

Novel Heterocycle-Based Two-Photon Absorbing Dyes

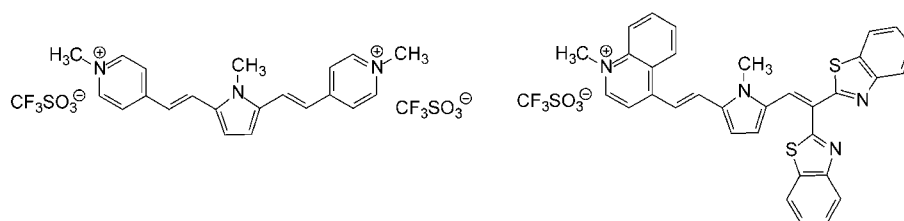
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ABSTRACT



The synthesis and nonlinear optical characterization of two novel heteroaromatic-based chromophores is described. The new dyes present an A- π -D- π -A general framework, where A is a π -deficient heteroaromatic ring (pyridine, quinoline, benzothiazole) and D a π -excessive pyrrolyl moiety. Both systems exhibit large two-photon absorption (TPA) values in the femtoseconds regime (TPA cross section as high as 150×10^{-50} cm⁴ s photon⁻¹ molecule⁻¹ with 150 fs laser pulses). Their TPA-based optical limiting activity is also shown.

Organic molecules that can simultaneously absorb two or more photons to be promoted to their excited states have recently been the subject of much research in the scientific community due to the growing interest in advanced photonic applications such as two-photon laser scanning fluorescence microscopy,¹ optical limiting,² three-dimensional optical storage,³ microfabrication,⁴ and upconverted lasing.⁵ Many of these applications take advantage of the fact that the two-photon absorption (TPA)⁶ activity scales quadratically with

the intensity of the incident laser radiation. Some of these applications are further based on the fluorescence properties of the two-photon excited molecule. Another important aspect is the fact that common organic molecules such as those present in biological tissues and organic coatings are linearly transparent in the wavelength domain where TPA occurs (near-infrared), providing increasing penetration.

To meet market criteria for these applications, molecules with large TPA cross-sections σ^7 are required. Although up to a few years ago only a limited number of systems could show relatively good σ values, it is only in very recent times that research has been reported on the design and development of very efficient TPA dyes.⁸ In particular, it is now apparent that an appropriate design strategy involves symmetrically substituted systems having a general structure of the type D- π -D or A- π -A, where A is an acceptor group, D a donating group, and π a conjugating moiety.

Although a number of efficient TPA dyes are now available, the vast majority of these systems are based on substituted conjugated benzene rings and rely on the

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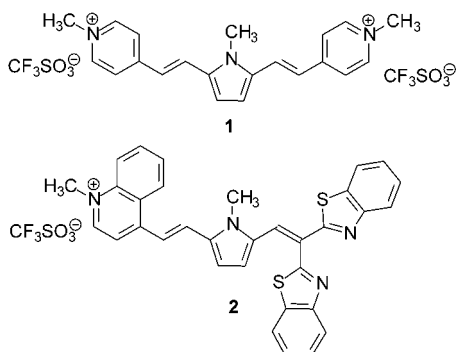
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(7) The molecular two-photon cross-section is the nonlinear absorption coefficient β normalized to a single quantum of excitation and to a single molecule.

electronic properties of primary organic simple functionalities such as OR, NR₂, NO₂, and CN. The lack of a systematic use of heteroaromatic compounds is surprising if one considers that π -deficient and π -excessive heterocycles may act as efficient acceptor and donor moieties, respectively.⁹ Furthermore, the intrinsic tunable nature of the heteroaromatic rings makes these systems particularly appropriate in order to finely control electronic and optical properties. The precious electronic properties of heteroaromatic rings have already been successfully employed for the design of efficient push–pull derivatives for second- and third-order nonlinear optical (NLO) activity.¹⁰ We have recently reported the design of new heterocycle-based push–pull dyes¹¹ and prepared new NLO-phores with large second-order NLO¹² and frequency-upconverted lasing activities.⁵

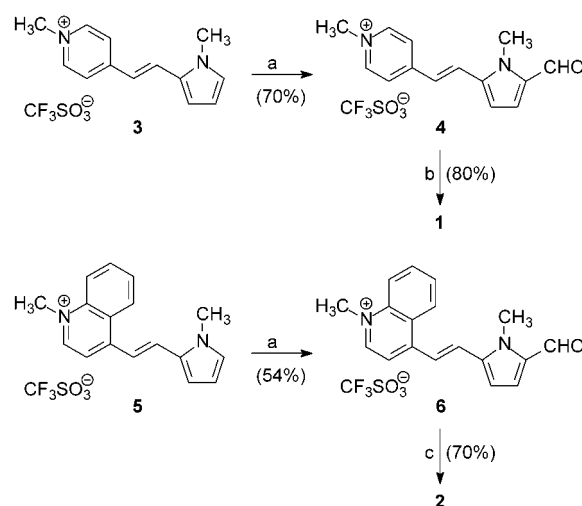
We herein report the synthesis, linear optical absorption and fluorescence, TPA properties, and TPA-based optical limiting activity of two novel heterocycle-based two-photon dyes **1** and **2**, possessing the general structure A– π –D– π –A, wherein A is a π -deficient and D a π -excessive heteroaromatic ring. By means of an extended multinuclear NMR investigation and using our commonly validated shift/charge relationships,¹³ we have previously established, in a quantitative manner, that the pyridyl, quinolyl, and benzothiazolyl substituents act as strong electron-withdrawing functionalities.¹⁴ On the other hand, it is known that the pyrrole ring is among the strongest donor heteroaromatics.⁹



