



Photo-tautomer of Br-porphyrin: a new frequency-selective material for ultrafast time–space holographic storage

Mikhail Drobizhev^{*,1}, Christophe Sigel, Aleksander Rebane

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

Abstract

We study spectral hole burning in the unstable tautomer form of free-base Br-tetraethylporphyrin in poly(vinyl butyral) film, which is created by photo-transformation of the stable tautomer form at low temperature. We report a Debye–Waller factor $\alpha = 0.7$ at 4 K, burning quantum efficiency $\varphi \sim 10^{-3}$ and thermal stability up to 115 K for this system. We observe for the first time that narrow-band illumination in the educt band leads to the formation of vibronic holes in the photoproduct band. Because the oscillator strength of the unstable form is at least one order of magnitude larger than that of the stable form, this new material is well suited for recording ultrafast time-and-space-domain holograms. Spectral hole burning with femtosecond pulses was achieved. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A unique property of spectral hole-burning (SHB) materials consists in the fact that they can capture simultaneously both the spatial as well as the spectral content of a light signal. By using holographic principle of recording and playback, SHB enables complete time-and-space-domain storage of optical signals [1–3]. Hole burning is especially useful for recording and coherent processing of sub-picosecond signals, because on the

ultrafast time scale there is no other method which allows simultaneous spatial and temporal acquisition of an optical wave [4].

Efficient recording of broad-band ultrafast signals requires from the SHB material several appropriate photophysical and photochemical properties. The most critical of them are a sufficiently broad inhomogeneous band width ($\Gamma_{\text{inh}} > 5$ THz) and a large ratio between inhomogeneous and homogeneous line widths ($\Gamma_{\text{inh}}/\Gamma_{\text{hom}} > 10^3$), but also a large oscillator strength for the resonant transition ($f > 10^{-3}$), a high quantum efficiency of phototransformation ($\varphi \sim 10^{-2}$) and a small degree of overlap between photoeduct and photoproduct bands. Meeting all these requirements is a serious challenge. In practice a compromise needs to be found between contradictory requirements.

* Corresponding author.

E-mail address: drobizhev@physics.montana.edu (M. Drobizhev)

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

Organic molecules such as porphyrins and phthalocyanines offer large oscillator strength ($f \sim 10^{-1} - 10^{-3}$), but suffer from low photochemical quantum yield and have often a substantial overlap between the educt and photoproduct inhomogeneous bands. Free-base porphyrins are known to show tautomerism involving two NH-protons in the center of the molecule. In the case of symmetrically substituted porphyrins, the two tautomers have very close ground and excited state electronic energies and, therefore their absorption spectra overlap considerably. The latter is a serious problem for recording of ultrafast signals, which requires broad bandwidth [5,6]. In symmetric molecules such as octaethylporphyrin, the overlap causes filling of the holes leading to loss of holographic information [7]. One way to solve this problem is to use non-symmetric molecules, such as dihydroporphyrin (chlorin), where the wavelength difference between the tautomer bands is large [8]. However, strongly asymmetric molecules often show increased phonon side-band and lower burning efficiency, making them less suitable for applications.

In this paper we present a novel approach, where we make use of the large difference between the oscillator strength of the two tautomer forms of slightly asymmetric porphyrins. According to Gouterman's four-orbital model [9,10], the oscillator strength of the long-wavelength transition Q_x (respectively Q_y) depends on the coupling coefficient to the optically allowed Soret state B_x (respectively B_y), with Q_y more intense than Q_x in most cases. For symmetrical porphyrins, upon tautomerization, the $H-H$ - and X -axis keep the same direction [9,10], leaving the relative intensities of Q_x and Q_y unchanged. For non-symmetrical porphyrins, it was shown experimentally [11,12] that the X - and Y -axis remain fixed while $H-H$ axis rotates 90° , resulting in an exchange of oscillator strength of Q_x and Q_y for each tautomer (because the relative transition strengths still follow the frame connected with $H-H$ axis). Practically, the Q_x transition oscillator strength of the phototautomer will be much higher than that of the educt Q_x transition, thus reducing the overlap problem.

