

Specroelectrochemical, Switching Kinetics, and Chronoamperometric Studies of Dibenzyl Derivative of Poly(3,4-propylenedioxythiophene) Thin-Film-Based Electrochromic Device

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ABSTRACT: The dibenzyl derivative of poly(3,4-propylenedioxythiophene) (PProDOT-Bz₂) thin film is deposited onto ITO-coated glass substrate by electropolymerization technique. The electropolymerization of ProDOT-Bz₂ is carried out by a three-electrode electrochemical cell. The cyclic voltammogram shows the redox properties of electrochemically prepared films deposited at different scan rates. The thin films prepared were characterized for its morphological properties to study the homogeniety. Classic six-layer structure of PProDOT-Bz₂ electrochromic device using this material was fabricated and reported for the first and its characterizations such as spectroelectrochemical, switching kinetics, and chronoamperometric studies are performed. The color contrast of the thin film and the device achieved are 64 and 40%, respectively, at λ_{max} (628 nm). The switching time is recorded and the observed values are 5 s from the coloring state to the bleaching state and vice versa. The chronoamperometry shows that the device performed up to 400 cycles, and it is capable of working up to 35 cycles without any degradation. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40717.

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INTRODUCTION

The change in optical properties of a material as a function of applied potential is known as electrochromism.^{1,2} Nowadays, due to the slow response time and low color contrast, inorganic materials are not much of interests to the scientific community.³⁻⁵ Electrochromic (EC) materials have been used in many technological applications such as automotive antiglazing mirror, smart window, and EC displays.⁶ The conducting polymers (CPs) are highly desirable for EC device applications because of its low oxidation potential, high color contrast, and ease of processing.^{7,8} Among the various CPs, polythiophene and its derivatives are widely used due to its faster switching, high conductivity, optical transparency, high spectral contrast between redox state, and good environmental stability.9,10 Nevertheless, $\alpha-\beta$ coupling between thiophene rings and high oxidation potential of the monomer during polymerization leads to a decrease or influence the values of the said properties. In order to overcome this problem, 3-substituted and 3,4-disubstituted thiophenes were synthesized and studied by different research groups.^{11,12} It was found that the addition of alkylenedioxy bridge across 3 and 4 positions increase the electron density to

aromatic ring and reduce the oxidation potentials which eventually led to the formation of highly stable CPs. 13

In addition, color contrast is also a defining property for display device performance. The color contrast is defined as the change in the percentage transmittance between oxidized and reduced state.¹⁴ The poly(3,4-ethylenedioxythiophene) (PEDOT) has been used as emerging material in EC applications, however due to its low color contrast, and insolubility in solvents limiting from commercial and industrial applications. This problem can be sorted out either by structural modification or incorporation of additional bulky substituent in alkylenedioxy ring. Recently, researchers have shown interest on poly(3,4-propylenedioxythiophene) (PProDOT) and its derivatives to increase EC properties such as color contrast, response time, stability and processing time. A monomer, dibenzyl derivative of ProDOT (PProDOT-Bz₂) was synthesized, and its polymer thin film with high color contrast (89%) was reported by Kumar and coworkers¹⁵ (thickness of the film was not given). The same group made an attempt to synthesize monosubstituted and disubstituted ProDOT and reported that the dibenzyl-substituted ProDOT material was insoluble in all the common solvents.¹⁶ In this article, we have



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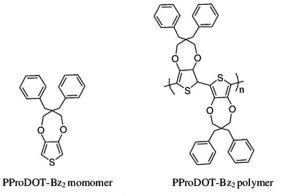


Figure 1. Chemical structures of ProDOT-Bz₂ monomers and polymers.

used the monomer synthesized by Kumar and coworkers¹⁵ and made an uniform EC thin film by applying only two cycles using cyclic voltammetry (CV) technique. Our attempt in this article is to characterize the film for the optical and morphological properties which was not reported in Ref. 15 and to fabricate a prototype EC device with high color contrast and to study the performance of the device without using a complementary coloring material for counter electrode. The novelty of this article is the fabrication of EC window based on dibenzyl-substituted ProDOT for the first time.

