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Research paper

Broadband two-photon absorption cross sections of benzothiazole derivatives and benzobisthiazolium salts

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Two-photon absorption (TPA) cross sections of conjugated donor-π-acceptor dipolar structures containing benzothiazole or benzobisthiazolium moieties are determined in a broad spectral range from 700 nm to 1000 nm using two-photon induced fluorescence technique. The TPA cross section values range from 150 GM to 4600 GM. The largest values are observed in near-infrared region. The dipolar derivative of benzothiazole has the largest TPA cross section of 4600 GM at wavelength of 890 nm. A combination of the large TPA in the near-infrared region and the high emission quantum yield makes these compounds excellent candidates for two-photon fluorescence microscopy.

1. Introduction

Two-photon absorption (TPA) cross section characterizes a simultaneous absorption of two photons in the same quantum event [1], quantitatively. TPA plays an increasingly important role in a number of areas, such as fluorescence microscopy [2–5], photodynamic therapy [6], optical switching [7], optical microfabrication [8] and signal processing [9]. More specifically, the TPA cross section is a figure of merit for fluorescence active compounds and the two-photon induced fluorescence microscopy.

The push-pull dipolar donor–bridge–acceptor (D–π–A) molecules remain at the frontline as the most important nonlinear optical chromophores. It has been shown that the TPA is strongly influenced by the photoinduced intramolecular charge transfer (ICT) occurring in these systems containing electron-donor and electron-acceptor groups [10]. Organic compounds based on benzothiazole core are used in various areas of biology and medicine [11–13] and are useful as biocompatible fluorescent markers of living cells. Derivatives of benzothiazole often serve as electron withdrawing part of molecules in push-pull systems. These donor-acceptor electron systems can effectively polarize electron density within a molecule without external electric field. In general, various structural properties such as conjugation length, planarity and dimensionality of the π-center, the vibronic coupling, and the donor-acceptor strength, can improve nonlinear activity [14,15] and therefore enhance the TPA cross section for absorbing molecules. Organic benzobisthiazolium [16] salts bring various advantages in the field of NLO materials, as improved solubility, greater stability (including photostability) and mainly enhanced ICT. Different organic compounds with high TPA cross section [17–19] were measured, achieving values as high as 8000 GM [20]. The largest value for push-pull chromophores with benzothiazole derivates in the electron acceptor end group was shown to be 2300 GM [21].

Generally, either direct or indirect techniques are employed in order to evaluate the TPA cross section (see e.g. [22] for an overview). Although direct techniques are straightforward to implement, the measured signals are derived from the cumulative effect of 2PA and excited state absorption (ESA), and the results could depend on pulse energy, pulse duration, or both. Therefore, it is typically very difficult to draw meaningful comparison between measurements obtained by direct and indirect methods and these comparisons, even if performed, are rather inconclusive (see e.g. [23,24]). Hence we opted for the two-photon excited fluorescence (TPEF, also known as TPIF) as a mean for the evaluation of TPA properties of the samples. Another advantage of TPEF is its direct relationship to two-photon excited microscopy.

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Our previous studies [21] were limited by the available tuning range of the laser source. Our motivation was twofold. Firstly, following our previous work, the aim was on extending the wavelength range by employing a broadly tunable optical parametric amplifier, since the larger TPA cross sections were assumed to be obtained in the near-infrared range. Secondly, the TPA was characterized for a range of new benzobisthiazolium salts which were recently designed and synthesized for bio-imaging application [16].

2. Materials and methods

Chemical structures of the derivatives with corresponding designation are shown in Fig. 1. Synthesis of octupolar (1) and dipolar (2) benzothiazole derivatives was published elsewhere [21]. Benzobisthiazolium salts, compounds (3) and (5), were prepared according to [16] and compound (4) was prepared according to [25]. All measurements were carried out in solution, where derivatives of benzothiazole (1) and (2) were dissolved in toluene and both benzobisthiazolium salts (3–5), and reference compound, Rhodamin B were dissolved in methanol at concentration of 1×10^{-5} mol dm^{-3}. Linear absorption and fluorescence spectra were measured using an Ocean Optics HR 4000 spectrometer with a wolfram-halogen lamp Ocean Optics LS-1 and fluorescence spectrophotometer Jobin Yvon Horiba Flourolog 3–11 with xenon lamp, respectively. The TPA cross section was determined by using the TPEF technique [26]. This indirect technique is based on the measurement of two-photon excited fluorescence signal in a solution, by employing an external reference. The two-photon excited fluorescence signal was generated by focusing a high intensity laser beam into the sample. An amplified Ti:Sapphire laser system (Coherent, Legend Duo USX/USP) was used as the laser source providing pulses at repetition rate of 3 kHz with central wavelength of 800 nm, energy of 4 mJ, and pulse duration of 100 fs. Subsequently, an optical parametric amplifier was applied to obtain wavelengths in the range from 700 nm to 1000 nm. The wavelengths in the range from 700 nm to 800 nm were obtained by frequency doubling the optical parametric amplifier signal output in a BBO crystal, while in the range from 800 nm to 1000 nm range, the idler output was frequency doubled. Laser peak intensity, at the point of the sample, was evaluated as approximately 5x10^{14} W/m^2 with a corresponding fluence of 50 J/m^2. The TPA cross-section measurement errors were mainly influenced by the short term stability of the laser source and by the laser power measurement error and would in total amount to approximately 20 percent.

