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Nonlinear optical and optical limiting properties of phthalocyanines in solution and thin films of PMMA at 633 nm studied using a cw laser

S.J. Mathews [a], S. Chaitanya Kumar [a], L. Giribabu [b], S. Venugopal Rao [a],*

[a] Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India
[b] Nanomaterials Laboratory, Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, Andhra Pradesh, India

Abstract

We present our results on nonlinear optical (NLO) and optical limiting properties of Tetra *tert*-butyl phthalocyanine and Zinc tetra *tert*-butyl phthalocyanine studied at 633 nm using a continuous wave laser. We have evaluated the sign and magnitude of the third-order nonlinearity from the closed aperture Z-scan data while the nonlinear absorption properties were assessed using the open aperture data. We have observed low power optical limiting, with low limiting thresholds, based on nonlinear refraction in both the samples. We also present results on the NLO properties of the same dyes doped in Polymethylmethacrylate (PMMA). These studies indicate that both the phthalocyanines are potential candidates for low power optical limiting applications.
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1. Introduction

The growth of interest in using all-optical devices in modern technology such as telecommunications has been prominent, especially in the last few years. For example, the substitution of electronic devices by the optical counterparts in communications technology, proved to be an impressive accelerator for processing, transport, and storage of data. In this respect, manipulation of amplitude, polarization, direction or phase of the optical beam gains significance. Such a control over light by light itself is possible through various NLO phenomena. In order to carry out these manipulations efficiently, an understanding of the underlying nonlinear optical phenomena is essential. The structural prerequisite for the verification of NLO phenomena in organic compounds is the presence of a network of delocalized π-conjugated electrons, which infer high polarizability and fast charge redistribution when the conjugated molecule interacts with rapidly varying intense electromag-

netic fields like those of laser pulses. Among the conjugated organic molecules possessing NLO properties Porphyrins, C_{60} [1–6] and Phthalocyanines [7–22] occupy a prominent position due to their versatile properties such as high thermal and chemical stability along with the ease of preparation and purification. Phthalocyanines offer great structural flexibility, and can host ∼70 different elements in the central phthalocyanine cavity. Moreover a large range of peripheral substituents of phthalocyanines is known, which were introduced in order to improve the poor solubility of unsubstituted phthalocyanine. The optical nonlinearities of phthalocyanines and their derivatives are being investigated mainly to explore their potential applications in optical devices such as optical limiters and all-optical switches [7–22]. Although many phthalocyanines have been investigated till date, their performance for optical limiting applications ranged from moderate to very good but for optical switching applications there is still much scope for investigation of novel structures with better credentials. We present here results of nonlinear optical studies of Tetra *tert*-butyl phthalocyanine (referred to as pc1) and Zinc tetra *tert*-butylphthalocyanine (referred to as pc2) in solution and thin film forms using a cw He–Ne laser at 633 nm. The advantage of

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* Corresponding author. Tel.: +91 361 2582718; fax: +91 361 2582749.
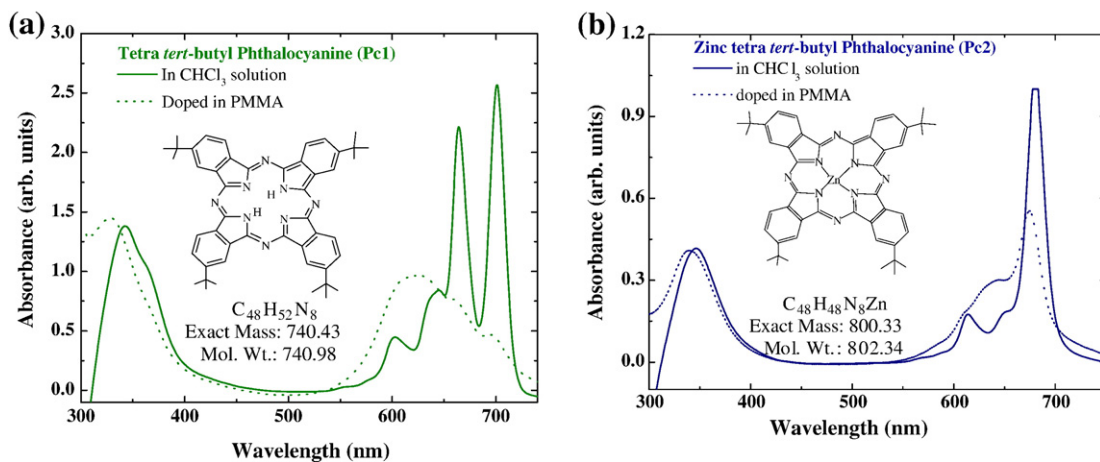*E-mail address:* soma_venu@iitg.ernet.in (S.V. Rao).