We demonstrate the possibility of recording broad-band ultrafast holograms by using SHB

in unstable (at room temperature) tautomer of 2,3,12,13,-tetraethyl-7-bromo-21H,23H-porphin (BrTEP). We estimate the quantum efficiency, Debye-Waller factor and thermal stability of hole burning in this new system.

2. Photochemical generation of T2 tautomer and burning of vibronic holes

BrTEP was synthesized by Dr. A.M. Shulga (Institute of Physics, National Academy of Sciences, Minsk, Belarus). Our samples were prepared by dissolving BrTEP in pyridine and mixing the solution into poly(vinyl butyral) dissolved in methylenechloride. Polymer films were prepared by allowing the solvents to slowly evaporate. The thickness of films was in the range 40–280 μm . The concentration of the dye in films was about 2×10^{-3} mol/l.

Fig. 1 shows the changes of the stable tautomer (T1) spectrum upon irradiation of its Q_y transition

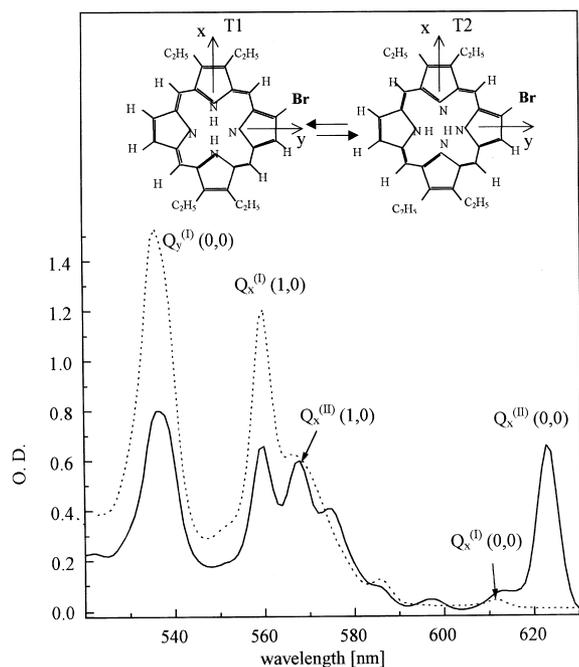


Fig. 1. Absorption spectrum of BrTEP in poly(vinyl butyral) at 4 K before (dashed line) and after (solid line) illumination with cw laser light at 532 nm. Inset shows the structure formulas of the stable (T1) and unstable (T2) tautomers.

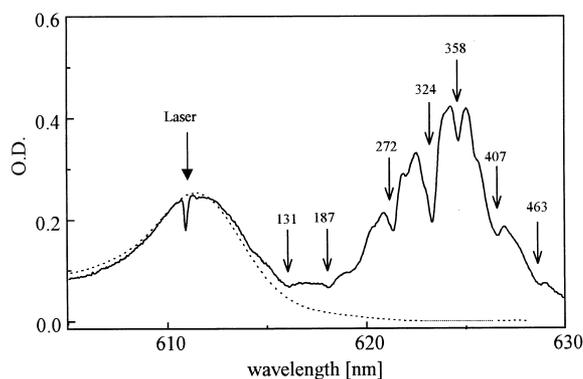


Fig. 2. Absorption spectrum of the system before (dashed line) and after (solid line) illumination with 110 J/cm^2 of cw laser at 611 nm. Arrows indicate vibronic holes along with their corresponding vibrational frequencies in wavenumbers.

at 4 K with a 532 nm cw light (Coherent Verdi frequency-doubled YAG laser). A strong band appears in the spectrum at a longer wavelength (623 nm). This band can be assigned [11,12] to the $Q_x(0-0)$ transition of unstable (at room temperature) tautomer (T2). From this figure it is evident that the $Q_x(0-0)$ oscillator strength of T2 is at least one order of magnitude greater than that of T1 and the energy separation between the lowest, $Q_x(0-0)$ transitions of two tautomers is about 260 cm^{-1} . The same T1 \rightarrow T2 photo-transformation can be observed also under direct irradiation of the T1 Q_x pure electronic and vibronic bands. Fig. 2 shows an absorption spectrum, obtained after selective irradiation of the $Q_x(0-0)$ band with a cw dye laser at 611 nm. As a result, the same long-wavelength T2 band appears in the spectrum simultaneously with a narrow spectral hole burnt in the T1 $Q_x(0-0)$ band. It is interesting to note that in this case the inhomogeneous profile of the emerging T2 $Q_x(0-0)$ band contains several spectral holes. The appearance of these holes can be explained if we suppose that illumination at 611 nm excites, in addition to T1 $Q_x(0-0)$ transition, several overlapping vibronic transitions of the freshly generated T2 species. In this case, several vibronic holes (Ref. [13], and references therein) can be observed in the pure electronic band of T2. From the spectral position of these holes with respect to the laser frequency we determine the vibronic frequencies in the T2 excited

