

Mechanism of electroluminescence in dye doped thiophene based conjugated polymer

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The optical and electrical properties of polymer light emitting diodes based on poly [2-(3-thienyl) ethanol butoxy carbonyl-methyl urethane] as emitting layer have been studied. The diode structures have been made by utilizing indium tin oxide coated glass as an anode and aluminum as a cathode. Polyaniline and tris(8-hydroxy-quinolino) aluminum have been employed as hole and electron transport layers, respectively. Enhanced electroluminescence (EL) near the turn-on voltage has been observed on addition of 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran dye. On the basis of current–voltage, luminance–voltage, capacitance–voltage, and impedance measurements, an attempt has been made to understand the mechanism of EL emission in these polymeric light emitting diodes. © 2001 American Institute of Physics.
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I. INTRODUCTION

An appreciable amount of research has been carried out in the field of organic electroluminescence (EL) based optoelectronic devices during the last decade. A variety of organic materials have been investigated as active layers for optimizing device performances. These organic materials can be broadly classified in four groups¹ namely: (a) conjugated polymer systems, (b) main chain polymers with isolated chromophores, (c) side chain polymers with pendant chromophores, and (d) low molecular weight EL active compounds. Of these, conjugated polymer based organic light emitting devices (OLEDs) have been of great interest specifically for their applications in large area display elements and considerable effort has been devoted to investigate their technological potential. The conjugated polymers such as poly (*p*-phenylene vinylene)^{2,3} (PPV) and its derivatives have presented many advantages in EL applications due to their good processability and high fluorescence efficiency. A wide range of materials have been subsequently reported that produce EL throughout the visible spectrum. Lee *et al.*⁴ fabricated ruthenium-phenanthroline complex based EL devices using self assembly. The fabricated EL devices exhibited high brightness but quantum efficiency was less than 1% with very high turn-on voltage. Gao *et al.*⁵ prepared blue EL devices by doping silyl substituted ter-(phenylene-vinylene) derivative in electron-transporting layer. Light emitting electrochemical cells⁶ have been developed by blending fluorescent polymer with ion conducting polymer composite between two metal electrodes. Although they were having very high brightness and high quantum efficiency, the phase separation due to blending with ion conducting polymer compos-

ite results into the degradation of the device. Very recently, Pei *et al.* have demonstrated a polymer solution light emitting device.⁷ The enhancement of device efficiency, turn-on speed, and device lifetime are still the major challenges.

Multifunctional conjugated polymers with electron, hole, and ion transport properties, and covalently functionalized electroluminescent properties can have a significant impact on the device performance. Most of the conjugated polymers in polythiophene family of polymers are stable under ambient environmental conditions. Further, their synthesis and structural modification can be brought about with ease. Unfortunately, they have received limited attention in comparison to the PPV family of polymers. The basic structure of organic EL devices consist of one or more organic films deposited between the two electrodes, at least one of which is transparent. The fundamental requirements for the organic layer are: an efficient luminescer, good charge transporter, and capability of efficient charge transfer to electrodes. In view of the earlier mentioned facts, a highly luminescent thiophene based conjugated polymer, i.e., poly [2-(3-thienyl) ethanol butoxy carbonyl-methyl urethane] (PURET) has been used in the present investigations. The chemical structure of PURET has been shown in Fig. 1(a). The EL emission of PURET lies in the yellow-orange region. The polymer shows a Stoke's shift ~140 nm and exhibits a small overlap of emission and absorption spectra which is a very important factor for designing high intensity polymeric light emitting diodes (P-LEDs). Enhanced EL has already been observed by some of the present authors when europium (III) and ruthenium (II) complexes were added in PURET.⁸

OLEDs using fluorescent dyes with conducting polymers have attracted great interest because of their emission in the visible region and for their applications to large area flat panel display devices driven at low voltages. A considerable enhancement in EL efficiency was observed by Ohmori *et al.*⁹ when poly (3-alkylthiophenes) were doped with

