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Organic/Polymeric Systems: Candidates for Optoelectronic Devices

K. S. NARAYAN
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064.

Abstract

Conjugated polymers have recently been shown to exhibit a wide variety of photo-induced and electric field - induced phenomena such as photoconductivity and electroluminescence. We present in this report the recent efforts in our laboratory related to the opto-electronic properties of certain conjugated polymers. The importance of electronic correlations leading to excitonic effects is observed in the photocurrent spectral responses of these polymers. We speculate on the mechanisms of absorption, photocurrent and luminescence on the basis of excitonic response in these polymers. A novel scheme to achieve a high degree of control in the mechanical and electronic properties of these polymers coupled with high photocurrent efficiency is also mentioned.

Introduction and Background:

There has been rapid intense activity in the study of electronic and optical phenomena in quasi-one dimensional organic semiconductors in recent times. It has been recently shown that polymers are attractive materials for active components in opto-electronic devices, flat-panel displays and sensors.[1–4] The main feature derives from the development of soluble precursors which permit convenient processing and fabrication of electroluminescent (light emission) and photovoltaic devices.[2,3] The flexibility of organic synthesis also permits a large number of substitutions and variations which can be used to modify the material properties. Desired properties for a device such as emission wavelength, absorption wavelength, polarization direction, can be tailored to meet the requirements. Even though the materials has entered into the technology market, most basic issues towards understanding the photophysics in the systems remain controversial.

Over the last decade the debate was on whether the initial photo-excitation in a conjugated polymer is ‘band-like’ generating free carriers as in semiconductors or ‘excitonic’ in nature as in molecular solids. The band to band transition approach was initially used and was based on single chain one electron model such as the Su Shcrieffer Heeger (SSH) model.[5] The SSH model was used to explain the bond alternation and the large energy gap in trans-polyacetylene which has a degenerate ground state. The model is a one-electron tight binding Hamiltonian which explicitly includes electron-phonon (e-p) coupling. The model highlights the existence of quasi-particle charged excitations such as solitons, polarons, and bipolarons originating from a quasi-1D system with a strong (e-p) coupling.[5] These excitations manifest as mid-gap states in the electronic structure and their signatures are expected to arise in photo-induced processes. The model explains certain features in trans-polyacetylene (PA), and polyaniline (PANI) such as metal insulator transitions.

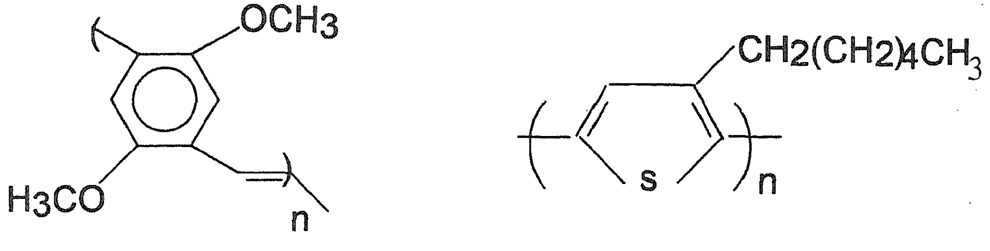
Within this framework luminescence has been interpreted in terms of recombination of electron hole pairs and the appearance of a stoke shift between absorption and emission being considered as evidence for polaron formation prior to recombination.

However the excitonic (strong electron correlations) models in the last few years have been used more successfully to explain several subtle and detailed features in the optical properties of poly(p-phenylene vinylene) PPV, polydiacetylene PDA, and polythiophene PTH systems.[6–9] The general picture out here is that photoexcitation produces a singlet exciton of mixed Frenkel- and Wannier like character that is localized to a conjugated segment. The exciton migrates to the lowest-energy segments of the sample. The 'apparent' Stokes shift is then largely due to spectral diffusion of photo-excited state to lower energy segments presumably with longer effective conjugation lengths. The remaining intrinsic shift after taking reflection, self absorption, and spectral diffusion gives information of the magnitude of the electron-phonon interaction which turns out to be small in magnitude (< 100 cm^{-1}). The other important questions are then the role of interchain coupling, the absolute magnitude of photoluminesence PL quantum yield and exciton binding energies, and the correlation between the EL and PL yields. In practically all cases almost perfect agreement is observed between (PL) and EL spectra which indicates that the excited state responsible for luminesence is the same for both cases, irrespective of the method for excitation. An important probe to answer some of these questions is to study the mechanism of the photoconduction process in these systems. The carrier generation mechanism responsible for photoconductivity has been the subject of enormous debate with explanations over the entire range from polaron pair dissociation, exciton dissociation to direct photogeneration of free carriers.