Vilsmeier formylation of the azinium salt **3**,^{11b} carried out under nitrogen in anhydrous acetonitrile, afforded aldehyde

4 as a bright yellow solid in high yields. Similarly, the previously unknown system **5** led to the quinolinium derivative **6**. Subsequent condensation of **4** and **6** with *N*-methyl-4-picolinium triflate and bis(benzothiazol-2-yl)methane¹⁵ in refluxing EtOH and in the presence of a catalytic amount of piperidine gave **1** and **2**, respectively, both as violet solids (Scheme 1). We have previously reported that the intermediate **3** itself shows enhanced TPA activity and frequency-upconverted lasing efficiency.⁵

Scheme 1^a



^a (a) i. DMF, POCl₃, anhyd CH₃CN, rt, 24 h, ii. NaHCO₃, H₂O; (b) *N*-methyl-4-picolinium triflate, piperidine, EtOH, reflux, 2 h; (c) bis(benzothiazol-2-yl)methane, piperidine, EtOH, reflux, 2 h.

Both dyes **1** and **2** show a strong intramolecular charge-transfer absorption band in the visible region and no significant NIR absorption. In addition, they show a fluorescence emission, which is an important prerequisite for TPA-based applications such as fluorescence microscopy¹ and upconverted lasing.⁵ Table 1 lists the main linear

Table 1. Linear Absorption and Emission Parameters of Compounds **1** and **2** in DMSO

compd	$\lambda_{\text{max}}(\text{abs})^a$ [nm]	$\lambda_{\text{cut-off}}$ [nm]	$\lambda_{\text{max}}(\text{em})$ [nm]	Φ^b [%]
1	524 (72 100)	610	620	14
2	559 (51 400)	670	669	0.4

^a Extinction coefficient ϵ in parentheses [mol⁻¹ l cm⁻¹]. ^b Fluorescence quantum yield; 9,10-diphenylanthracene was used as a standard ($\Phi = 90\%$ in cyclohexane).

absorption and fluorescence properties of **1** and **2**. The linear absorption and fluorescence spectrum of **2** in DMSO is shown in Figure 1.

The TPA cross sections of molecules **1** and **2** have been measured by open aperture Z-scan experiments performed

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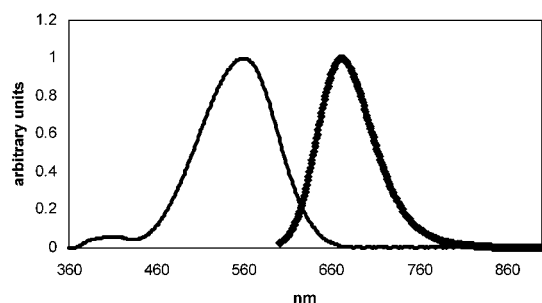


Figure 1. Linear absorption and emission spectra in DMSO of compound **2**.

with a femtosecond (fs) laser source. Open aperture Z-scan allows one to measure the nonlinear absorption of samples by recording the transmittance as a function of the input intensity. To this end, the sample position is moved along the propagation direction (z -axis) of a focused beam, the energy of which is kept fixed, while the intensity increases by approaching the focal plane. Far from the focus position, only the linear transmittance contributes to the signal, while in the vicinity of the focus, the intensity increases very rapidly and the nonlinear absorption process generates a dip in the transmittance. The dip is symmetric with respect to the focal plane position.

The fs-laser measurement is able to discriminate between coherent two-photon processes and multiphoton sequential absorption implying excited states populated by nonradiative processes. The latter does not contribute to the measured signal when fast (~ 100 fs) pulses are used, since most nonradiative processes occur on a picosecond (ps) or nanosecond (ns) time scale. Figure 2 shows the Z-scan data

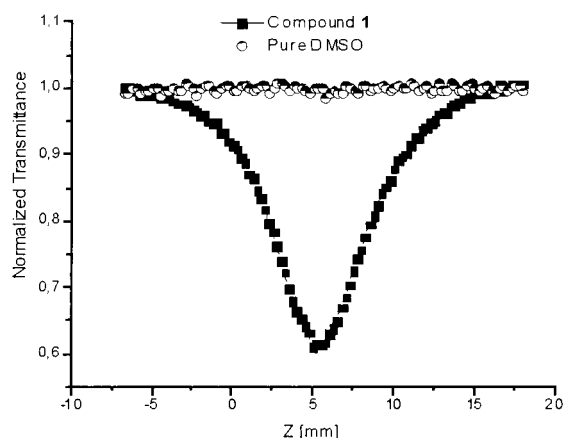


Figure 2. Z-scan experimental data of compound **1** in DMSO (3×10^{-2} M) (squares) and of pure DMSO (circles) in a 1 mm cell, using an input intensity laser beam of $0.35 \mu\text{J}$.