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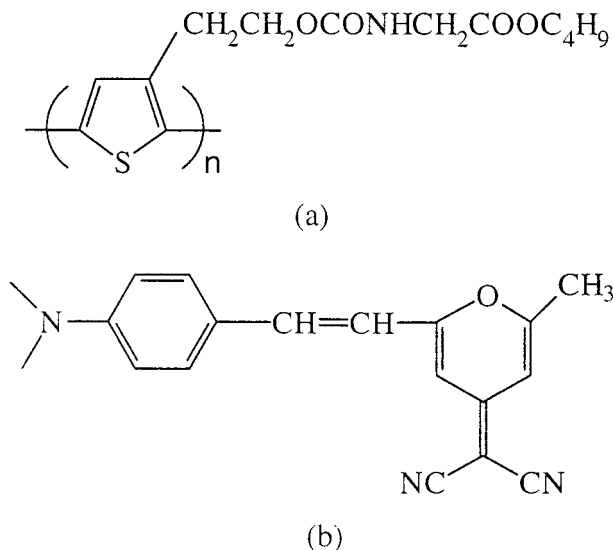


FIG. 1. Chemical structures of (a) Puret and (b) DCM dye.

(1,2,3,4,5-pentaphenyl, 1-3-cyclopentadiene). In addition to efficient color tuning, dye doping¹⁰ can enhance the probability of electron-hole recombination and stability of the device. Moreover, by shifting the emission from the vicinity of the hole or electron transporting layer to the dye, the quantum efficiency of the device can be improved significantly. Hence, it is of interest to combine the merits of organic fluorescent dye molecules with those of conducting polymers. 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) has been chosen for the present investigations. The chemical structure of DCM has been shown in Fig. 1(b). The selection criterion is based on the fact that its fluorescence color is in the orange region and electron hole recombination can be efficiently mediated by the dye.¹¹ We have doped Puret with varying amounts of DCM dye. Enhanced electroluminescence ~ 1000 cd/m² could be achieved by incorporating a very small amount of dye. The devices are stable under atmospheric conditions. The experimental results in atmospheric conditions are similar within the accuracy of $\pm 2\%$ to those taken in the inert atmosphere of dry nitrogen (N₂) gas. An attempt has been made to understand the mechanism of charge transport. This helps in identifying the possible reasons for the enhancement of EL emission as a function of dye concentration and allows for further optimization of device performance.

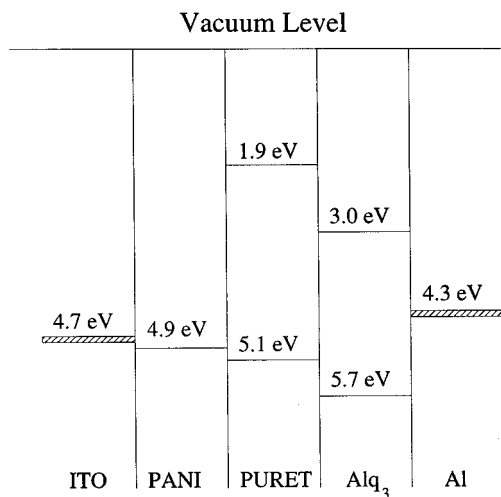
II. EXPERIMENT

Puret was synthesized according to the procedure reported elsewhere.¹² 1 wt % of polymer solution was prepared by dissolving the Puret in the solvent propylene glycol methyl ether acetate (PGMEA) and was subsequently filtered through 0.2 μ m Gelman (Teflon) filter. The solution was spin coated on precleaned glass slides for absorbance and fluorescence measurements. Films of thickness ~ 1000 Å were obtained when spin coating was performed at 1800 rpm. Our device is a three layered structure. Indium tin oxide (ITO) coated glass with surface resistivity of 10 Ω/\square was used as the anode with ~ 800 -Å-thick polyaniline (PANI)