In order to assume technological importance as a candidate for flat panel device the stability and efficiency needs to be improved. Recent reports have indicated electroluminesence EL efficiency of greater than 2% and lifetimes of the order of 1000 hours.[10] Further improvements to enhance the charge recombination need a closer understanding of the photophysical process and the transport mechanism of the charge carriers at the interface and in the bulk. The organic molecular solids such as Alq_3 also electroluminesce with an added advantage of vapor phase deposition techniques.[11] This paper focuses on derivatives of PPV and PTH which are prototypical of non-degenerate ground-state conjugated polymers

Charge transport at the metal/polymer interface occurs largely by tunneling with diffusion and thermionic emission as secondary factors. However, this simplistic rigid band model does not explain many experimental results and ignores interactions between the electrodes and the polymer surface states. The EL observed in these systems require understanding and control of the four factors involved: (a) *Hole injection* (b) *Electron injection-* (c) *Transport of the carriers in the bulk;* d) *Recombination kinetics.*

Since the bulk carriers in the active medium *i.e.*, the polymer layer, have a much greater hole mobility, the recombination occurs closer to the electron injecting layer. The problems associated with the low work function metal oxide formation at the interface is an important factor in deciding the efficiency and stability. An important factor for EL yield is a balanced injection of both holes and electrons. this is normally achieved by



(a) (b)

FIG. 1. Chemical structures of DMPPV and PTH.

matching the Ferim energies of the electrode materials to the HOMO and LUMO energies of the semiconducting polymer either by choosing the appropriate materials or by tuning the redox properties by introducing subtle substituents. where the degree of disorder, crystallinity, and orientation are decisive factors for the transport, energy levels and life times associated with the recombination sites decide the emission rate.

Several strategies have been employed to increase the EL and photoconduction quantum efficiencies such as dilution of the active material in an inert matrix, incorporation of a non-conjugated segments into the polymer backbone, multilayer designs using organic charge transport layers between the contacts and the actual emissive material, or doping the active material into a charge transporting matrix.[12,13]

We discuss in these papers the photophysics of poly(2,5-dimethoxy-p-phenylene vinylene), DMPPV and poly(hexylthiophene) P3HT (Fig. 1) on the basis of our initial results and also highlight couple of different strategies adopted to enhance the opto-electronic properties.

Experimental

Absorption, dc measurements, photoconductivity and electroluminescene studies were carried on thin polymer films. For the photoconductivity studies the polymer was generally loaded into an optical cell in the ITO/sample/Aluminum sandwich configuration Fig. (2). In the transverse cell or sandwich cell configuration the samples were sandwiched

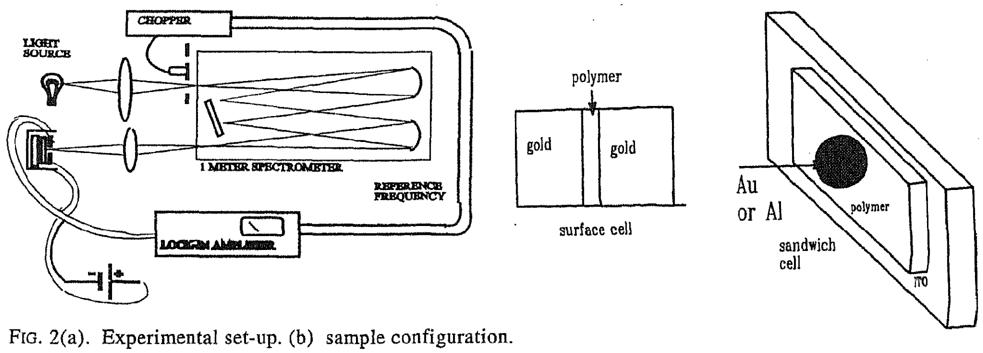


FIG. 2(a). Experimental set-up. (b) sample configuration.

