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Enhanced two photon absorption cross section and optical nonlinearity of a quasi-octupolar molecule

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ABSTRACT

Two photon absorption (2PA) cross sections of two quasi-octupolar molecules (*E*,*E*,*E*)-2,4,6-tris [2-(4-*N*, *N*-diphenylaminophenyl)vinyl]pyridine (DPATSP) and (2,4,6-tris((*E*)-4-(diphenylamino)styryl)-1-methylpyridine-1-ium iodide, DPATSP-Me) have been estimated. It has been found that by introducing the pyridinium ion, the 2PA cross section of DPATSP-Me increases with respect to the parent molecule, DPATSP. Z-scan experiments on the two samples reveal that DPATSP-Me is a better candidate for optical limiting applications.

1. Introduction

Synthesis and characterization of new multiphoton absorbing materials is an active area of research due to their widespread technological applications in optical limiting [1–3], up-converted lasing [4,5], microfabrication [6–8], 3-D optical data storage [9,10], bioimaging [11,12] and photodynamic therapy [13]. Organic molecules with electron rich donor (D) and electron deficient acceptor (A) motifs connected with a π-bond constitute the easiest and most effective class of nonlinear optical (NLO) materials compared with other inorganic NLO materials. Depending upon the symmetry, these organic molecules are classified into dipolar (D-π-A), quadrupolar (D-π-A-π-D, A-π-D-π-A, ...), and octupolar (A_3-D, D_3-A, . . .) types. The simplest among them, the dipolar has a nonzero dipole moment in the ground state and has limitations with respect to assembling, in addition to polarization dependence of the second order optical nonlinearity, $\chi^{(2)}$. In contrast, quadrupolar molecules have no ground state dipole moment and their $\chi^{(2)}$ values are identically zero due to center of inversion symmetry. Compared with both dipolar and quadrupolar systems, octupolar molecules possess a non-polar ground state, non-centrosymmetric assembling, isotropic structure and polarization independence of the $\chi^{(2)}$ process [14,15]. Owing to these properties, octupolar molecules have been found to be better candidates for multiphoton applications [16–20].

In an earlier paper, we reported the synthesis and characterization of a quasi-octupolar molecule, (*E*,*E*,*E*)-2,4,6-tris [2-(4-*N*,*N*-diphenylaminophenyl)vinyl]pyridine (DPATSP) (Fig. 1, panel A) [21]. Its 2PA cross section (σ_2) was estimated using the two-photon induced fluorescence (2PIF) method. The *N*-methyl derivative of DPATSP (abbreviated as DPATSP-Me, (Fig. 1, panel B)) is expected to have a red shifted absorption and emission spectra compared with DPATSP because of the increased amount of intramolecular charge transfer (ICT). This led to a considerable spectral overlap and Förster resonance energy transfer (FRET) between DPATSP and DPATSP-Me was observed to be efficient [21].

Molecules with pyridinium core with donor moiety other than diphenylamino group have been studied and are reported to possess large value of σ_2 [22,23]. Since the pyridinium ion will attract electrons more strongly than pyridine it is expected that replacing pyridine with pyridinium can further augment the ICT to yield an increased 2PA cross section. However we observed that although the pyridinium derivative exhibited a 2PIF signal under *fs* pumping at 800 nm, the fluorescence yield of DPATSP-Me was considerably lower than that of DPATSP. This indicates that the 2PIF method is not very efficient for the estimation of σ_2 in this case. Therefore, the nonlinear transmission technique of Z-scan [24] has been used for the determination of σ_2 for DPATSP-Me. The nonlinear optical coefficients for DPATSP have also been measured for comparison purposes. By using the techniques of open and

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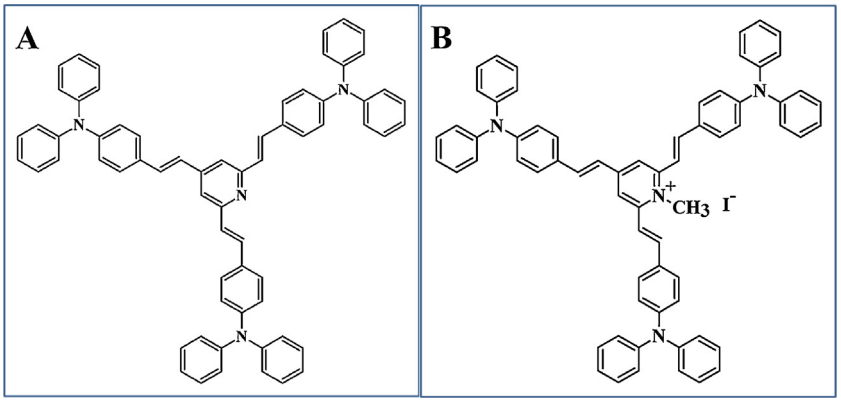

Fig. 1. Molecular structure of DPATSP (panel A) and DPATSP-Me (panel B).

closed aperture Z-scans, the effects of increased acceptor strength on the 2PA cross section and third order optical nonlinear susceptibility have been measured and are discussed in this paper.

