



Persistent spectral hole burning by simultaneous two-photon absorption

Mikhail Drobizhev¹, Aliaksandr Karotki, Aleksander Rebane^{*}

Department of Physics, Montana State University, Bozeman, MT 59717-3840, USA

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Abstract

We show for the first time persistent spectral hole burning by simultaneous absorption of two 1138 nm photons in an inhomogeneously broadened $S_1 \leftarrow S_0$ (Q_y) transition of unstable photo-tautomer of chlorin in polymer film at low temperature. Spectrally selective hole burning is achieved due to high (10%) quantum efficiency of photo-transformation in that system and high peak intensity (tens of GW/cm^2) of near-infrared femtosecond pulses used for excitation. Two-photon absorption cross-section is measured for both stable and unstable photo-tautomers to be $\sigma_2 = (0.5 \pm 0.2) \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Spectral hole burning (SHB) is a promising technique for optical recording of information with a potential to achieve storage capacity in excess of 10^4 – 10^5 bits per every λ^3 -volume [1]. The fundamental advantage of SHB over conventional optical recording methods consists in a capability to write and read data not only in the spatial dimensions, but also in the dimension of frequency (and related to it via Fourier transform dimension of time). Addressing of data in the frequency dimension makes use of frequency-specific photo-induced transformation, which is present in systems with inhomogeneously broadened absorption spectra such as dye molecules in polymers and rare

earth ions in crystals at low temperature [1]. The ultimate number of bits, which may be recorded in a λ^3 -volume is given by the ratio of inhomogeneous band width, Γ_{inh} , to much narrower homogeneous width of zero phonon line, Γ_{ZPL} . So far, bit-by-bit hole burning [2] as well as holographic hole burning [3–5] have been implemented. In both of these approaches the spatial degrees of freedom are addressed only in the plane perpendicular to the laser beam. Exploiting in full the capacity provided by the depth of the recording medium, however, has remained a challenging task. This is because propagation of the writing beam through the bulk of the SHB material brings along an intrinsic loss due to one-photon absorption. In bit-by-bit storage, the beam has to penetrate a thick layer of the medium to address a small volume inside the sample, which leads to attenuation of intensity and erasure of data at other spots. In holographic approach similar harmful effects occur, which makes angular multiplexing of SHB holograms inefficient.

^{*} Corresponding author. Fax: +1-406-994-4452.

E-mail address: rebane@physics.montana.edu (A. Rebane).

¹ Permanent address: Lebedev Physics Institute, Leninsky Prospekt 53, 117924 Moscow, Russian Federation.

In principle, this problem may be overcome if one could excite the zero-phonon transition by simultaneous absorption of two infrared photons [6,7]. In this case the medium will remain essentially transparent for the writing beam, while allowing unrestricted penetration and focusing in the depth of the bulky sample. Two-photon absorption (TPA) has been used earlier to demonstrate conventional spectrally non-selective recording in TPA photochromic materials by focusing two perpendicularly directed laser beams (with photon energies $\hbar\omega_1$ and $\hbar\omega_2$) onto one spot [8]. Since the sample is transparent for each beam separately, TPA occurs only at the intersection of the beams. In some molecules doped into a polymer matrix, TPA initiates a photochemical reaction, which has been used to record data in the volume of the sample [8]. In these experiments the possibility to add the third spatial dimension increased the capacity of optical memory device (3D memory) by several orders of magnitude.

In this Letter we investigate the possibility to extend the principle of 3D memory via TPA for frequency-selective recording in materials such as polymers doped with organic dye molecules. The main difficulty that we encounter consists in the fact that most SHB-active molecules have a low probability of two-photon transition, which is orders of magnitude lower than corresponding one-photon transition probability, even at a high laser illumination intensity (GW/cm^2). We identify three key conditions, which need to be fulfilled to achieve our goal. (1) Two-photon cross-section of the lowest purely electronic transition should be at least, $\sigma_2 \sim 1 \text{ GM}$ ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$). A much smaller value of σ_2 cannot give a reasonable probability of excitation with existing laser sources. (2) This transition should be spectrally selective; i.e. the homogeneous spectrum (zero-phonon line plus phonon side band) should be at least 10 times narrower than inhomogeneous distribution. (3) Quantum efficiency of photochemical transformation has to be sufficiently large for spectral changes to be observable at reasonable irradiation times.