layer spin coated as the hole transport layer. PANI solution was prepared in trifluoroacetic acid and filtered through 0.2 μ m Gelman (Teflon) filter. The films were dried overnight in vacuum at 40 °C. Puret films were spin coated on an ITO/PANI electrode and dried overnight in vacuum at 50 °C. A 600-Å-thick tris(8-hydroxy-quinolino) aluminum (Alq₃) layer was thermally evaporated at the pressure of $\sim 10^{-5}$ Torr. A 1500-Å-thick aluminum was thermally evaporated at the pressure of $\sim 10^{-6}$ Torr to form the metal electrode. The effective area of the device is 0.12 cm². A stock solution of 1 wt % DCM dye in PGMEA was prepared and was added to the Puret in order to get dye contents of 0.5, 0.7, 1, 2, and 5 wt % in Puret solutions. In the present investigations, the P-LEDs prepared for the varying dye concentrations mentioned earlier are referred to as P1, P2, P3, P4, and P5, respectively. The device prepared from Puret having no DCM dye has been referred to as P0. All the P-LEDs were prepared under similar conditions. The light output from P-LEDs was measured with an optical power meter using a calibrated radiometric photodetector having an effective area of 1 cm² and effective diameter of 1.13 cm. The luminance is then calculated¹³ as $683V_{\lambda}R_0/A$ where R_0 is the radiant intensity along the forward direction (taking into account the solid angle), V_{λ} is the relative luminosity coefficient derived from the Commission Internationale de l'Eclairage definition of photopic response of the average human eye, and A is the effective light emitting area of the device. I - V characteristics were simultaneously recorded with the help of Keithley's 177 microvolt digital multimeter. Capacitance-voltage and impedance were recorded in the frequency range of 20 Hz–10 MHz at various bias using HP 4284A precision LCR meter.

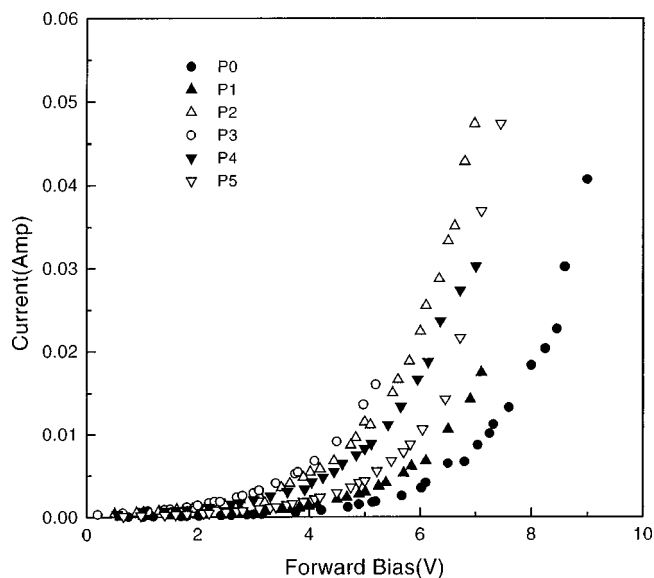
III. RESULTS AND DISCUSSION

The efficiency of electron-hole recombination in the bulk polymer can be enhanced by improving the charge injection and transport properties of the electrode materials. One way to achieve this is by matching the barrier for electron and hole injection by judicious selection of work functions of electrodes. Although calcium is the most suitable metal electrode,¹⁴ unfortunately, it is highly reactive and not suitable when in contact with air. The choice of calcium thus complicates the sample preparation and operation of these devices. A somewhat different technique to improve charge injection is by incorporating the electron injecting and the hole injecting layers on each side of the emitting polymer. Polyaniline, which has been reported as an effective hole injecting material by Yang *et al.*,^{15,16} has been chosen for the present investigations. Alq₃ has been used as electron injecting layer. Alq₃ itself electroluminesces, but its contribution with an emission maximum at 520 nm (with a full width at half maximum of ~ 100 nm) is negligible compared to the EL output of the Puret, which emit orange-red light with a maximum at ~ 600 nm⁸. Puret was used in its undoped form. The doped conducting polymer layers partially contribute to the enhancement of carrier injection and transport with low operating voltage. However, doping severely quenches molecular fluorescence.¹⁸ Figure 2 shows the sche-