between transparent ITO coated glass, serving as the front contact, and the aluminum or gold coated plates as the second electrode. A Spex monochromator with a 150 W tungsten-halogen source was used to illuminate the sample in the energy range from 1.0 eV to 3.5 eV. The incident light was chopped nominally at 10-20 Hz range and the photocurrent was detected by a lock-in amplifier (Stanford SR830). The zero frequency measurement was done using the Keithely 6512 electrometer. The intensity dependence of the photocurrent was done using neutral density filters. All data was normalized to incident photon density using a commercial calibrated photo-diode under similar experimental conditions. The incident photon flux at the sample position in the visible wavelength range measured by the photo-diode was in the order of 1 $\mu W/cm^2$. The data presented is the normalized photocurrent per unit incident photon I_{ph}. The above technique can be modified to study the electroluminesence with a modulating voltage source as a reference for the lock-in amplifier. The total intensity from the sample however has to be monitored due to the instability in the emission during the spectral scan. This final spectra has to be normalized with respect to the fluctuating total intensity to obtain the corrected EL spectra.

Studies of the chemical and morphological aspects of the conjugate polymer membrane composite were done using a Bruker IES-48 FTIR and Leica S440 SEM.

P3HT was prepared from the monomer using electrochemical synthesis procedure in a solution of nitrobenzene with tetrabutylammoniumphosphate as the electrolyte in nitrogen gas atmosphere at 5°C. The polymer is soluble in common organic solvents and films were obtained by casting and spin coating techniques. DMPPV thin films used for photoconductivity measurements were prepared by solution casting the dimethoxy precursor in chloroform on both glass and NaCl pellets. Solution concentrations were controlled to get films thickness in the range of 0.5–5 μm (measured using Dektak surface profiler and SEM). The precursor films were then subjected to an elimination reaction under a stream of HCl gas at 180–200°C for 2–3 hours [3a,3b] to get free standing DMPPV films.[14] These films obtained on glass plates, or by dissolving the NaCl pellet were vacuum dried for a period of 8–10 hours to ensure removal of HCl and moisture impurities.

Composites of the polymers mentioned above were made. Polyvinylene di-flouride (PVDF), and polytetra-fluoroethylene (PTFE) and Nylon membranes obtained commercially were chosen for their robust mechanical properties and stability under elimination reaction conditions. The membrane thickness was in the 110–140 μm range with effective pore sizes of 0.44 μm and 0.22 μm. P3HT and DMPPV were incorporated in these membranes to obtain the composites.

Results and Discussion:

The direct absorption spectra of the P3HT solutions and the films are shown in Fig. 3. The film absorption spectra are red shifted from the solution by ~ (0.4 eV), showing additional low-energy oscillator strength below the solution absorption onset. It is to be mentioned that the data is not corrected for refractive index differences and reflection. This and other solid state phenomena can be ruled out noting the relatively significant shift of the spectrum. A possible effect is the effect of oxygen which has been observed in case of PPV

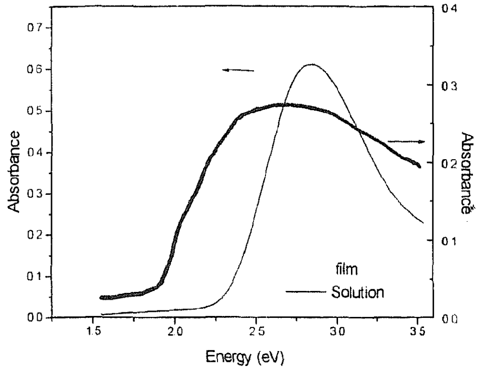


FIG. 3. Abosrption curves of P3HT in solution and thin films.

and results in significant PL quenching. Photoconductivity spectrum of P3HT (not shown here) shows a difference upon introduction of air but this difference is in the range < then 1.9 eV, the comparison of the photoconductivity spectra with abs. spectra as a function of processing and effect of oxygen are being currently investigated. Nevertheless, the red shift in the film samples clearly indicates the presence of additional, low energy directly accessible excitations in the film samples. The absorption spectra of DMPPV was done only in the film phase because of its insoluble nature and shows at an absorption edge at 2.0 eV with a max. at 2.7 eV.