Note that satisfying simultaneously conditions (1) and (2) requires that the spectral selectivity of zero-phonon lines persists upon two-photon exci-

tation. Indications that this can be achieved in non-symmetric molecules at low temperature may be found in [9], where the hole burnt with usual one-photon excitation was detected in TPA spectrum, and in [10], where the authors observed two-photon excited fluorescence line narrowing. It is well known that if a molecule has a center of symmetry, then the dipole selection rules for one- and two-photon absorption are mutually exclusive. In the first case only transitions $g \leftrightarrow u$ are allowed, whereas in the second case only $g \leftrightarrow g$ or $u \leftrightarrow u$ are allowed [11]. On the other hand, for molecules without inversion symmetry, the same excited state may be accessed by absorption of one visible or two infrared photons [12,13], provided that the energy of the infrared photons add up to the energy of the transition.

Based on the requirements described above, our preference to perform the experiment was given to chlorin molecule (7,8-dihydroporphin, H_2Ch) doped in polymer film. At room temperature this molecule exists in a form with N–H...H–N axis parallel to reduced C–C bond (T1-form, Fig. 1) [14]. At liquid helium temperatures it undergoes photoinduced tautomerization yielding perpen-

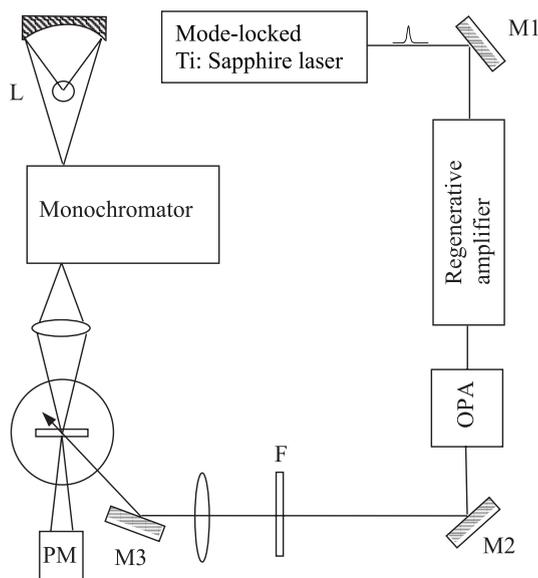


Fig. 1. Schematic of experimental setup. L: filament lamp; PM: photomultiplier; F: set of infrared filters; OPA: optical parametric amplifier.

dicular direction of N–H...H–N axis with respect to the reduced bond (T2-form) [15]. SHB has been shown in both educt and photoproduct tautomers of H₂Ch in Shpolskii matrices [15], and polymer films [16–19]. As compared to T1 → T2 photo-transformation, a drastic (10²–10³ times) increase of the rate of back T2 → T1 process has been observed [15,18,19], giving rise to up to 10% quantum efficiency of this process in polymer matrices [18,19]. This value is probably the highest one known for monomolecular SHB systems. On the other hand, H₂Ch, as well as its tautomer, have no center of symmetry and, therefore, are assumed to meet the condition (1). This assumption is further supported by the fact that the closely related chlorophyll *a* molecule reveals a coincidence of one- and two-photon absorption spectra [20]. Finally, using spectrally broad femtosecond pulses in our experiments imposes one further practical constraint, which requires that the spectral separation between the educt and product absorption bands needs to be larger than the spectral width of the femtosecond pulses, i.e. more than 100 cm⁻¹. Femtosecond excitation of tautomers of H₂Ch is easily performed because their absorption bands are separated by more than 1000 cm⁻¹ [15,17–19].

In this Letter we start by measuring the TPA cross-section for stable tautomer of H₂Ch by relative fluorescence method. We proceed to show the possibility of two-photon-induced isomerization of unstable photo-tautomer of H₂Ch molecules and to measure the TPA cross-section basing on the kinetics of this reaction. Finally, we demonstrate spectrally selective hole burning by direct two-photon excitation of unstable tautomer at low temperature by using time-delayed pairs of high-intensity femtosecond infrared pulses.