This study, systematically addresses the preparation and characterization PProDOT- Bz_2 thin film. These thin films were used to fabricate EC windows and the window was characterized for its performance such as color contrast, switching time, and stability.

EXPERIMENTAL

PProDOT-Bz₂ Thin-Film Deposition

Dibenzyl derivative of ProDOT (Figure 1) was electropolymerized using a three-electrode electrochemical cell onto

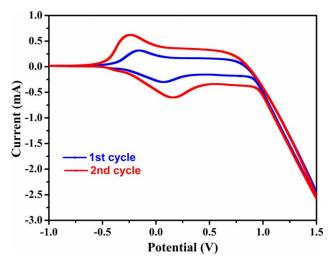


Figure 2. Cyclic voltammogram during electropolymerization of PPro-DOT-Bz₂ on ITO-coated glass substrate from 0.01M respective monomers in 0.1M TBAP/ACN solution in the potential range of 1.5 to -1.0 V at 100 mVs⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

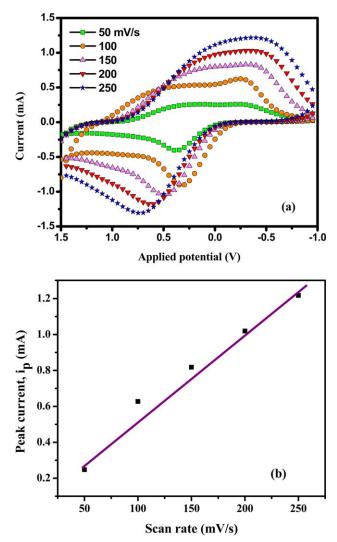


Figure 3. (a) Cyclic voltammograms of PProDOT-Bz₂ on ITO-coated glass at different scan rates, (b) A plot of scan rates against oxidative peaks current (I_p) during cyclic voltammetry of PProDOT-Bz₂ thin film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ITO-coated glass substrate as a working electrode. Platinum foil and $Ag/AgNO_3^+$ were used as counter and reference electrode, respectively.¹⁷ The PProDOT-Bz₂ thin film was deposited on to ITO/glass substrate by CV in 0.01*M* ProDOT-Bz₂ monomer dissolved in 0.1*M* TBAP/acetonitrile (ACN) medium at potential between 1.5 and -1.0 V with scan rate of 100 mVs⁻¹ shown in Figure 2. The obtained polymer film was homogeneous and adherent to the electrode. Reduction and oxidation reaction of the conductive polymer took place at -0.23 and 0.16 V, respectively. After electropolymerization, the obtained PProDOT-Bz₂ films were rinsed thoroughly with ACN to remove unreacted monomers and electrolytes then dried at room temperature.

Preparation of Gel Electrolyte

The electrolyte used for the EC device has been prepared according to the previous report.¹⁸ About 0.75 g (3%) of LiClO₄ was dispersed in 13.65 mL (70%) of ACN followed by

Table I. Scan Rates Against Oxidative Peaks Current (I_p) and DiffusionCoefficient (D) of PProDOT-Bz2 Thin Film

Scan rates (mVs ⁻¹)	Cathodic peak current (l_p) $ imes$ 10 $^{-4}$	Diffusion coefficient (D) $\times 10^{-10} \text{ cm}^2 \text{s}^{-1}$
50	2.5233	0.1758
100	6.3428	0.5559
150	8.2507	0.6271
200	10.26	0.7274
250	12.24	0.8288

1.75 g (7%) of poly(methyl methacrylate) and heated under magnetic stirrer for 6 h at 70°C for complete dissolution. Then 5.95 mL (20%) of propylene carbonate as plasticizer was added to this solution under stirring. This viscous transparent gel was then cooled and preserved for device fabrication.

