

# Enhancement of a two-photon absorption cross section (TPACS) — design and synthesis of a novel class of photochromic molecules with large TPACS

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Two novel photochromic compounds were designed and synthesized; the two-photon absorption (TPA) cross section of both were measured with a nanosecond laser pulse; their TPACS ( $\delta$ ) values are around  $25 \times 10^{-46} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$  in acetonitrile; the molecular structure of the target compounds have a 3-methyl-1-benzothiophen-2-yl moiety, which can greatly enhance the two-photon absorption cross section.

In the early 1930's two-photon absorption (TPA) of an atom was introduced into the literature as a new concept by Göppert-Mayer.<sup>1</sup> The TPA can be defined as the simultaneous absorption of two photons through a virtual state in a molecule or medium. Theoretical studies have been done to define a unit of two-photon absorption cross section ( $\delta$ ) as GM.

$$1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$$

After that, the experimental studies were not developed very well for about forty years. In the 80's and especially in the 90's an upsurge of research on TPA followed the fast development of various lasers and advanced techniques in different fields, such as three dimensional (3D) optical storage;<sup>2-4</sup> the pioneer work being contributed by Rentzepis *et al.*<sup>2</sup> Other fields included 3D fluorescence imaging,<sup>5,6</sup> 3D microfabrication,<sup>7,8</sup> optical limiting<sup>9-11</sup> and two-photon photodynamic cancer therapy.<sup>12,13</sup> Most of the advanced techniques are interlinked between different sciences and techniques. Most of them are based on TPA or multi-photon absorption (MPA).

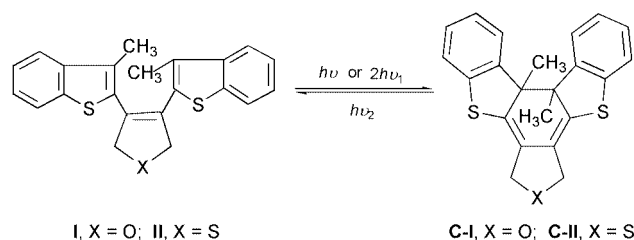
Studies of TPA can be carried out by nanosecond, picosecond or femtosecond laser pulses. TPA or MPA are based on nonlinear properties of a molecule or medium. The main advantage of TPA is that the excitation spatial area can be selected accurately in a volume medium through a tightly focused laser beam, so volume (3D) or multi-layer devices can be exploited.

It is well known that systematic research on photochromism was started from the 1950's. Until the end of the 1980's photochromism was studied basically on molecules and systems.<sup>14</sup> Two-photon induced photochromism was studied from 1989.<sup>2</sup> Recently, Belfield and Fan *et al.*<sup>15</sup> used a femtosecond laser to study one beam two-photon induced photochromism of 2-[1-(1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-3-isopropylidene succinic anhydride (indolyl fulgide). The TPACS ( $\delta$ ) was measured through a Z-scan technique. The  $\delta$  value of indolyl fulgide is  $10.3 \times 10^{-48} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ . It is almost the same as that of the D- $\pi$ -D type molecule, 1,4-bis[[4-(4-dibutylamino)phenyl]buta-1,3-dienyl]-2,5-dimethoxybenzene<sup>7</sup> (as large as  $12.5 \times 10^{-48} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ ), but indolyl fulgide is a D- $\pi$ -A type molecule.

Unfortunately, design and synthesis for molecules with a large TPA cross section have not been well developed. It is well known that a large  $\delta$  value of a medium is a fundamental property to make 3D or multilayer volume devices. The study of the relationship between molecular structure and  $\delta$  value is quite

important. Some molecular models are designed as D- $\pi$ -D, D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A.<sup>7,16</sup> Kim *et al.*<sup>17</sup> studied  $\pi$  systems and they found that the dithienothiophene chromophore as the center  $\pi$  system can greatly enhance the TPA.

We find the connecting chromophore (D or A) can also greatly affect the TPA. Two novel kinds of photochromic compounds will be reported in this communication. The chemical structure of these compounds has been identified by NMR, MS and elemental analysis. They are 3,4-bis(3-methyl-1-benzothiophen-2-yl)-2,5-dihydrofuran (**I**) and 3,4-bis(3-methyl-1-benzothiophen-2-yl)-2,5-dihydrothiophene (**II**). The photochromic reaction is described as follows.