2. Experimental

The laser system comprised a mode-locked Ti:sapphire femtosecond laser (Coherent Mira 900) and a 1 kHz repetition rate Ti:sapphire regenerative amplifier system (Clark MRX CPA-1000). The amplified pulses had duration of 100 fs, energy of 1 mJ at 780 nm. An optical parametric amplifier, OPA (TOPAS, Quantronix), converted these

pulses to near infrared (1100–1500 nm). Laser spectrum was recorded with a Lambda 900 Perkin Elmer spectrophotometer and pulse temporal profile were measured with an autocorrelator.

Fig. 1 shows the scheme of our experiment on two-photon-induced photochemistry. A thick stack of glass color filters was used to cut off any residual visible light from the laser. Infrared pulses were focused with a 50 cm lens on a mask with 1 × 0.6 mm² opening placed just before the sample. The pulse peak intensity at the sample was varied from 20 to 80 GW cm⁻². The mask was used to be sure that the same spot of the sample was irradiated and probed. The sample of a chlorin-doped 0.2-mm thick polyvinylbutyral (PVB) film was contained in helium cryostat at *T* = 4 K.

For measurement of transmission spectra, a chopper-modulated light from a filament lamp was dispersed in a TRIAX 550 Jobin Yvon/Spex spectrometer and then focused onto the sample. The intensity transmitted through the sample was recorded with a Hamamatsu photomultiplier and a lock-in amplifier.

TPA cross-section was measured by comparing the fluorescence intensity under two- and one-photon excitation as described in [21,22]. In our case, one-photon excitation was carried out with a cw YAG laser (532 nm). Central part of both OPA and YAG beams were carefully selected with a pinhole to achieve equal spatial intensity distribution for both beams. The sample was placed 90 cm after a *f* = 100 cm focusing lens. Fluorescence was detected with a digital CCD camera (Xillix Microimager). A stack of color glass filters was used cut off excitation light.

3. Results and discussion

To the best of our knowledge, there are no prior communications concerning TPA properties of chlorin molecule. Therefore, we aimed to evaluate its TPA cross-section in the spectral region of our interest, i.e. near the lowest one-photon electronic Q_y transition, which occurs at 634 nm in PVB film [16–18]. Owing to a presence of well-detectable fluorescence under 1265-nm pulse excitation, we were able to estimate the TPA absorption cross-

section by using the method described in [21,22]. For sech² temporal profile of excitation pulses and under the assumption that fluorescence quantum efficiency is the same for both one- and two-photon excitation, the two-photon cross-section writes as follows (cf. [22]):

$$\sigma_2 = \frac{F_2 I_1 t_1 (h\nu_2)^2}{F_1 I_2^2 t_2 h\nu_1} \frac{\tau r (1 - 10^{-OD_1})}{0.3Cl} \quad (1)$$

Here indexes 1 and 2 refer to the values measured under one- and two-photon excitation, respectively, F is the fluorescence signal recorded during time t , C is the molecule concentration (in molecule cm⁻³), l is the sample thickness (in cm), τ is the pulse duration (full width at half maximum, in s), r is the pulse repetition rate for two-photon excitation, I is the average intensity (in W/cm²), ν is the laser frequency (in Hz), OD_1 is the optical density of the sample at one-photon excitation wavelength. Using Eq. (1), we have found $\sigma_2 = 0.5 \pm 0.2$ GM at 1270 nm at room temperature. The latter value correlates well with that measured for other dyes, near lowest one-photon allowed transition [13].

Despite the fact that we are apparently exciting a strong fluorescence signal by TPA of the stable T1 tautomer of H₂Ch, our attempts to induce a detectable change of the absorption by illumination with focused femtosecond near-IR beam were failed³, even for irradiation times as large as several hours. This is because this tautomer has very small quantum efficiency of photo-transformation [15,18,19]. Therefore, we turn to the metastable (at low temperatures) tautomer T2. This form is known to have much higher quantum efficiency of photo-transformation [15,18,19], but a low Debye–Waller factor in polymer matrices [18,19]. Nevertheless, it has been shown that the T2 inhomogeneous band still has some degree of spectral selectivity [17,18]. As described below, this relatively small selectivity proved sufficient for us to demonstrate the effect of two-photon SHB.