Characterization Technique

Electropolymerizations and electrochemical studies of the PPro-DOT-Bz₂ thin films were performed using cyclic voltammetry (CH Instrument electrochemical analyzer model CHI6005D). The optical transmission and absorption spectra were recorded using a UV-Visible optical spectrophotometer (Ocean optics model DH-2000-BAL). The morphology of the PProDOT-Bz₂ thin film was studied using FEI ESEM Quanta 200 and atomic force microscopy (AFM; model A100-SGS AFM) analysis was carried out in AFM facility, Department of MRC, Indian Institute of Science, Bangalore, India. Raman scattering analysis was carried out using Jobin Yvon LabRAM HR. Argon ion laser having a wavelength of 514 nm was used as the excitation source. Bruker IFS 66v/s vacuum Fourier transform interferometer was used for FTIR characterization.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Figure 3(a) shows the redox properties of electrochemically prepared PProDOT-Bz₂ thin film observed using CV at potential between 1.5 and -1.0 V in 0.1*M* TBAP/ACN solution with different scan rates of 50, 100, 150, 200, and 250 mVs⁻¹, respectively. Nevertheless, the current densities were directly proportional to the scan rates, there was an anodic shift in corresponding oxidation peak at increasing scan rate that indicated the polymeric film was electroactive and well adhered to the electrode surface. Electrochemically prepared PProDOT-Bz₂ thin film changed the color from deep blue to transparent light blue, accompanying to a further redox reaction. The linear relationship between the peak current with scan rates in Figure 3(b) also demonstrated that the electrochemical processes were reversible in nature even at high scan rates.^{19,20}

Diffusion Coefficient

The diffusion coefficient (*D*) values of PProDOT-Bz₂ thin film has been calculated using the CV and Randles–Sevick equation:²¹

$$I_p = (2.69 \times 10^5) n^{2/3} AD^{1/2} CV^{1/2}$$

where I_p is the cathodic peak current from CV measurement, n is the electron number involved in redox reaction, A is the film

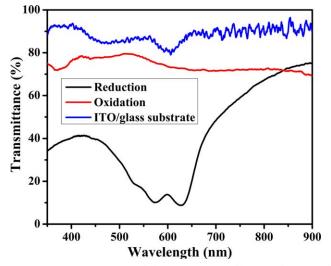


Figure 4. (a) UV–vis spectra of the PProDOT-Bz₂ film as a function of applied potential between -1.5 and +1.5 V in 0.1M TBAP/ACN solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

active area, C is the concentration of electrolyte, V is the scan rate of CV measurement.

The calculated ion diffusion coefficient of the PProDOT-Bz₂ thin film was 0.55×10^{-8} cm² s⁻¹ for 100 mVs⁻¹ scan rate in 0.1M of electrolyte concentration and 1 cm² film area. This diffusion coefficient indicates that the film has the capability to modify color in fraction of seconds. Table I gives the diffusion coefficient values at different scan rates.

Transmittance Spectrum

The UV–vis spectrum of PProDOT-Bz₂ thin film coated onto ITO/glass was recorded in a monomer-free LiClO₄/ACN electrolytic solution at applied potential between -1.0 and +1.5 V is shown in Figure 4. This EC thin film depicts the reversible switching between a deep blue and transparent light blue color

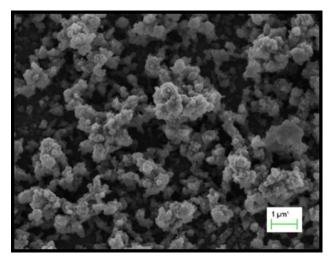


Figure 5. The SEM image of PProDOT-Bz₂ film deposited on ITO-coated glass substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



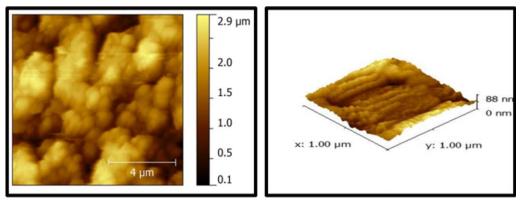


Figure 6. AFM images for PProDOT- Bz_2 film (left) and the 3D image (right) of the film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and this film gives the maximum absorption and transmission in the visible region. The color contrast ($\Delta\% T$) between fully colored (deep blue) and bleached state (light blue) was 64% at $\lambda_{\rm max}$ of 628 nm which was significantly higher than the value of PEDOT.⁸ This indicates that the incorporation of dibenzyl groups on 3,4-propylene dioxythiophene rings have enhanced the color contrast of PProDOT.¹⁵