Fig. 1. (a) Absorption spectra of pc1 in chloroform (Solid line) and in PMMA (350 K) (dotted line). (b) Absorption spectra of pc2 in chloroform (Solid line) and in PMMA (350 K) (dotted line).

these robust class of phthalocyanines, compared to others, are (a) Planar structure and facile synthesis procedure (b) Easy dissolution in all common solvents implying that it can be embedded in majority of the polymers easily (c) Excellent chemical and thermal stability along with long shelf life.

2. Experimental

Both the phthalocyanines were synthesized according to the procedures reported in literature [23] and were purified before being used in the NLO studies. Chloroform was used as the
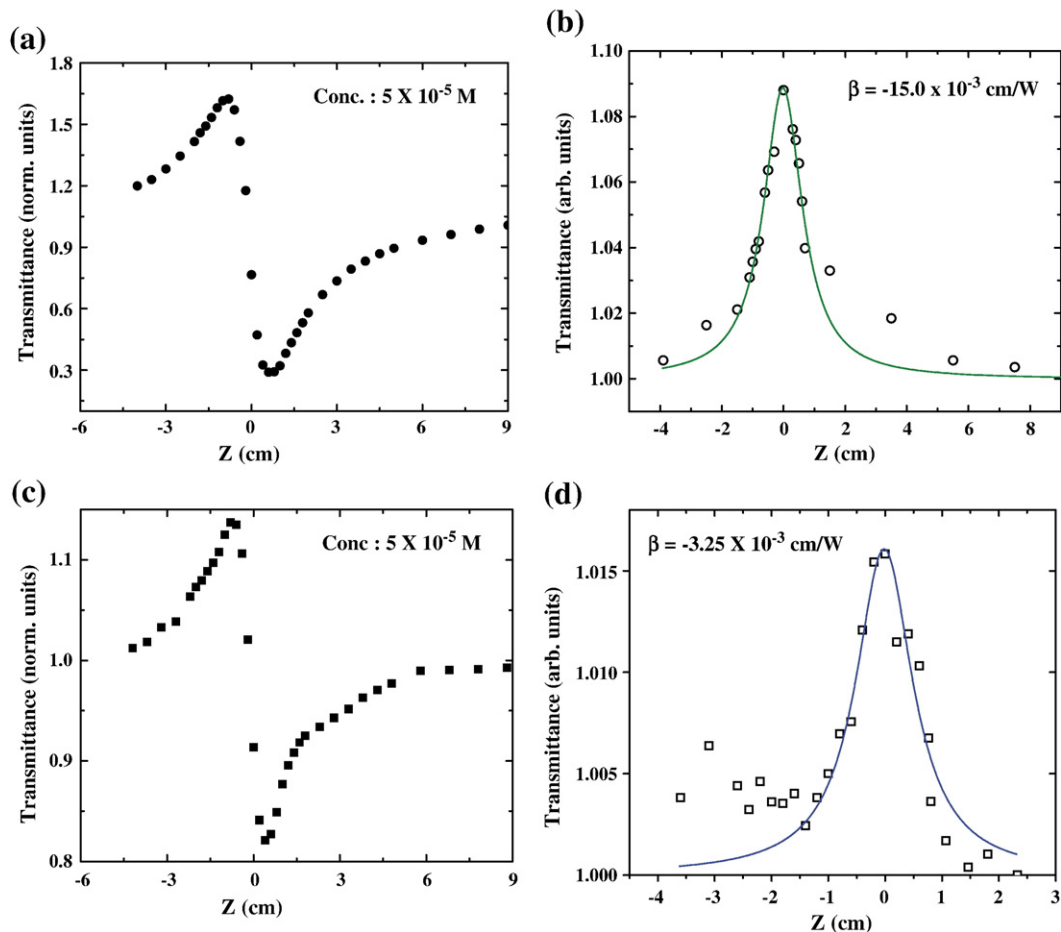

