Synthesis and characterization of strongly two photon absorbing and photoswitchable azo molecules

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ABSTRACT

Here we describe the synthesis and characterization of a range of symmetric two photon absorbing chromophores containing photoswitchable Disperse Red-type donors. These have been incorporated into D–π–D molecules with 1-(2-ethylhexyloxy)-4-methoxybenzene and 9,9-bis(2-ethylhexyl)-fluorene π-cores, and D–π–A–π–D molecules based on a (2,6-dimethyl-pyran-4-ylidene)propanedinitrile acceptor core. The TPA cross section measured by z-scan at 780 nm was up to 298 GM for the D–π–A–π–D molecules and up to 1250 GM for the molecules with D–π–D architectures. As all of the compounds have azo groups as part of the π linker the cis/trans isomerisation of these materials was also explored. It is found that dyes based on the D–π–D architecture are more amenable to isomerisation and are also more stable in the cis form when compared to D–π–A–π–D chromophores.

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1. Introduction

Recently there has been much interest in chromophores with high two photon absorption (TPA) cross sections due to their applications such as optical switching [1], two photon initiated polymerization [2], and fluorescence microscopy [3–6]. The advantage of TPA is that chromophores are able to be excited by photons with energies outside of their one photon absorption band. Furthermore, the rate of two photon absorption is quadratically dependent upon the excitation intensity, I, compared to the linear dependence of one photon absorption on I [7]. Using an intense focused laser beam TPA only occurs in the immediate vicinity of the focal point. This is because the TPA cross section falls off rapidly and only occurs where there is a high photon density. Consequently, focused TPA is useful for obtaining high precision in laser micromachining [8] and micro-paterning/readout in rewritable optical data storage applications [9].

For two photon data storage, materials which show both TPA and photo-switching functionality are of particular interest [10]. Azo-benzene – along with a number of other azo containing compounds – are some of the best known photochromic materials and the characteristic trans–cis photo-isomerisation of the azo-family of molecules has been extensively studied. Azo molecules typically exist as the trans isomer as opposed to the less stable cis isomer.

These two isomers can be easily interconverted by illumination with light at an appropriate wavelength, reaching a photostationary state where the two isomers are at equilibrium [11]. Although there have been previous studies done on the TPA activity of azo compounds [9,12], most studies have concentrated on their second order nonlinear optical properties. As a result there have been few studies to date focusing on the optimisation of TPA within azo systems [13].

Symmetric D–π–D and D–π–A–π–D chromophores (where D is an electron donor, A is an electron acceptor and π is a π-conjugated bridge) have been reported as promising molecular architectures for high TPA cross section materials [7,14]. For example chromophore 1 (Fig. 1) is based on such a D–π–D molecular architecture, with a 9,9-bisoctyl-fluorene core, and has a reported TPA cross section of 1140 GM [14]. As part of our studies into multifunctional materials for laser micromachining we are interested in developing compounds that combine both a high TPA cross section along with an ability to undergo photo-switching in order to realise either a refractive index or volume change. Consequently we report here the synthesis and characterization of a range of symmetric D–π–D chromophores with either a 1-(2-ethylhexyloxy)-4-methoxybenzene (**phenylene**) or 9,9-bis(2-ethylhexyl)-fluorene (**fluorene**) core, as well as D–π–A–π–D molecules with a (2,6-dimethyl-pyran-4-ylidene)propanedinitrile (**pyran**) core. We have also measured their TPA cross sections by z-scan at 780 nm as well as their photo-switching properties. Combining this large TPA cross section with photoswitchable structures make these interesting novel chromophores.

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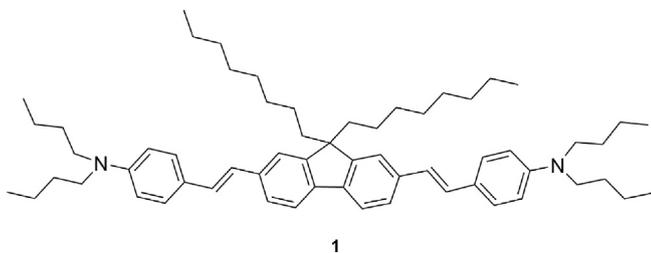
Fig. 1. Structure of a D−π−D chromophore based on a 9,9-bisoctyl-fluorene core with reported TPA of 1140 GM [14].

2. Experimental

2.1. Reagents and procedures

Commercially available reagents were obtained from Sigma Aldrich and were used without additional purification. The solvents used were of analytical grade and were also used without further purification. Flash column chromatography was carried out on Silicycle SiliaFlash F60 silica (230−400 mesh) with the stated solvent systems. Analytical thin-layer chromatography (TLC) analyses was performed on pre-coated plates (Merck aluminium sheets, silica gel 60F 254, 0.2 mm). Visualisation of chromophores was achieved by illumination under ultraviolet light (254 nm).