The photocurrent increases more gradually compared to the absorbance with respect to the photon energy for 2.0 eV <hv < 2.7 as shown in Fig. 4 The photocurrent continues to rise even as the absorption decreases for hv >2.7 eV and reaches a maximum at $hv_{max} \approx 3.3$ eV. hv_{max} was seen to be marginally dependent on the sample thickness for the thickness ranging from 1-5 μm. I_{ph}^{sur} and I_{ph}^{san} in the forward bias for DMPPV show similar spectral response in contrast to results on other conjugated polymer systems.The similarity in the spectral response indicates the absence of bulk anisotropy effects in the phototransport behaviour of the polymer system.[15,16] A direct photogeneration of free carriers via an interband transition cannot explain the entire spectral response. It has been argued that for PPV the initial photoexcitation creates hot intrachain excitons and subsequently interchain charge transfer occurs to form bound polaron pairs. Dissociation of either of these neutral excitations will result in photocurrent. The photocurrent in this case could arise from the dissociation of the weakly bound excitons at the defect sites, field and thermal ionization of excitons, exciton interaction with trapped carriers, exciton-exciton interaction or exciton-photon interaction. The spin-coated and drip cast films of DMPPV have been shown to have a high degree of disorder with a high density of defect sites. These defect sites can enhance the photocurrent generation as observed in case of PPV.[17] The presence of the methoxy groups will make the hot intrachain excitons more mobile along the chain and may directly contribute more significantly to the photocurrent than other processes, and may be the cause for the differences observed in the I_{ph} spectral response in PPV and DMPPV.[15] The significant difference in the electric field response of the photoconductance in the surface configuration at different photon energies highlights