Fig. 2. (a) and (c) Closed aperture Z-scans of pc1 and pc2 in chloroform solution indicating a negative type of nonlinearity. (b) and (d) Open aperture Z-scans for pc1 and pc2 indicating a saturable absorption type of nonlinearity.

solvent for dissolving the samples. For obtaining thin films, initially PMMA (350 K, purchased from Sigma Aldrich) was dissolved in chloroform and left in an ultrasonic bath for few hours to obtain a clear solution. In the next step phthalocyanines (pc1 and pc2) were added to these solutions with the doping carried out according to weight percent. Pc1 and Pc2 were doped by 1 wt.% in the PMMA solutions. Clear uniform films were obtained after spin coating using a home-made spin coater with varying speeds. The thickness of films determined by the m-line technique (Metricon prism coupler 2010) varied from 9 µm to 15 µm depending on the spin speed. The measurements for determining the thickness were performed on plain PMMA films. We used 9 ± 1 µm thick films of pc1 and 12 ± 1 µm thick films of pc2 for the present NLO studies.

We employed the standard Z-scan technique [24,25] for evaluating the nonlinear optical properties at 633 nm. A Helium–Neon laser was the source used for exciting the sample solutions and thin films. Typical values of the parameters used for the experiment were input beam of size (diameter) 0.70 mm focused to a spot size of ~ 30 µm (~ 65 µm) using 5 cm (10 cm) lens, with input powers in the 5–14 mW range. The sample solutions (in chloroform) were placed in a 1-mm quartz cuvette. Thin films were coated on to commercially available microscope slides. The molecular structures and corresponding absorption spectra of the phthalocyanines studied are shown in Fig. 1(a) and (b). Solid line represents the absorption spectra for solutions and the dotted line represents the absorption spectra for phthalocyanine doped thin film (PMMA). A characteristic double peak structure in the 600–700 nm range (Q-band) was observed for pc1 solution while the peaks were suppressed in thin film. Pc2 had a single absorption peak near 700 nm (Q-band) in both solution and thin film forms.

3. Results and discussion

Fig. 2(a) and (b) shows the closed aperture and open aperture Z-scan curves obtained for pc1 (metal-free phthalocyanine). A signature of peak–valley indicating a negative type of nonlinearity from closed aperture and saturable absorption type behaviour from open aperture scan was observed. Fig. 2(c) and (d) shows the closed aperture and open aperture Z-scan traces for pc2 (metal phthalocyanine) again indicating negative and saturable type of nonlinearities.

The nonlinear refractive index (n_2) was calculated using the standard relations [24,25]

$$n_2 = \frac{\Delta n_0}{I_0} \text{ with}$$
$$\Delta n_0 = \frac{\Delta\phi_0}{kL_{\text{eff}}} \text{ and} \tag{1}$$
$$\Delta T_{p-v} \cong 0.406(1-S)^{0.25} * |\Delta\phi_0|, \text{ where}$$