$h\nu$  is UV light;  $h\nu_1$  is visible light, it is a 532 nm laser beam in this paper;

$h\nu_2$  is blue light. C-I and C-II are the colored forms of I and II.

The target compounds can be defined as 1,2-diarylethenes,<sup>18</sup> but the 3,4-bis(3-methyl-1-benzothiophen-2-yl)heterocyclopentene derivatives having photochromic properties have never been reported before and never studied as TPA materials.

The one-photon absorption spectra were measured by a spectrometer (Hitachi F-4500). Their maximum wavelengths ( $\lambda_{\text{max}}$ ) are listed in Table 1.

In the transmittivity measurements, the second harmonic wave of a Q-switched Nd:YAG laser (Spectra-Physics GCR Series) with pulse duration of 10 ns was used as a pump source, and a laser energy meter (Laser Precision Corp., Model Rj-7200) with double detector was used as a recorder. The light beam from the laser was firstly divided into two beams by an optical splitter. The weaker one was used as a reference beam, which entered directly into the detector of the laser energy meter

**Table 1** Maximum wavelength ( $\lambda_{\text{max}}$ ) of absorption spectra of the target compounds and their colored forms (C-I and C-II)

Compd.	$\lambda_{\text{max}}/\text{nm}$	
	Cyclohexane (CHX)	Acetonitrile (ACN)
I	263, 310	263, 312
II	230, 264	230, 266
C-I	375	380
C-II	350	350

**Table 2** TPACS values of the target compounds in different solvents under nanosecond laser pulse

Compounds Solvent	I CHX <sup>a</sup>	I ACN <sup>b</sup>	II ACN <sup>b</sup>
Concentration/10 <sup>-2</sup> mol L <sup>-1</sup>	1.00	1.00	1.00
Pulse duration/ns	10.0	10.0	10.0
I <sub>in</sub> /10 <sup>-2</sup> GM cm <sup>-2</sup>	4.433	4.822	6.178
I <sub>out</sub> /10 <sup>-2</sup> GM cm <sup>-2</sup>	3.367	3.903	3.827
NLO absorption coeff. β/cm GM <sup>-1</sup>	21.59	42.59	39.59
δ <sub>TPA</sub> /10 <sup>-18</sup> cm <sup>4</sup> GM <sup>-1</sup>	3.585	7.053	6.575
δ <sub>TPA</sub> /10 <sup>-46</sup> cm <sup>4</sup> s photon <sup>-1</sup> mol <sup>-1</sup>	13.38	26.41	24.55

<sup>a</sup> CHX = cyclohexane. <sup>b</sup> ACN = acetonitrile.

in order to monitor the intensity of the pump beam. The other beam was focused into the solution of the compounds, and the transmitted energy was measured by another detector of the same laser energy meter. The diameter of the laser beam in the sample was 0.6 mm.

The TPACS are calculated by a method in the literature.<sup>10</sup> The results are collected in Table 2.

Compound I can be assigned as a D-π-A-π-D type molecule based on the difference of electronegativity between oxygen and sulfur. The benzothiophenyl could act as an electron donor and the oxygen as an acceptor. On the other hand, there is no difference in electronegativity of heteroatoms in compound II. It is difficult to say how the photoinduced electron transfer between different moieties of the molecule occurs. The δ values of studied compounds are almost the same in spite of the difference in the centre moiety between dihydrofuran and dihydrothiophene. In fact, the moieties on the left and right hand side of the target molecules are the same, 3-methyl-1-benzothiophen-2-yl.

The conclusion is that 3-methyl-1-benzothiophen-2-yl can greatly enhance the TPA cross section of a molecule. Based on papers we have checked in the literature, the δ values of the target compounds are the largest in acetonitrile. The reason for the TPA enhancement of the 3-methyl-1-benzothiophen-2-yl moiety could be owing to the lone electron pairs of 3p electrons on the sulfur atom. We propose that the enhancement

mechanism of dithienothiophene chromophore<sup>17</sup> could also be the same as that of 3-methyl-1-benzothiophen-2-yl. The magnitude of the δ value is a fundamental property of a molecule or medium in making three dimensional optical devices.

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