Morphological Studies

SEM of Electrochromic Film. The surface morphology of PPro-DOT-Bz₂ thin film was demonstrated by the SEM image as shown in Figure 5. It depicted that the surface of the PPro-DOT-Bz₂ film was homogeneous and well-separated agglomerations of particles with less than 200 nm in size. The morphological image also confirmed that the PProDOT-Bz₂ film which formed on ITO/glass substrates was uniform without any pores or cracks.¹⁷

Atomic Force Microscopy. The electropolymerized PProDOT-Bz₂ thin film appeared uniform and exhibited high color contrast of ~64%. Nevertheless, on microscopic scale measurement, it was apparent that the film lacked consistency in morphology and it also showed the surface was rough. The 3D image from Figure 6 indicates the morphology of PProDOT-Bz₂ was spherical, and pile shaped due to the formation of undulated

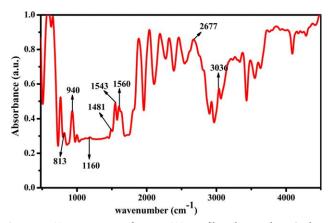


Figure 7. FTIR spectrum of PProDOT-Bz₂ film electropolymerized on ITO/glass substrate at the scan rate 100 mVs^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

premature microstructured aggregation of particles, which may be due to limited solubility.

FTIR Analysis

The FTIR characteristic peaks depicted the assignment of corresponding functional groups of the obtained PProDOT-Bz₂ thin film on ITO/glass substrates as shown in Figure 7. The region between 1530 and 1560 cm⁻¹ was known to contain absorptions due to aromatic ring deforming vibrations and the position and strength of these features were strongly dependent on the substitute attached to the ring.²² The peak observed at 1543 cm⁻¹ was due to the deformation of phenyl rings with attached sulfonate groups. The band at 1481 cm⁻¹ and the peak at 1160 cm⁻¹ showed the stretching of C=C bond and C-O-C bond correspondingly. The bands at 813 and 3036 cm⁻¹ were attributed to aromatic C-H bonding and stretching, respectively.^{23,24}

Raman Spectral Analysis

The Raman spectra of PProDOT-Bz₂ thin film is shown in Figure 8 that describes the structural information. The C-H strong bonds were observed at 2842 and 2930 cm⁻¹ and the main Raman lines at 1508, 1411, 1089–1215, and 958 cm⁻¹ were attributed to the vibrational modes: C=C vibration, CH₂ and

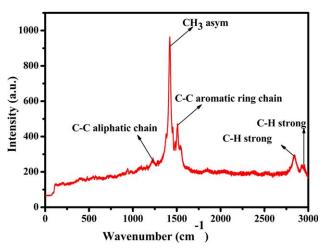


Figure 8. Raman spectrum of electropolymerized $PProDOT-Bz_2$ thin film on ITO/glass substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 Table II. Raman Frequency of Dibenzyl Derivative of PProDOT Film and Its Functional Groups

Frequency (cm ⁻¹)	Intensity	Functional groups
1215, 1089	Medium	Aliphatic C-C chain vibration
502.77	Strong	Si-O-Si
1411	Medium	CH ₂ , CH ₃ asym
1508	Strong	C=C vibration
958	Medium	C-O-C
2842, 2930	Strong	C-H
1508	Strong	Aromatic C-C chain ring

CH₃ asymmetric vibration, aliphatic C-C chain vibration, and C-O-C vibration subsequently.²⁵ Raman frequency, intensity, and its functional groups of PProDOT-Bz₂ thin film are given in Table II.