2.2. Measurements and instrumentation

Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker Avance 500 MHz spectrometer with solvent peaks used as reference. Liquid chromatography-mass spectrometry (LCMS) was run on a Waters Q-TOF Premier™ Tandem Mass Spectrometer. Melting points were recorded with an EZ-Melt automated melting point apparatus and are uncorrected. UV visible absorption spectra of the chromophores at a concentration of 1×10^{-5} mol/L in DMSO were collected using a Perkin Elmer Lambda 1050 spectrophotometer. Spectra were then normalized to unity at their maxima for easier comparison. To characterize the photochromic behaviour of the chromophores an ocean optics fibre optic spectrometer was used to obtain absorption spectra while the solutions were illuminated at different wavelengths using high power LEDs.

An open aperture z-scan setup was used to study the two photon absorption properties of the chromophores. A schematic of the apparatus used is shown in Fig. 2. The change in transmittance is measured while the sample is moved through the focal point of the lens using a translation stage. A Toptica femtosecond fibre laser

with pulse duration of 100 fs, a repetition rate of 80 MHz and operating at a wavelength of 780 nm was used. The resulting optical intensity in the focal point was 2.4 GW/cm^2. Due to the high repetition rate thermal effects can have a profound effect and influence the measurement. Therefore a modified z-scan setup was used and an optical chopper was incorporated to manage and minimize thermal effects [15−18]. The chopper frequency was set at 100 Hz and had a duty cycle of 0.82%. This resulted in the sample being illuminated for 82 μs every 10 ms. The rise time was 6 μs due to the finite size of the beam at the chopper and the transmittance through the sample was measured exactly after the rise time using a digital oscilloscope. The reference detector (D1) was used to account for fluctuations in the laser intensity and was also used as the trigger for the oscilloscope. A solution of Rhodamine 6G in methanol was used as the reference standard to verify the setup and resulted in a TPA cross section of 28 GM, which is consistent with the values reported in the literature [19]. All measurements were performed on solutions in DMSO with concentrations ranging from 9.5×10^{-3} mol/L to 2.4×10^{-2} mol/L.

The open aperture scan can be used to directly obtain the nonlinear absorption coefficient (β). When the third order nonlinear losses are small ($\beta IL_{eff} \ll 1$), the normalized change in transmittance due to two photon absorption can be approximated by [20];

$$\Delta T(x) = \frac{-q_0}{2\sqrt{2}} \frac{1}{1+x^2} \qquad (1)$$

With $q_0 = \beta I_0 L_{eff}$ and $x = z/Z_0$, where Z_0 is the Rayleigh length, I_0 is the peak intensity. $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective sample length which in this case is approximately equal to the sample length due to the low absorbance at the wavelength used. The molecular two photon cross section σ_{TPA} can be obtained from β using the following relation;

$$\sigma_{TPA} = \frac{\hbar\omega\beta}{N_a C} \qquad (2)$$

where N_a is Avogadro's number, C the concentration, $\hbar$ the reduced Planck constant and ω the angular frequency.

2.3. Preparation of chromophores

The synthetic procedure used to prepare the chromophores used in this study is shown in Scheme 1. The azo aldehydes 4-((4-(ethyl(2-hydroxyethyl)amino)phenyl)diazenyl) benzaldehyde (**2**) and 4-((4-(bis(2-hydroxyethyl)amino)phenyl)diazenyl) benzaldehyde (**3**) were synthesised by the methods of Su et al. [21] and Ledoux et al. [22] respectively. Tetraethyl ((9,9-bis(2-ethylhexyl)-
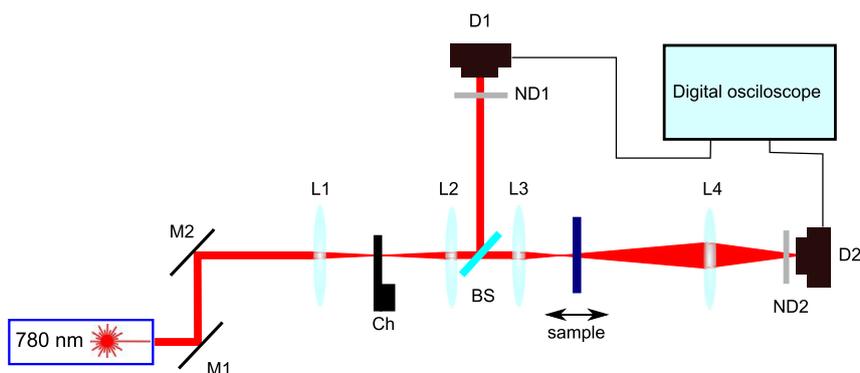

Fig. 2. Schematic of the used z-scan setup, (Ch = chopper, L = lens, D = photodiode, M = mirror, ND = neutral density filter and BS = beam splitter).