2. Experimental

The detailed synthesis procedure of two quasi-octupolar dyes DPATSP and DPATSP-Me is given elsewhere [21]. All solvents were used as received and dye solutions of suitable concentrations were made by dissolving in toluene (SD Fine Chem., Ltd./VWR International). The steady-state absorption and fluorescence spectra of the samples were recorded by a UV visible dual beam spectrometer (Varian, Cary 400) and a fluorimeter (Jasco, FP-6600), respectively. The spectrograde solvents were checked for the purity by recording the absorption spectra, as well as by the fluorescence measurements at the excitation wavelengths. For the Z-scan experiments, laser pulses at 800 nm of 30 fs duration at a pulse repetition rate of 82 MHz were obtained from a Coherent Micra oscillator. The laser was focused using a 100 mm focal length double convex lens on the sample. The front iris was used to control the input power and the Rayleigh range. The samples were held in a 1 mm thick cell that moved in the focal plane of the lens. Another 100 mm diameter (focal length of 200 mm) lens was kept at the far field in order to collect all the transmitted light. The collected light was fed to a fast photodiode (Thorlabs, DET10A) connected with an oscilloscope (Tektronix, TDS3032B).

Time correlated single photon counting (TCSPC) technique [25] was used for the time-resolved characterization. The samples were excited using a ps diode laser (50 ps, 1 MHz, PiL040 (406 nm,) and PiL047 (470 nm), Advanced photonics systems, Germany) while the fluorescence was collected in a back scattering geometry by an epifluorescence microscope (E400, Nikon), dispersing by a monochromator (Oriel, 77250). A photomultiplier tube (PMT) (Hamamatsu R928) was used as a detector. The decay curves were recorded with the help of a TCSPC card and the software (T900, Edinburgh Instruments). A commercial software package (FAST, Edinburgh Instruments) was used for the data analysis. The goodness of the fit was judged by the value of the χ^2 and the distributions of the residuals [26].

3. Theoretical aspects: closed aperture (CA) and open aperture (OA) Z-scans

The rate of change of light intensity in a pure 2PA process is given by [27],

$$\frac{dI}{dz} = -\beta I^2 \tag{1}$$

where β is the 2PA coefficient. It is a macroscopic parameter for characterization of the material.

The β and σ_2 are related by,

$$\beta(\omega) = \frac{N}{E}\sigma_2 \tag{2}$$

where N is the concentration (in units of cm^{-3}) and E is the photon energy. Hence the σ_2 (in units of 1 GM = 10^{-50} cm^4 s^{-1}) of a single solute molecule can be determined by using the following relationship,

$$\sigma_2 = \frac{\beta h\upsilon}{N_A d \times 10^3} \tag{3}$$

where N_A is the Avogadro number, d is the concentration of the sample, h is Planck's constant, and υ is the frequency of the incident light.

The value of β can be experimentally determined by performing Z-scan experiments. The normalized transmittance in the closed aperture (CA) Z-scan in the low irradiance limit for Gaussian type profiles is given by [24],

$$T(z) = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\varphi - \frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\psi \tag{4}$$

where $x = z/z_0$, where z_0 is the Rayleigh range, $\Delta\varphi$ and $\Delta\psi$ are the on-axis phase shifts due to refractive nonlinearity and absorptive nonlinearity, respectively and L_{eff} $(=1-\exp(-\alpha_0 L/\alpha_0))$ is the effective path length. The nonlinear absorption (β) and refractive (η_2) indices of the sample are related to the $\Delta\psi$ and $\Delta\varphi$, respectively as follows,

$$\beta = \frac{2\Delta\psi}{I_0 L_{eff}}(\mathrm{m/W}) \tag{5}$$

$$\eta_2 = \frac{\Delta\varphi}{kI_0 L_{eff}}(\mathrm{m^2/W}) \tag{6}$$

Here I_0 is input irradiance at $z = 0$ and k is the propagation vector.

For the case of open aperture (OA) Z-scan, the transmittance is insensitive to the beam distortion and depends only on the nonlinear absorption of the material [28]. Therefore, the normalized transmittance will be,

$$T(z) = 1 - \frac{1}{(x^2+1)}\Delta\psi \tag{7}$$