Performance of PProDOT-Bz₂ EC Devices

Fabrication of Solid Electrochromic Device. The six-layered EC device shown in Figure 9(a) was prepared by sandwiching the conducting gel electrolyte between the PProDOT-Bz₂ thin film coated ITO/glass (working electrode) and the as-prepared ITO/glass (counter electrode). While applying potential the electrolyte allows the transport of ions through the device, one layer acts as the positive electrode (e.g., bare ITO/glass) and another layer (e.g., PProDOT-Bz₂ thin film/ITO/glass) plays as the negative electrode and vice versa. The potential range between -2.0 V (deep blue) and +2.0 V (colorless) were applied to the device and the picture is shown in Figure 9(b,c), respectively. The life span of the device was studied up to 400 cycles and after 35

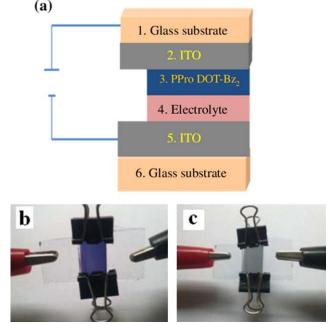


Figure 9. (a) Schematic diagram of the electrochromic device; from top to bottom: ITO glass, PProDOT-Bz₂, gel electrolyte, ITO glass, and photo-graphic images of (b) colored and (c) bleached states of PProDOT-Bz₂ device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cycles the peak current slightly decreased and beyond 250 cycles the peak current was almost constant. The color contrast of the device observed was 40% at $\lambda_{\rm max}$ (628 nm). The time required to change from colored to bleached state and vice versa was 5 s.

Spectroelectrochemistry of PProDOT-Bz₂ Device. *Absorbance spectra.* The absorbance spectra shown in Figure 10(a) were investigated for the PProDOT-Bz₂ device maintained at potential range between +2.0 and -2.0 V using DC power source. As the applied potential was increased cathodically from +2.0 to -2.0 V, the color of the device changed from transparent blue to deep blue color. The figure revealed that the bleached state possessed no variation in absorbance but showed a small hump at 600 nm. But in colored state, it was observed that the absorbance increased with decreasing potential from -1.0 to -2.0 V. Upon reduction, the spectrum of the device indicated that the absorption peak split into two peaks at 587 and 627

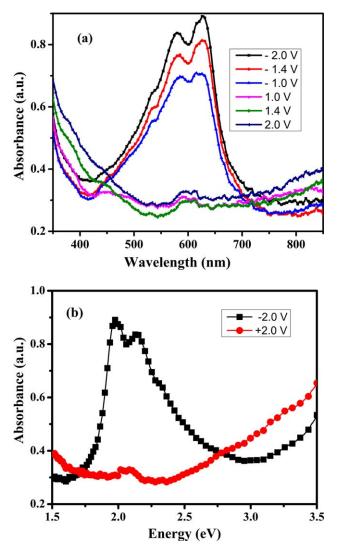


Figure 10. (a) The absorbance spectra of PProDOT-Bz₂ thin-film-based electrochromic device between -2.0 and +2.0 V, (b) optical absorption spectra of PProDOT-Bz₂ for applied voltages -2.0 and +2.0 V. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]



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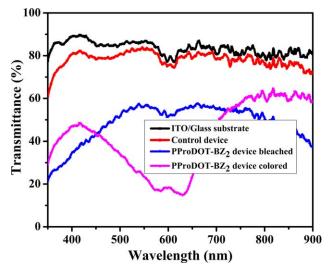


Figure 11. UV–vis spectra of ITO/glass substrate, control device, PPro-DOT- Bz_2 thin-film-based electrochromic device bleached and colored states from -2.0 to +2.0 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nm, respectively, for -1.0 V potential as shown in Figure 10(b). Since the carbon–oxygen double bond of the PProDOT-Bz₂ material has the π electron as a part and it has a lone pairs on the oxygen atom. The peak at 587 nm revealed the π to π^* absorption, which means, it absorbs light of a higher wavelength. Since, the absorption peak moved towards the lower wavelength as the amount of the delocalization in the molecule increased. The peak at 627 nm occurred due to n (non-bond-ing) to π^* absorption in the presence of the chromophore.⁹ The activation energy was less between the bonding and antibonding orbitals as the amount of delocalization increased as shown in Figure 10(b).