$L_{\text{eff}} = \frac{(1-e^{-\alpha L})}{\alpha}$ with $I_0 = 2P/\pi\omega_0^2$ defined as the peak intensity within the sample and ΔT_{p-v} the peak–valley distance. $|\Delta\Phi_0|$ is the on-axis phase-shift, L is the thickness of the sample, α is the linear absorption coefficient and S is the linear transmittance of the
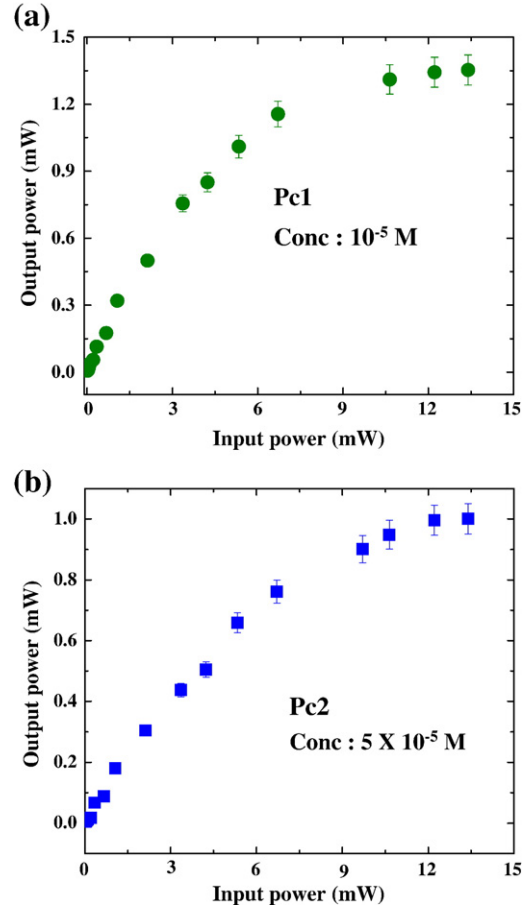

Fig. 3. (a) Optical limiting curve recorded for pc1 in chloroform solution for a concentration of 10^{-5} M (b) Optical limiting curve for pc2 in chloroform for a concentration of 5×10^{-5} M.

aperture given by $S=1-\exp(-2r_a^2/w_a^2)$ where r_a is the radius of the aperture and w_a is the radius of the laser spot before the aperture. Using the peak–valley distances measured from the closed aperture Z-scans we estimated the values of n_2 as $\sim 20.0\pm4.0\times10^{-7}$ cm^2/W for pc1 and $\sim 2.5\pm0.5\times10^{-7}$ cm^2/W for pc2.

The imaginary part of the third-order nonlinear optical susceptibility [$\chi^{(3)}$] was estimated using the value of nonlinear absorption coefficient β obtained from open aperture Z-scan data and using the relations:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \text{ for } |q_0(0)| < 1, \tag{2}$$

where

$$q_0(z) = \beta I_0 L_{\text{eff}}/\left(1 + z^2/z_0^2\right) \tag{3}$$

$$\text{Im}\left[\chi^{(3)}\right] = 10^{-2}\frac{\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2}\beta (\text{cm/W}) \tag{4}$$

$$\text{Re}\left[\chi^{(3)}\right] = 10^{-4}\frac{\varepsilon_0 n_0^2 c^2}{\pi}n_2 (\text{cm}^2/\text{W}) \tag{5}$$

z_0 is the Rayleigh range, I_0 is the peak intensity within the sample, n_0 is the linear refractive index of the sample, ϵ_0 is the permittivity of free space.

In case of saturation type of nonlinear absorption we can estimate the value of $Im[\chi^{(3)}]$ from the nonlinear absorption coefficient β (cm/W) using the relation $\beta = \sigma_0 / I_s$ where σ_0 is the ground state absorption coefficient in cm^{-1} provided the value of I_s (Saturation Intensity) is $> I_0$ (Peak Intensity). The solid lines in Fig. 2(b) and (d) are the theoretical fits using Eqs. (2) and (3) to obtain the nonlinear absorption coefficient β. The third order nonlinear susceptibilities for pc1 and pc2 measured using relations (4) and (5) were $10.0 \pm 2.0 \times 10^{-5}$ esu and $1.4 \pm 0.25 \times 10^{-5}$ esu, respectively, clearly indicating that the metal free phthalocyanine possessed stronger nonlinearity. These values represent an average of two independent set of measurements. The errors in estimating these values arise from the uncertainties in the estimation of focal spot size, peak intensities, Rayleigh range, and absorbance. We expect the maximum error in such measurements to be $\sim 20\%$.