Initial absorption spectrum of stable, T1 form of H₂Ch at 4 K is shown in Fig. 2, dotted line. The strong band at 633 nm corresponds to pure electronic transition, polarized along the reduced C–C bond. This figure also shows the spectrum of the

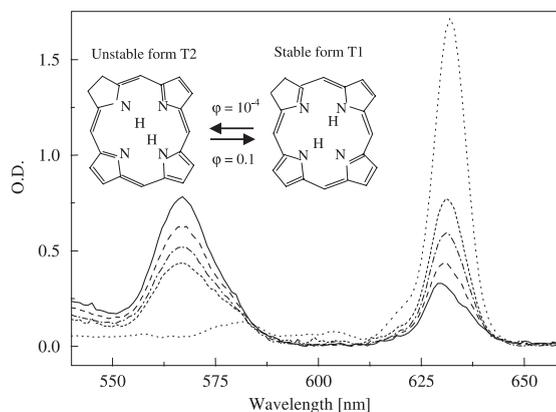


Fig. 2. Absorption spectrum of stable chlorin tautomer T1 in PVB film at 4 K, dotted line. Spectrum of the sample after illumination with second harmonic of OPA (633 nm, 1 W/cm² average power density at 1 kHz repetition rate) for 20 min, solid line. The band at 567 nm corresponds to unstable T2 tautomer, see inset for chemical structures. Dashed, dash-dotted, and short dashed lines correspond to spectra after illumination of T2 form with 3.6, 4.7, and 6.1 kJ/cm² total fluence of 1134 nm OPA pulses, respectively.

sample after its illumination with 633-nm pulses (second harmonic of OPA tuned to 1265 nm), solid line. One can see the strong band appearing at 567 nm, which was observed earlier at low temperatures in the same system [17,18] and attributed to H₂Ch tautomer (T2) with perpendicular arrangement of N–H...H–N axis [15]. Note that this tautomer is unstable at room temperature, revealing spontaneous conversion to T1 form. Excitation of the sample now with 1134 nm femtosecond pulses yields an orange fluorescence. Prolonged illumination results in a decrease of absorption at 567 nm and simultaneous increase of the initial band at 633 nm (dash, dot–dash, and short dash lines in Fig. 2). These facts suggest that the TPA of the photoproduct T2 takes place and leads to T2 → T1 back transformation. To verify that the TPA is indeed responsible for photochemistry, we measured the dependence of integrated absorption changes as a function of applied laser fluence and intensity.

Fig. 3a shows the dependence of integrated (from 530 to 570 nm) T2 absorption as a function of the total accumulated dose D applied. Experimental points were obtained by applying different

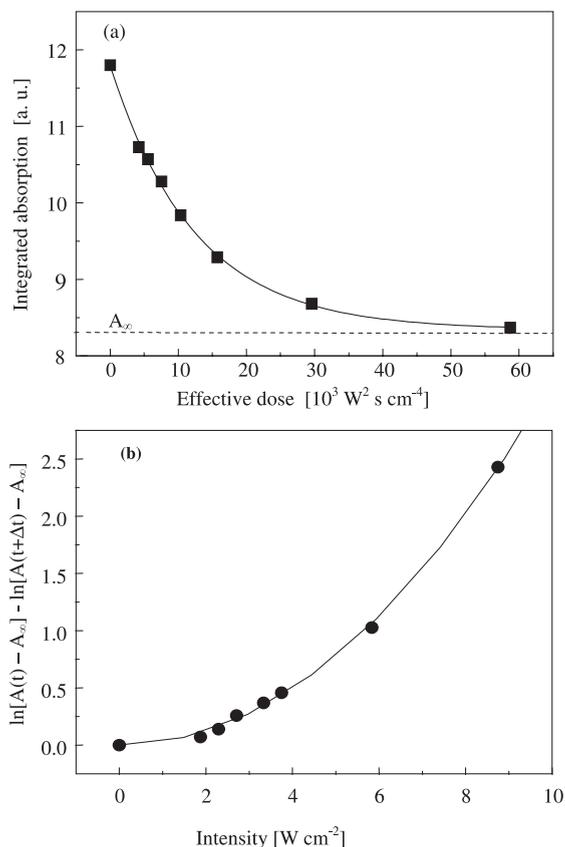


Fig. 3. (a) Dependence of integrated absorption of T2 form as a function of effective irradiation dose, $\sum I^2 \Delta t$. Solid line presents a best fit to Eq. (2). (b) Dependence of normalized changes in T2 absorption (see text) on average laser intensity I (Average intensity of 10 W/cm^2 corresponds to 90 GW/cm^2 peak intensity). Solid line presents a square dependence fit.

