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Nonlinear absorption properties of ‘axial-bonding’ type tin(IV) tetratolylporphyrin based hybrid porphyrin arrays

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Abstract

The nonlinear absorption properties of ‘axial-bonding’ type hybrid porphyrin arrays based on a tin(IV) *tetratolylporphyrin (SnTTP)* scaffold are studied with picosecond and nanosecond pulses. The effect of different central metal atoms substituted adjacent to the tin(IV) porphyrin in the oligomer structure is discussed. In the picosecond regime the lifetimes of the excited singlet states and two-photon absorption (TPA) processes dominate leading to interesting switching of nonlinear absorption behaviour. The TPA cross-section (σ_{TPA}) is found to be as high as 396×10^{-46} cm^4 s photon^{-1} molecule^{-1}, for an oligomer with Sn and Ni porphyrin macrocycles. However, in the nanosecond regime the optical limiting performance has increased considerably with increasing number of porphyrins in the array and excited state absorption is found to play a major role.

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1. Introduction

Nonlinear absorption is a phenomenon defined as an increase or decrease in the absorption coefficient with increasing intensity. The former response is called as reverse saturation of absorption (RSA), while the latter is known as saturation of absorption (SA). Organic materials with delocalized electrons are of great importance because of their large nonlinear optical absorption coefficients, architectural flexibility, and ease of

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fabrication. Recently materials showing RSA behaviour have been in focus for optical limiting applications [1]. SA in various materials has been studied for applications in laser pulse compression and laser amplification [2,3]. An intense laser pulse redistributes the molecular population between the ground and excited states causing a transient modification in the optical properties of the material. The dependence of transmission of organic molecules on light intensity can yield considerable information on the molecular level system that can lead to variety of nonlinear optical processes like limiting, switching and bistability. Metalloporphyrins and metallophthalocyanines form an important class of electronic materials because of the large π-electron conjugation over two-dimensional molecular structure [4,5]. Interest in advanced electronic and photonic materials recently has led to the exploration of conjugated polymers of more complex units, such as porphyrins [6]. The high polarizability and optical oscillator strength of the porphyrin macrocycles gives these materials remarkable nonlinear optical (NLO) behaviour, making them potentially useful for ultrafast switching technologies. High values of the nonlinear refractive index n_2 (which is proportional to the real part of the third order susceptibility $\chi^{(3)}$) are essential for electro-optical and all-optical switching [6], whereas high nonlinear absorption coefficients, β (proportional to the imaginary part of $\chi^{(3)}$) are important for optical limiting [7]. The architecture of the porphyrin macrocycles is important for developing materials with optimum nonlinearity and response times [8]. Structural modifications to the porphyrin ring can be expected to yield molecules with diverse photophysical and photochemical properties that will in turn affect their optical nonlinearity. This would lead to an increase in a variety of excited state processes including enhanced internal conversion and intersystem crossing (ISC), ion-association, excitation energy transfer, photoinduced electron transfer, etc. [9]. Such effects can be conveniently harnessed to enhance the third order nonlinearity and nonlinear absorption properties, hence to develop promising materials for various applications. Excited state absorption (ESA) is the most important mechanism leading to optical limiting in porphyrins [10–12]. Our group has been involved in studies on a class of porphyrins, known as tetratolylporphyrins, for achieving higher optical limiting performance and nonlinear absorption. The tetratolylporphyrins synthesized have higher third order nonlinearities [10,11,13] and efforts are being made to attain large excited state absorption cross-sections through structural modifications. In this paper, we discuss the nonlinear absorption properties of oligomers based on Sn(IV)TTP scaffold that lead to an interesting nonlinear switching behaviour.

2. Molecular structure and linear optical properties

The nomenclature of monomer and dimer molecule is *meso*-5,10,15,20-(tetratolyl) porphyrinato tin(IV) dihydroxide; $[(TTP)Sn^{IV}(OH)_2]$ and [μ-[5,10,15-tri(*p*-tolyl)-20-[4-[2-[4-[10,15,20-tri(*p*-tolyl)-5-porphyrinyl]phenoxy]ethoxy]phenyl] porphyrinato]] di(tin)(IV)tetrahydroxide; $[(TriTP)-Sn^{IV}(OH)_2]–O(CH_2)_2O–[(TriTP)Sn^{IV}(OH)_2]$, respectively. Dimer molecule has two monomers linked at *meso* position with ethoxy spacer. Monomer and dimer are synthesized following the procedure reported in the literature [14,15]. For simplicity we mention them as SnTTP and $Sn–Sn(TTP)_2$ in this paper. Sn^{IV} porphyrin based, 'axial-bonding' type hybrid trimers and hexamers are constructed by employing 'building-block' approach. The approach involves simple inorganic reactions such as axial bond formation of main group element containing porphyrins and insertion of metal/metalloid ions into the porphyrin cavity. The architecture of the trimer arrays [16] is such that Sn^{IV} complex of *meso*-5,10,15,20-(tetratolyl)porphyrin forms the basal scaffolding unit, the free-base, Ni^{II} porphyrins occupy the two axial sites via an aryloxy bridge. The nomenclature of the porphyrin trimer arrays discussed here is as follows: (free-base porphyrin)$_2$ (tin(IV) porphyrin) ≡ $[(TTP)–Sn^{IV}(H_2TriTP(O))_2]$ and (nickel(II) porphyrin)$_2$ (tin(IV) porphyrin) ≡ $[(TTP)–Sn^{IV}(NiTriTP(O))_2]$. For simplicity these trimers are referred as $Sn–(H_2)_2(TTP)_3$ and $Sn–Ni_2(TTP)_3$, respectively. The scheme of construction of