP and NiTCTMP are presented in Figure 2a [40]. Freebase porphyrin H_2OMP and H_2TCTMP 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_2OMP and H_2TCTMP 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

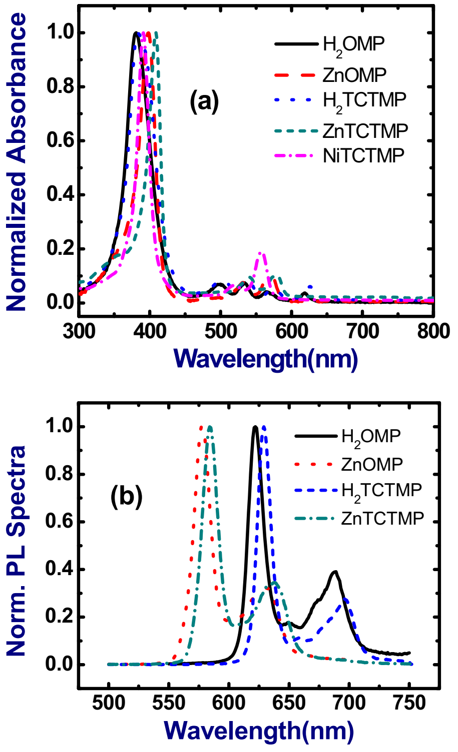

Figure 2. (a) UV–vis spectra of the studied porphyrins (in chloroform) demonstrating strong absorbance near 400 nm. (b) Emission spectra of H_2OMP, ZnOMP, H_2TCTMP, ZnTCTMP in chloroform. NiTCTMP did not show any detectable fluorescence.