laser intensities I during equal exposure time Δt ($= 10 \text{ min}$). Therefore, we suppose that $D = \sum I^2 \Delta t$. Experimental dependence is well fitted to a single exponential

$$A(t) = (A_0 - A_\infty)e^{-kD} + A_\infty. \quad (2)$$

Note a pronounced offset absorption A_∞ , which is about two times as large as the maximum change $A_0 - A_\infty$. This offset can be related to those T2 molecules, which cannot be accessed with a focused laser beam, but still probed with a spectrometer because the mask opening is larger than the effective laser waist. This observation can give us an idea about independent estimation of the

effective illumination area because the mask opening has a well-defined size.

As a next step, we shall present absorption changes as a function of the average intensity I . For this purpose we rewrite Eq. (2) as follows:

$$A(t + \Delta t) = [A(t) - A_\infty]e^{-kI^n \Delta t} + A_\infty. \quad (3)$$

Now we do not assume a priori any particular value for the power exponent n , but only suppose A_∞ value to be the same as obtained from Fig. 3a. Presentation of experimental data in $\ln[(A(t) - A_\infty)/(A(t + \Delta t) - A_\infty)]$ vs. I coordinates should give an n -power dependence (see (3)) because Δt is kept equal each time. Fig. 3b shows this dependence, which is fitted to the power law, giving $n = 2.03 \pm 0.04$. This result demonstrates that the T2 \rightarrow T1 transformation is undoubtedly due to TPA by tautomer T2.

Knowing the coefficient k from this experiment ($5 \times 10^{-5} \text{ cm}^4 \text{ W}^{-2} \text{ s}^{-1}$), we can now estimate the value of TPA cross-section for T2. It is easy to show that:

$$k = \frac{0.3\varphi\sigma_2}{\tau r(h\nu_2)^2}. \quad (4)$$

Here φ is the quantum efficiency of photochemical transformation. Taking $\varphi = 0.1$ [19], we obtain $\sigma_2 = 0.5 \pm 0.1 \text{ GM}$. Note that this value is within experimental error equal to that obtained for T1 tautomer. This fact is unlikely just accidental because the values were measured with different methods, i.e. based on fluorescence intensity and photochemical kinetics, respectively. It makes more sense that both tautomers possess equal cross-sections for some reason. Further discussion, as well as an independent measurement of σ_2 for T2 with the fluorescence technique will be addressed in a subsequent work.

As can be seen from Fig. 2, the T2 absorption band decreases upon illumination as a whole. This is due to the fact that the laser spectrum has almost the same width and maximum as the inhomogeneous absorption band. To prove the feasibility of frequency-selective hole burning, we modulated the laser spectrum by passing the near-IR pulses through a Michelson interferometer (replaced mirror M2 in Fig. 1). At the output of

the interferometer there were two spatially overlapping equal intensity beams, with a time delay of $\Delta\tau \approx 180$ fs between them. Fig. 4 demonstrates the changes in T2 absorption band as a result of irradiation of sample with such pairs of pulses. Experimental dots (closed and open) were obtained as follows. Absorption spectrum before burning was subtracted from that after burning. Then, this differential spectrum was approximated with a Gaussian envelope function. Finally, the Gaussian fit was subtracted from experimental differential spectrum and the result was smoothed with standard method using 10 adjacent points. Two different data sets correspond to two different exposure times.

In the usual case of one-photon hole burning, it is well known [23] that an irradiation with pairs or trains of pulses with $\Delta\tau \ll T_2$, where T_2 is the total dephasing time, results in a periodically modulated spectral hole profile with a period $\Delta\nu = (c\Delta\tau)^{-1}$. Naturally, for ordinary modulated hole spectrum will be centered at the carrier laser frequency and will have a period $\Delta\nu = 180 \pm 20$ cm^{-1} . Our expectation was that a modulation will show up also in the TPA hole burning spectrum, but centered around the twice laser frequency. However, the question about the exact shape of spectral hole structure is not so evident. Our preliminary model calculations show that the period of the grating will again be determined by time delay between