Transmittance spectra. Figure 11 shows the investigation of the coloration of PPoDOT-Bz₂ EC device with voltages ranged from

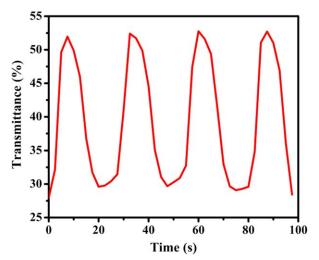


Figure 12. Switching time characteristics between the colored and bleached states for the PProDOT-Bz₂ electrochromic device measured at ± 2.0 V with transmittance wavelength of 628 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

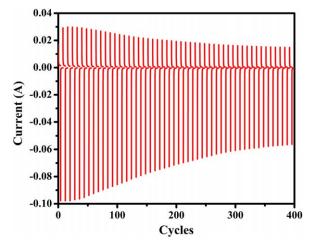


Figure 13. Chronoamperometric investigation of PProDOT-Bz₂ thin-filmbased electrochromic device in the potential between -2.0 and +2.0 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

-2.0 to +2.0 V. Transmittance of an EC device depends on the thickness of the EC materials.^{26,27} The maximum color contrast of the device achieved was 40% at λ_{max} (628 nm) for the thin film with thickness of about 256 nm measured using zeta analysis instrument. The EC device depicted the reversible switching between a deep blue and transparent light blue color and it showed the maximum absorption and transmission in the visible region. The color contrast of the device can be increased with increasing film thickness and using high transparent TCO coated glass electrode. This was significantly higher compared with low transmittance of the control device and as-prepared ITO/glass substrates.²⁸

Switching Kinetics. The EC reversibility of PProDOT-Bz₂-based EC device studied between reduced and oxidized state was measured at stepping potential between -2.0 and +2.0 V as shown in Figure 12. The response time is defined as the time required to achieve maximum percentage of the desired response, the response time was found to be 5 s from the coloring state to the bleaching state and vice versa. This slower response time is due to the additional bulky structural unit of dibenzyl derivative in PProDOT and due to slower diffusion rates of the neutral species in the EC gel upon neutralization.²⁹ PProDOT-Bz₂ device gives good EC reversibility and stability compared to the device prepared from other CPs.

Chronoamperometry. The stability and lifetime of PProDOT-Bz₂ EC device were examined at potential range from +2.0 to -2.0 V (Figure 13). It shows that the switching of the device was stable up to 35 cycles. After 35 cycles both anodic and cathodic current was decreased with increase in number of cycles.³⁰ However, the decrease in anodic current was smaller than the cathodic current as shown in figure, and it was nearly constant after 300 cycles. It shows that the device was stable to attain its colorless state. The reduction in current was due to the electronic leakage of solid-state inorganic electrolyte layers in the device. It was observed that there was a reduction in color contrast, slow switching speed, because of the leakage current in the device.

CONCLUSIONS

The CV showed that the PProDOT-Bz₂ thin film was electroactive and well adhered to the working electrode. The linear relationship between the current with scan rates demonstrated that the redox properties were reversible in nature even at high scan rates. The morphological study using SEM revealed that the PProDOT-Bz₂ film was uniform and homogeneous and the particles of size less than 200 nm were also observed .The AFM study suggests that the morphology of PProDOT-Bz₂ thin film was uniform in nature with some granular particles. The characteristics peaks of FTIR and Raman confirmed the presence of dibenzyl derivative in the polymer chain. The color contrast of the device achieved was 40% at λ_{max} (628 nm) whereas, for the same wavelength, the contrast of the film was about 64%. The time taken to switch the device from colored to bleach state and vice versa was 5 s. The chronoamperometry study of the device shows that beyond 35 cycles the colored and bleached state decreased slightly, and it worked as a switch up to 400 cycles.

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