For optical limiting experiments the sample solution in a 1-mm quartz cuvette was placed just after the focus of lens (focal length of 10 cm) where the defocusing occurred. At very high peak intensities (closer to the focus) we could observe diffraction type pattern with concentric ring structures probably due to self-phase modulation. However, for limiting experiments we ensured that there was no ring pattern formation by placing the sample away from focus, yet in the nonlinear regime. Fig. 3 depicts the optical limiting curve in chloroform solutions recorded for concentrations of 10^{-5} M and 5×10^{-5} M for pc1 and pc2 respectively. We could reproduce this behaviour several times within some experimental errors. It is evident from the figure that the threshold was low and was estimated to be ~ 7 mW. We could not verify the behaviour (damage or breakdown threshold) above 14 mW due to limitations with our laser source power. We observed a low threshold of ~ 8 mW for pc2 also. The limiting behaviour observed in both the samples is attributed mainly to nonlinear refraction. Since the samples were pumped with cw laser beam the arising nonlinearities are predominantly thermal in nature. Our results are comparable to some of the recent reports of low power optical limiting in porphyrins [26].

For thin film studies the samples were doped in high molecular weight PMMA (350,000) which could be utilized for fabricating nonlinear waveguides in direct writing applications. Fig. 4(a),(b) and (c),(d) shows the close aperture and open aperture z-scan results obtained for pc1 and pc2 respectively. It is evident that both the samples exhibit *negative* nonlinearity as indicated by the peak–valley structure in closed aperture Z-scans and saturable absorption kind of behaviour as indicated by the open aperture Z-scans. The values of n_2 and $\chi^{(3)}$ evaluated for Pc1 thin film were 12.0×10^{-6} cm^2/W and 7.00×10^{-4} esu respectively. The corresponding values were 14.2×10^{-6} cm^2/W and 8.6×10^{-4} esu respectively for pc2. Pc1 had a higher
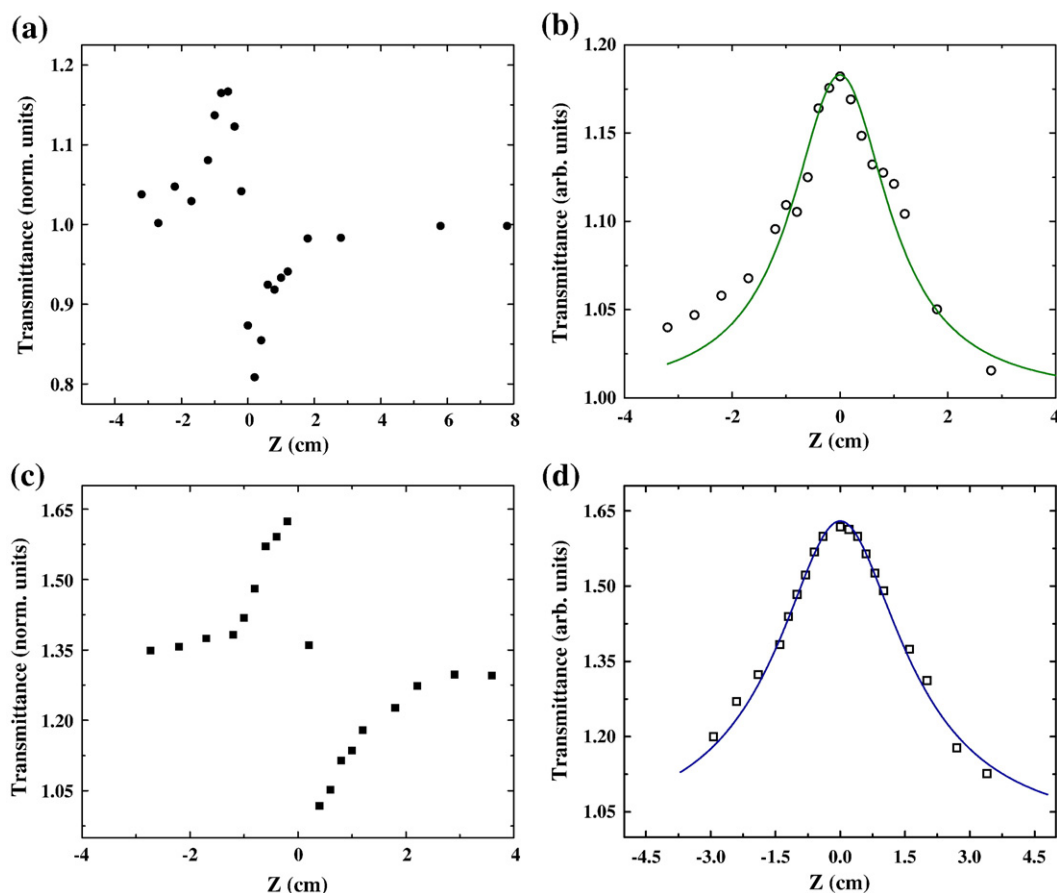

Fig. 4. (a) and (c) Closed aperture Z-scans of pc1 and pc2 (doped 1% by weight) in PMMA (350 K) film indicating a negative type of nonlinearity. (b) and (d) Open aperture Z-scans for pc1 and pc2 films indicating a saturable absorption type of nonlinearity.