state (see Fig. 2). To our knowledge this is the first time that vibronic holes in the photoproduct band are observed simultaneously with the irradiation of the educt band.

3. Estimation of Debye–Waller factor and quantum efficiency

In this section we present hole-burning results obtained with a multimode cw dye laser ($\sim 1 \text{ cm}^{-1}$ line width). The holes were detected in absorption with a Perkin-Elmer Lambda 500 spectrophotometer. To estimate the value of Debye–Waller factor we used a method based on the measurement of the burning kinetics of the zero-phonon hole (ZPH) and the pseudo-phonon side-band hole (PPSH) [14,15]. In our experiment the laser has a nearly Gaussian spectral profile with a width much broader than that of the zero-phonon line (ZPL). The ZPH profile can be then expressed as follows:

$$H_{zz}(v, t) = C \left\{ 1 - \exp \left[-k_z t \exp \left(\frac{4(v - v_1)^2}{\delta^2} \right) \right] \right\}, \quad (1)$$

where $v_1 \sim 16050 \text{ cm}^{-1}$ is the laser central frequency, $k_z = 2I\sigma\varphi\alpha/(\pi)^{1/2}\delta$ is the hole burning rate, I is the burning photon flux, σ is the absorption cross-section integrated over the inhomogeneous band, φ is the quantum efficiency of burning, α is the Debye–Waller factor, δ is the laser linewidth (full-width at e^{-1} of maximum) and C is the maximum hole depth. In Eq. (1) the hole profile $H_{zz}(v, t)$ is taken as a difference between the spectra before and after burning. If we assume that the phonon wing has a Gaussian profile with width Γ_p , we can similarly have for the PPSH [15,16],

$$H_{pz}(v, t) = C \left\{ 1 - \exp \left[-k_p t \times \exp \left(-\frac{4(v - v_1 + \Delta)^2}{\Gamma_p^2} \right) \right] \right\}, \quad (2)$$

where now $k_p = 2I\sigma\varphi(1 - \alpha)/(\pi)^{1/2}\Gamma_p$ and Δ is the Stokes shift between the maxima of ZPL and phonon wing. Note that one can use in Eq. (2) the same value for C as in Eq. (1) when Δ and Γ_p are

much smaller than the inhomogeneous distribution width.

To compare to the experimental spectra, the hole profiles (1) and (2) need to be convoluted with the slit function of our spectrometer (3 cm^{-1}). Experimental hole profiles at each exposure time can be well approximated by a sum of two Gaussians separated by 17 cm^{-1} and possessing the widths 5 and 27 cm^{-1} , which correspond to the ZPH and PPSH, respectively.

Fortunately, for the evaluation of the Debye–Waller factor we only need integrals of the hole profiles, which are independent of the slit function. One can show [15] that at moderate burning fluences ($k_z t, k_p t < 30$),

$$A_{zz} = \int_{-\infty}^{\infty} H_{zz}(v, t) dv = \frac{C}{2} \sqrt{\pi} \delta k_z t \exp\left(\frac{\sqrt{k_z t}}{2}\right) \quad (3)$$

and

$$A_{pz} = \int_{-\infty}^{\infty} H_{pz}(v, t) dv = \frac{C}{2} \sqrt{\pi} \Gamma_p k_p t \exp\left(-\frac{\sqrt{k_p t}}{2}\right). \quad (4)$$