of dye **1** in DMSO (squares) and of pure DMSO (circles), measured in a 1 mm cell, with $0.35 \mu\text{J}$ pulses. In this Figure,

the normalized transmittance (i.e., $I(z)/I(\infty)$, with $I(\infty)$ being the linearly transmitted intensity far from the focal plane) is reported as a function of the sample position (z). The normalized transmittance of pure DMSO is flat, indicating that nonlinear absorption from the solvent does not occur at $0.35 \mu\text{J}$, the upper limit of pulse energies used. Conversely, system **1** shows a deep dip typical of nonlinear absorption.

Table 2 reports the fs TPA coefficients of compounds **1** and **2** compared to those of the most representative literature examples measured with fs pulses.

Table 2. TPA Cross-Section Coefficient of Compounds **1** and **2** in DMSO Compared to Literature Data of TPA Cross-Section Coefficients of Different Compounds

compd	pulse laser		β	σ
	λ [nm]	fwhm [fs]	$[\text{cm}^4/\text{GW}] \times 10^{21}$	[GM] ^a
1	790	150	0.08	119
2	790	150	0.02	150
AF50 ¹⁶	796	150	1.10	22
AF250 ¹⁶	796	150	1.20	30
TP-DTT-TP ¹⁷	796	150	0.12	270
PRL-701 ¹⁸	796	173	2.4	600

^a 1 GM (Goppert-Mayer) = $1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$.

N,N-diphenyl-7-[2-(4-pyridyl)ethenyl]-9,9-di-*n*-decyl-9*H*-fluoren-2-amine (AF50) and (7-(7-benzothiazol-2-yl-9,9-diethylfluoren-2-yl)-9,9-diethylfluoren-2-yl)diphenylamine (AF250) are two of the most representative TPA dyes so far reported in the literature.¹⁶ It can be easily seen that both systems **1** and **2** overcome by almost 1 order of magnitude the TPA performances of these two examples. The TPA coefficient of the *N,N*-diphenylamine-dithienothiophene derivative TP-DTT-TP is larger.¹⁷ However, it should be considered that the TPA measurements of **1** and **2** have been carried out at the nonoptimized 790 nm wavelength position. Indeed, recent results, which will be reported elsewhere, demonstrate that the 790 nm laser source is far away from the peak position of the TPA spectrum of **1** and that a significant enhancement of the σ value is expected at optimized parameters. Finally, we compare in Table 2 the performances of **1** and **2** to that of a particular case, PRL-701,¹⁸ which exhibits one of the largest σ values so far known

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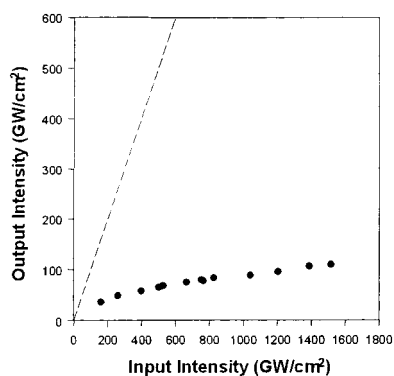


Figure 3. Input–output intensity profile for a DMSO solution of chromophore **1** for a fs laser source. The straight line corresponds to the linear transmission of the solution.

in the fs regime.¹⁹ Although our systems compare well to PRL-701, it must be said that the high value of the latter

(19) A larger value of $\sigma = 11\,000$ GM, measured with fs pulses, has been recently reported for a 29-repeat-unit dendrimer: Drobizhev, M.; Karotki, A.; Rebane, A.; Spangler, C. W. *Opt. Lett.* **2001**, 26, 1081.

originates from its multibranched trimeric structure, where a cooperative effect enhances σ by more than six times with respect to the “monomer” system ($\sigma = 87$ GM, where 1 GM (Goppert–Mayer) = 1×10^{-50} cm⁴ s photon⁻¹ molecule⁻¹).¹⁸ Multibranched structures based on heteroaromatic donor and acceptor units have been developed in our laboratories and will be published in due course.

As an example of TPA-based applications, we show in Figure 3 the optical limiting properties of chromophore **1** obtained in the fs time scale. The expected^{17,18} much larger ns multiphoton absorption of **1** and **2**, due to an additional contribution of the linear absorption of the two-photon allowed excited state, makes these new heterocycle-based systems very attractive for a number of applications operating in the ns regime.

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Supporting Information Available: Experimental procedures and characterization for compounds **1**, **2**, and **4–6** (¹H and ¹³C NMR data). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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