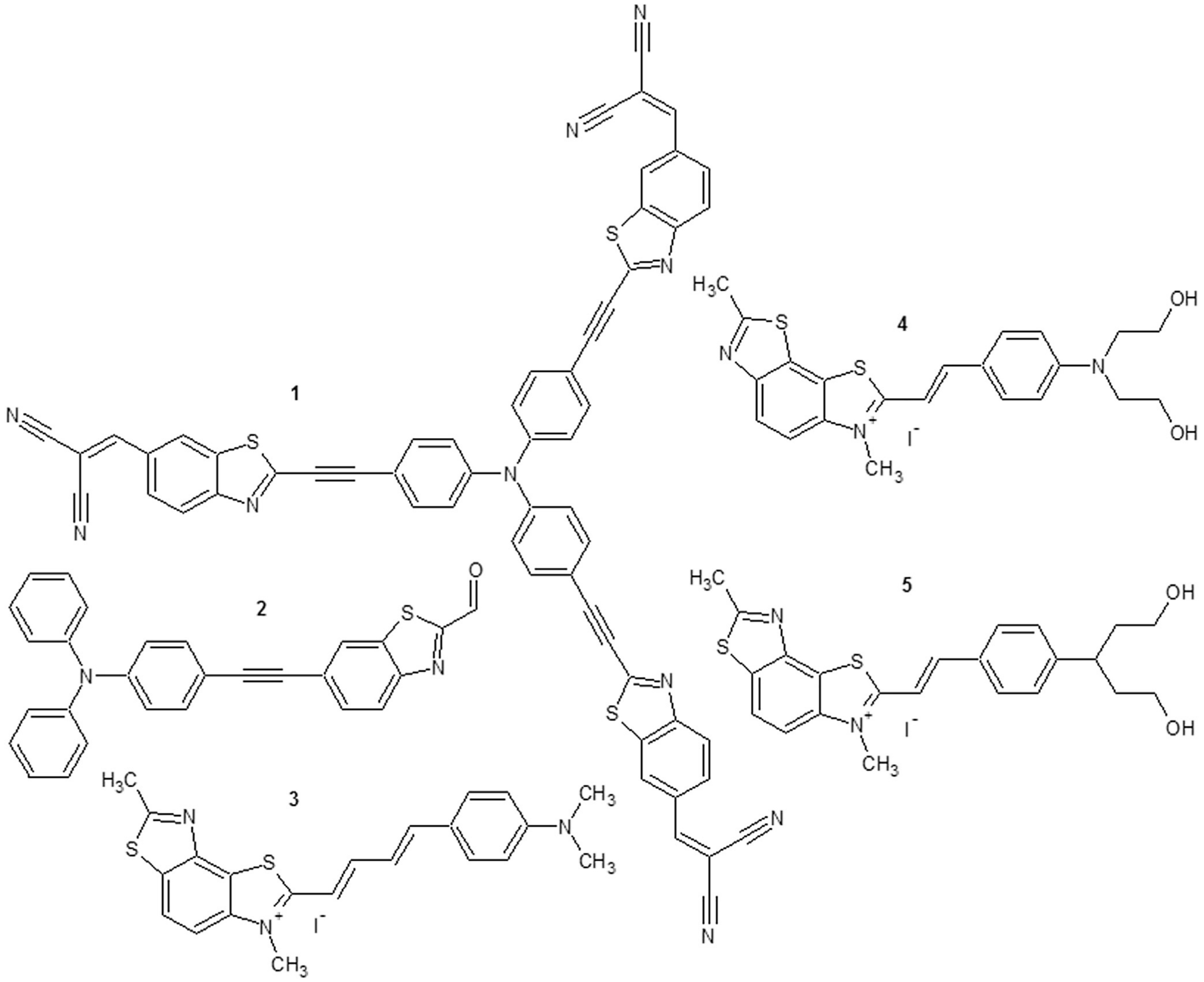

Fig. 1. Molecular structures of benzothiazole derivatives (1–2) and of benzobisthiazolium salts (3–5).