Therefore, by taking the ratio,

$$\frac{A_{pz}(t)}{A_{zz}(t)} = \frac{1 - \alpha}{\alpha} \exp\left(\frac{\sqrt{k_z t} - \sqrt{k_p t}}{2}\right), \quad (5)$$

we obtain α by plotting the experimental data in coordinates $\ln(A_{pz}/A_{zz})$ versus \sqrt{t} . The intersection point of the straight extrapolation line with the ordinate axes is, $\ln((1 - \alpha)/\alpha)$, and the slope is, $(\sqrt{k_p} - \sqrt{k_z})/2$. Fig. 3a presents our data in these coordinates, where the intersection point yields the value of the Debye–Waller factor, $\alpha = 0.70 \pm 0.02$. This value is comparable to those obtained previously for some symmetrical free-base porphyrins and phthalocyanines at $T \leq 10 \text{ K}$: $\alpha = 0.54\text{--}0.87$ [17–21]. On the other hand, for nonsymmetrically substituted tetrapyrrolic molecules it has been observed that α decreases considerably by going from the stable tautomer to the unstable one [18,22].

As the next step we evaluate the efficiency of hole burning in the T2 $Q_x(0-0)$ band. For this purpose we use Eq. (2). It does not suffer from the convolu-

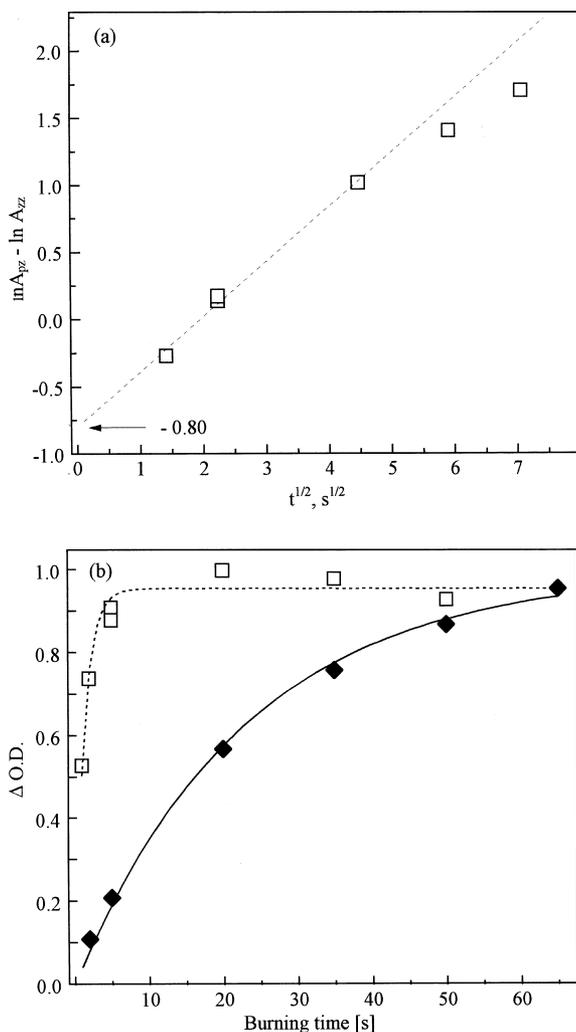


Fig. 3. (a) Logarithm of ratio of the integrated PPSH to the integrated ZPH as a function of square root of burning time. Debye–Waller factor is determined from the straight line extrapolation to zero burning time. (b) Dependence of ZPH depth (open squares) and PPSH (filled diamonds) on burning time.

tion with the slit function because the pseudo phonon side hole feature is much broader than the latter. For the hole depth as a function of burning time, we obtain

$$H_{pz}(v - \Delta, t) = C(1 - \exp[-k_p t]). \quad (6)$$

We fit this simple equation to our experimental data by varying both k_p and the maximum side

hole depth, C . Fig. 3b shows that the best fit is obtained with $k_p = (4.3 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$ at $I = 3 \times 10^{17} \text{ photons s}^{-1} \text{ cm}^{-2}$ (60 mW/cm^2). Fig. 3b presents also the kinetics of the observed ZPH hole depth and its approximation by exponential function.