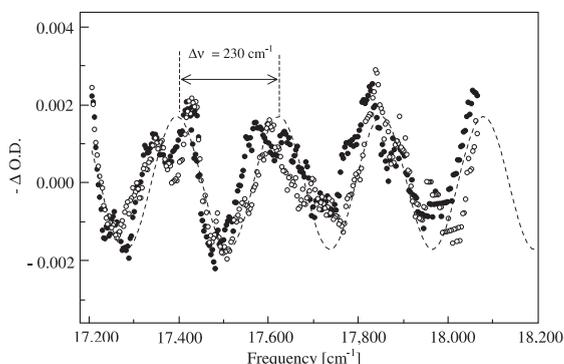


Fig. 4. Spectral modulation in T2 absorption band induced by two-photon absorption from pairs of pulses with 180-fs time delay between them after irradiation time of 45 (closed dots) and 285 s (open dots), $I = 3$ W/cm^2 . Solid line represents a cosine function with a period of 230 cm^{-1} .

pulses and equal to $(c\Delta\tau)^{-1}$. The first experimental results, presented in Fig. 4, shows that the modulation period of the holes is, $\Delta\nu = 230 \pm 30$ cm^{-1} . This value coincides within experimental error with the expected modulation period.

A poor contrast of the holes presented in Fig. 4 occurs because of low Debye–Waller factor (<0.1) mentioned above. However, it is known that if both the phonon wing of homogeneous spectrum and laser spectrum are narrower than inhomogeneous distribution function, one can still observe the spectral selectivity [24,25]. At low irradiation fluence, a relatively broad hole will appear exactly at laser maximum frequency. During the burning process the hole will broaden and shift towards the maximum of inhomogeneous distribution to coincide with it when almost all the centers will be burnt. This effect was confirmed by model calculations [24] and experiment [26]. We can use this effect here as another convincing demonstration of spectrally selective hole burning via simultaneous TPA.

Successive changes of the hole shape as a function of irradiation time upon illumination with spectrally modulated laser with a maximum tuned to 1138 nm are shown in Fig. 5. One can definitely see that at the earlier stages the maximum of the broad envelope continuously shifts to

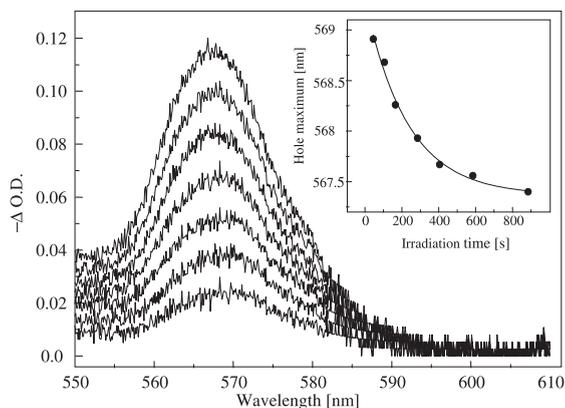


Fig. 5. Spectral changes in T2 absorption band upon successive irradiation with pairs of pulses with carrier wavelength at 1138 nm, $I = 3$ W/cm^2 . Curves from bottom to top correspond to increasing irradiation time. Inset shows the position of spectral envelope maximum of each curve as a function of that time (points) with exponential decay fit (solid line).

the center of inhomogeneous distribution (567 nm), as is to be expected if molecules with different transition frequencies become gradually involved in the photo-transformation.

In conclusion, we would like to emphasize that the effect of SHB via non-resonant TPA differs radically from the well-known photon-gated SHB [1]. The latter implies sequential absorption of two photons with the first one in resonance with material absorption, thus precluding its use in 3D memory devices.

The use of SHB via TPA in 3D-memory devices, which could be called now 4D-memory, may result in a drastic increase of information density because of addition of the fourth dimension. Also, it can open the possibility to monitor fourth-order field correlation functions of non-classical light in those cases, when the degree of non-classicity (e.g. quantum photon indistinguishability) depends on frequency of light [27,28].

4. Conclusions

In this Letter we have demonstrated for the first time the possibility of spectral hole burning via simultaneous TPA in organic molecular system. The choice of chlorin photo-tautomer for this demonstration is based on its attractive one-photon hole burning properties: one of the highest quantum efficiencies of transformation, high oscillator strength, large spectral separation of educt and product bands. New technique of measurement of two-photon absorption cross-section, σ_2 , based on kinetics of photochemical transformation is proposed. The σ_2 value of both photo-tautomers of chlorin molecule is measured for the first time.

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