Table 1
Summary of the nonlinear optical properties of pc1 and pc2 evaluated from Z-scans

Form of sample →	Thin films (in PMMA) solvent: $CHCl_3$		Solution solvent: $CHCl_3$	
Sample	Pc1	Pc2	Pc1	Pc2
% by weight/concentration	1%	1%	5×10^{-5} M	5×10^{-5} M
Nonlinear RI n_2 (cm^2/W)	-12.0×10^{-6}	-14.2×10^{-6}	-20.0×10^{-7}	-2.5×10^{-7}
Nonlinear absorption coefficient β (cm/W)	-0.49	-1.1	-15.00×10^{-3}	-3.25×10^{-3}
$|\chi^{(3)}|$(esu)	$7.0 \pm 1.4 \times 10^{-4}$	$8.6 \pm 1.7 \times 10^{-4}$	$10.0 \pm 2.0 \times 10^{-5}$	$1.4 \pm 0.3 \times 10^{-5}$

nonlinearity compared to pc2 in solution form. The difference is not clear from the values in thin film form and probably stems from the fact that amount of linear and nonlinear absorption will be slightly different in solution and thin film forms for both the phthalocyanines. Moreover, the errors in the measurement of thickness and n_2 values suggest that the behaviour of $\chi^{(3)}$ in thin films is a bit complex. Our initial studies do not suggest appropriate limiting behaviour in the thin films probably due to scattering or bleaching. Table 1 summarizes the values of nonlinear refractive indices, nonlinear absorption coefficients, and third order susceptibilities of both the phthalocyanines in solution and thin film form. These values correspond to one of the highest reported in literature for molecules with cw excitation [27,28].

With cw pumping we expect major contribution to the observed third-order nonlinearities to be thermal in nature. The energy from the focused laser beam is transferred to sample through linear absorption and is manifested in terms of heating the medium leading to a temperature gradient and there by the refractive index change across the sample which then acts as a lens. The phase of the propagating beam will be distorted due to the presence of this thermal lens. The peak–valley separation of more than 1.7 times the Rayleigh range of ~ 0.38 cm (~ 5 times in solutions and ~ 3 times in thin films) also suggests the presence of thermal component in our case. It is well established that a separation of $\sim 1.7 z_0$ indicates Kerr-type of nonlinearity [29]. The values reported are one of the largest and a plausible explanation could be the relative strong absorption at 633 nm combined with a high thermo-optic coefficient for these molecules. We are investigating the behaviour of nonlinear optical response in time domain for understanding further the origin of this strong nonlinearity. Studies to this extent are in progress and will be a subject of our future publication. We strongly feel that these molecules are potential candidates for optical limiting applications with cw and nsec excitation particularly in the 400–650 nm spectral regions. We also believe that these molecules possess ultrafast relaxation times which could be exploited for switching applications.

4. Conclusions

In conclusion we have reported the nonlinear optical properties of two phthalocyanines (metal and metal-free) obtained using cw excitation at 633 nm. The observed nonlinearities were large and negative in nature. For samples Pc1 and Pc2, in solution form, the nonlinear refractive indices

obtained from the Z-scan data were $\sim 2.0 \times 0.4 \times 10^{-6}$ cm^2/W and $\sim 2.5 \pm 0.5 \times 10^{-7}$ cm^2/W. The reported nonlinearities are primarily thermal in nature owing to the cw excitation. Based on nonlinear refraction both the samples behaved as good optical limiters even at low powers with thresholds of ~ 7 mW and ~ 8 mW indicating these samples find potential applications in optical limiting and signal processing applications.

Acknowledgements

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