To estimate the quantum efficiency we need to know the value of the integrated absorption cross-section of the T2 $Q_x(0-0)$ band. This value can be estimated as $\sigma \approx (2\pi)^{1/2} \Gamma_{\text{inh}} \sigma_{\text{max}}$, where σ_{max} is the cross-section at the absorption maximum. For our system, the standard Gaussian width, $\Gamma_{\text{inh}} = 60 \text{ cm}^{-1}$ (corresponding full width at e^{-1} of maximum is 170 cm^{-1}). Our estimation of σ_{max} is based on the observation that the T1 $Q_y^I(0-0)$ band (at 536 nm) shows equal (but with opposite sign) changes in optical density as the T2 $Q_x^II(0-0)$. This is observed for both photochemical T1 \rightarrow T2 (Fig. 1) and dark thermal T2 \rightarrow T1 transitions. This is possible only if $\sigma(Q_y^I(0-0)) = \sigma(Q_x^II(0-0))$. The same relation between these transitions was also found in Ref. [11,12]. We have measured $\sigma(Q_y^I(0-0)) = 6.1 \times 10^{-17} \text{ cm}^2$ ($\epsilon = 16,000 \text{ M}^{-1} \text{ cm}^{-1}$). Therefore, $\sigma \approx 0.9 \times 10^{-14} \text{ cm}$. Using the above expression for k_p and substituting all other experimentally determined parameters, we obtain, $\varphi = (1 \pm 0.5) \times 10^{-3}$.

4. Temperature-induced dark T2 \rightarrow T1 transformation

As mentioned above, the T2 species are stable only at low temperatures because its ground state energy is higher than that of T1. Generally speaking, this state is metastable, because even at very low temperature there exists a finite although small probability of tunneling to the T1 state. Here we study the T2 \rightarrow T1 transformation as a function of temperature. Fig. 4 shows the dependence of integrated $Q_x^II(0-0)$ band as the temperature is increased from 4 K to 200 K. The waiting time at each temperature was about 5 min. Upon increasing temperature, the intensity of T2 $Q_x(0-0)$ absorption band decreases and that of T1 absorption band increases, with equal absolute changes of optical densities in $Q_x^II(0-0)$ and $Q_y^I(0-0)$ bands. We can describe this dependence in terms of a simple model [23,24], which assumes a distribution of potential

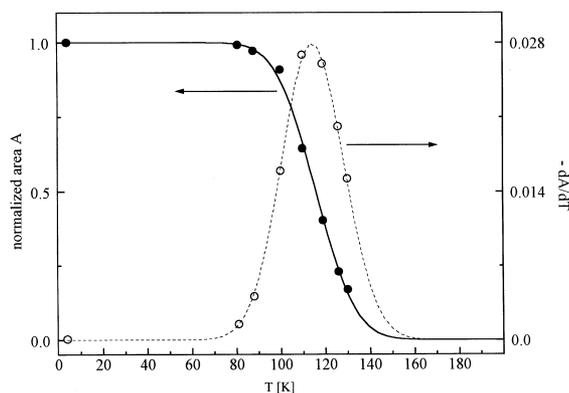


Fig. 4. Thermal stability of the T2 tautomer. Integral over absorption band is plotted versus increasing temperature (filled circles) with 5 min waiting time at each temperature. Open circles correspond to the temperature derivative of the absorption. See text for description of fitting curves.

barriers heights, $p(V)$. The model also assumes that at a certain temperature only those T2 molecules will overcome such barrier, for which $V < kT$. In this case a derivative of the absorption as a function of temperature will give us the barrier distribution function (for a given experimental time) [23]. This experimental distribution function is shown in Fig. 4 (open circles), fitted with a Gaussian (dashed line). From there we find a critical temperature, $T_c = 115 \text{ K}$, where the absorption reduces to one half of its initial value. The width of the barrier height distribution is, $\sigma_b = 14 \text{ K}$.

Among other porphyrins with proton tautomerization, our system shows almost the same thermostability as symmetrical tetrabenzoporphyrins, tetraphenylporphyrins, [24] and asymmetrical naphthalocyanines [18], far exceeding that of chlorin [18].