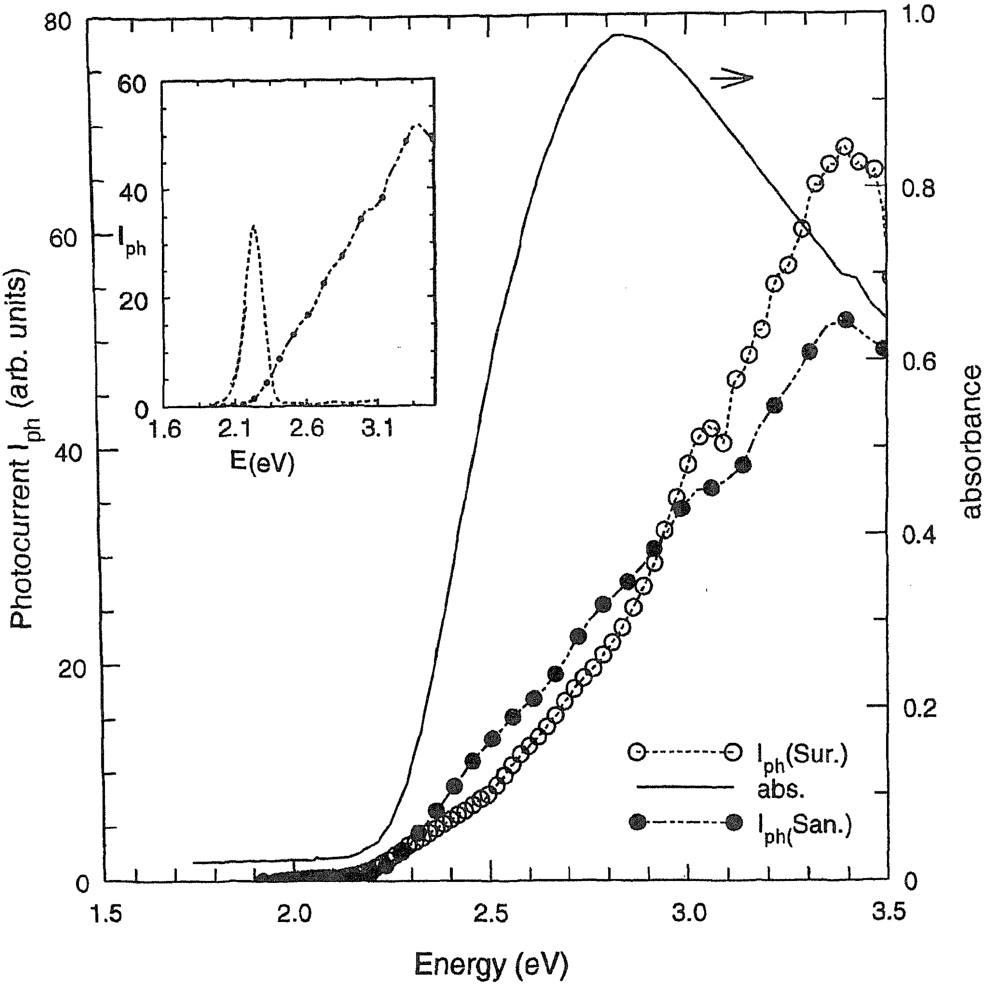


FIG. 4. Photoconductivity spectra of DMPPV; inset shows the comparison of forward bias and reverse bias spectra. (dashed line is a guide to the eye).

the contribution of the electric field assisted exciton dissociation. The probability of the generation of the charge carriers is higher for excitons near the surface. The linear dependence of I_{ph} at low light intensities and a sublinear dependence at higher light intensities has been attributed to the exciton-surface mechanism.[15] I_{ph} in the sandwich configuration shows entirely a linear behavior with respect to the intensity suggesting a monomolecular recombination kinetics. The difference in the chopper frequency dependence in the two configurations highlight the differences in the long lived kinetics.

However, for the ITO/DMPPV/Al configuration the model predictions totally deviate from the experimental results. The reverse bias photocurrent peak at 2.2 eV which is significantly shifted from the forward bias photocurrent peak at 3.3 eV, cannot be explained solely on the basis of the differences in the electron and hole mobility in the bulk. The feature of the red shifted peak in the reverse bias spectral response has been attributed to the comparable magnitude of the absorption depth and mean range of the photogenerated carriers in the bulk.[17] It was reported that the photocurrent peak is decided by the polymer film thickness, and the peak shifts towards the lower energy as thickness increases in the range 50 nm to 150 nm . However the film thickness for DMPPV films in the present case is an order of magnitude higher and as seen from the results of the model predictions, assuming reasonable values of the mean range of the carriers, do not qualitatively explain the large shift towards the lower energy side. Neither can a model used on basis of field assisted exciton dissociation at the polymer/Al interface can explain the results.[18] The fact that the red shifted reverse bias feature is not observed for the symmetric Au/polymer/Au device with the illuminated surface biased negative seem to indicate that interfacial effects seem to be the dominant factor giving rise to this feature.

For PTH the spectral response is sensitive to the ambient conditions, but the general trend is that the photocurrent distinctly precedes the absorption. Experiments are underway to quantify the effect of impurities, orientation factors controlled in spin coated films, and thickness dependences.[19] Preliminary experiments on studying light emission properties were done for PTH devices. The I-V curves in these devices have been explained on the basis of different models such as Shottky barrier type injection and Fowler-Nordheim tunneling injection. [20] The field dependent I-V behavior can be explained using the Fowler Nordheim tunneling theory which predicts that I is proportional to $E^2\exp(-k/E)$ where E is the electric field strength and k is a parameter which depends on the barrier shape ~ $8\pi (2m^*)^{1/2} \chi$ with electric field E, electron mass m, and barrier height χ. The ITO/P3TH/Al device has non-linear I-V characteristics. The device emits light for currents exceeding approximately 1 mA. As, indicated in Fig. 5, the turn on voltage for emission does not correlate with the band-gap. The electric field controls the device characteristics rather than the applied bias. The tunneling theory considers semiconductors having delocalized band states into which carriers are injected but in case of organic systems with a density of localized states the probability of injection also depends on the energetics and the kinetics of the carriers at the interface. This factor can explain the deviations observed in the results (Fig. 5 inset).