5. Hole burning in T2 absorption spectrum with femtosecond pulses

Fig. 5 shows the profile of a broad spectral hole created by illumination with 200 fs duration pulses at 620 nm , 0.6 mW/cm^2 average power, and 1 kHz repetition rate, as a function of the illumination time. At short illumination times, the hole maximum coincides with that of the laser spectrum,

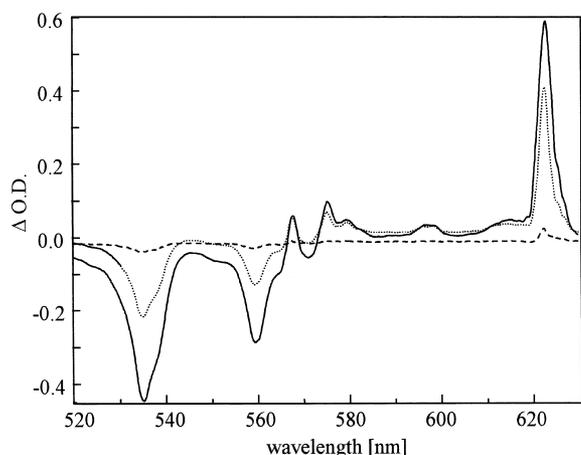


Fig. 5. Burning of the T2 band upon illumination with spectrally broad femtosecond pulses at three exposure levels, 20 mJ cm^{-2} (dotted line), 420 mJ cm^{-2} (dashed line), 1220 mJ cm^{-2} (solid line).

whereas at longer times it continuously shifts towards the center of the inhomogeneous band. Note that we were able to burn out almost 90% of the initial optical density. We estimate the quantum efficiency in this case to be $\varphi = (2 \pm 1) \times 10^{-3}$. Within the limits of experimental error, this value agrees with that obtained in cw burning mode. This result confirms that the mechanism of hole burning (i.e., tautomerism of protons) is the same, both for pulsed and cw excitation. To our knowledge, the highest value, $\varphi \approx 0.1$, was observed in the less-stable tautomer form of chlorin [18]. But, the Debye–Waller factor in that system is very small. Symmetrically substituted OEP possesses also a relatively high quantum efficiency, $\varphi \approx 2.5 \times 10^{-2}$ [18]. However, the energy separation between the two tautomers is very small. Higher burning efficiency in OEP, as compared to BrTEP, correlates with its longer triplet state lifetime, $\tau \approx 22 \text{ ms}$ at 77 K [25], versus $\tau \approx 1.8 \text{ ms}$ in BrTEP [11].

Fig. 6 demonstrates the burning of a spectral grating with a sequence of femtosecond pulse trains. We see that at a moderate exposure of 20 mJ cm^{-2} , the material already records a spectral structure, corresponding to the Fourier power spectrum of the incident pulse train, which verifies the possibility for efficient recording of ultrafast

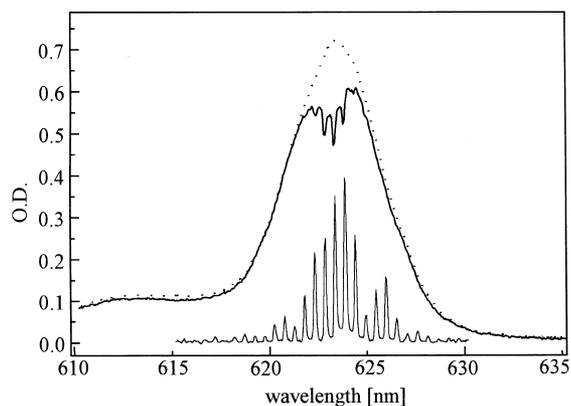


Fig. 6. Burning of a spectral grating with a train of femtosecond pulses. Absorption spectrum of T2 before (dotted line) and after (bold line) exposure with 20 mJ cm^{-2} . Intensity spectrum spectrum of the laser pulse train is shown for comparison (thin line).

time-and-space-domain holograms. We have also performed preliminary experiments on holographic recording in the T2 band, by splitting the femtosecond laser beam into object and reference beams. More details about these experiments will be given in following reports.

6. Conclusions

To summarize, we have introduced and characterized a new persistent spectral hole burning material for broad bandwidth recording, Br-tetraethylporphyrin in poly(vinyl butyral). We showed that hole burning can be performed in this material in the $S_1 \leftarrow S_0$ band of the unstable tautomer, rather than in the usual stable tautomer. We showed that because the stable form has a much lower oscillator strength, the spectral overlap between the tautomers has no practical consequences, which is an important advantage for ultrafast holographic storage applications.

Acknowledgements

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