The membrane composites show remarkable photoinduced properties. A high degree of control in the mechanical and electronic properties of these polymers can be achieved.[21] Fibrous membranes provide a viable option both in terms of the reinforcement through the porous network and their substantial wetting properties. Polymer microstructures get formed in membranes such as nylon, polyvinylene di-flouride, and polytetra-fluoroethylene etc. The efficiency of photoconduction in derivatives of PPV supported by the membranes depend on the network of the polymer through the bulk, and is governed by the membrane morphology and the chemical nature of the membrane surfaces. PVDF and PTFE are inert membranes and the electronic transport properties of the conjugate polymers in these matrix show a scaled behaviour as expected. The membrane with pore diameters <0.1 microns have shown to make a difference in the dc conductivity by introducing an anisotropy by constraining the chain axis to be largely parallel to the porous cylinder axis. The charge nylon membranes with polar additive groups as a membrane

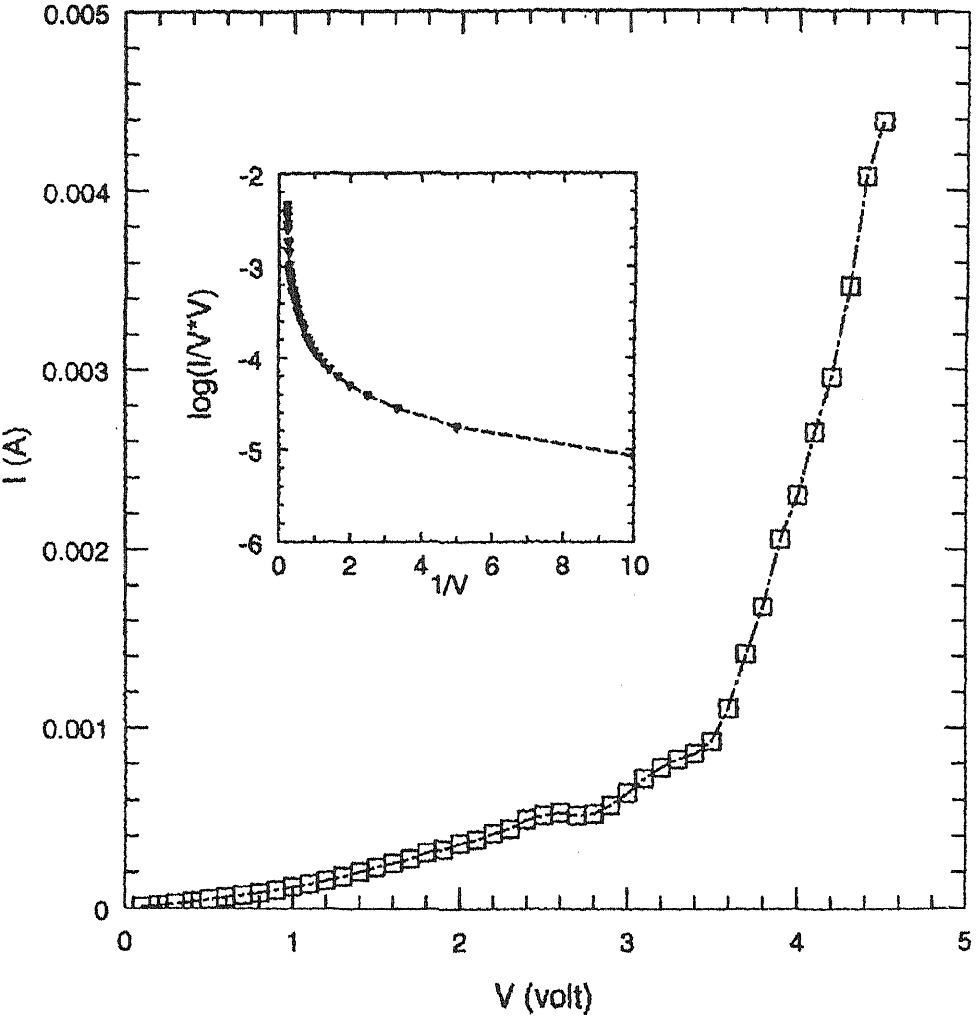


FIG. 5. I-V of P3HT device. inset plot of log(I/V^2) vs I/V.

matrix apart from providing morphological constraints introduce additional types of interactions such as dipolar, charge transfer between the conjugated polymer and the polar moieties on the membrane surface. Large photocurrents with unique properties are observed as a consequence[22,23].

The opto-electronic properties of the polymers mentioned above and its various composite forms offers an attractive alternative for several sensor devices. The microscopic mechanism, the lifetime and the mobility properties of the charge carriers in these systems and their dynamics have to be studied experimentally along with inventive chemical synthesis strategies to introduce subtle changes in the electronic structure. This coupled approach will help us develop better understanding of the phenomena in these kind of systems.

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