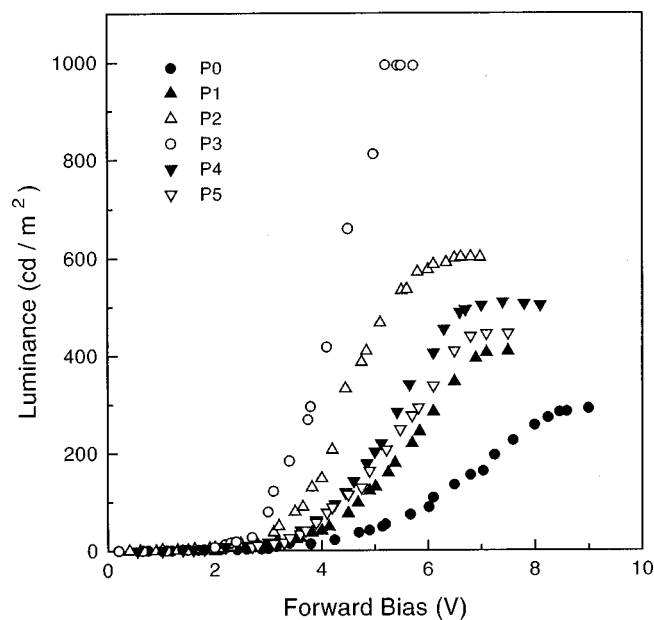
FIG. 2. Band diagram for three layer ITO/PANI/PURET/Alq₃/Al devices.

matic representation of energy band diagrams of various layers for the better understanding of the mechanism of EL emission from the device. The work functions of ITO, PANI, and Alq₃ were taken from literature^{19,20} and the highest occupied molecular orbital and lowest unoccupied molecular orbital (LUMO) for PURET were determined by cyclic voltammetry and the threshold wavelength of the UV/visible absorption spectrum. The band gap of the PURET encompasses the work functions of the cathode and the anode. Barrier height of holes for the injection from ITO is 0.4 eV, and it is reduced to 0.2 eV in the presence of PANI. The LUMO of PURET is ~ 1.9 eV below the vacuum level where as that of Alq₃ is ~ 3.0 eV below the vacuum level, which makes Alq₃ an efficient electron transport material. Moreover, Alq₃ acts as a barrier for the diffusion of Al into PURET and therefore, it prevents the quenching effect of metal ions on PURET. The barrier at the interface between PURET and Alq₃ for the holes is ~ 0.8 eV and for electrons is ~ 1.1 eV. The electrons and holes injected from the two electrodes are expected to get blocked and recombine at this interface.

The forward bias I - V characteristics for various P-LEDs namely P0, P1, P2, P3, P4, and P5 having different weight concentrations of DCM are shown in Fig. 3. The rectification constant (ratio of forward bias current to the reverse bias current at a given voltage) for various samples has been calculated with the help of reverse bias characteristics (results not shown). The values of the rectification constant at 5 V for P0 and P1 are ~ 3400 where as for P2 ~ 7400 , for P3 ~ 9000 , for P4 ~ 6800 , and for P5 ~ 4200 . The highest rectification constant has been obtained for P-LEDs having 1 wt% of DCM dye. The optimum concentration of DCM in PURET for exhibiting highly enhanced EL output was estimated by studying the EL behavior, which is shown in Fig. 4. It is evident from Fig. 4 that the maximum luminance of ~ 290 cd/m² for P0 has been obtained at around 9 V. An increase in EL power has been observed in the presence of dye up to 1 wt%. The highest luminance of ~ 1000 cd/m² has been obtained for the sample having 1 wt% of DCM dye. The turn-on voltage for P0 is about 3.4 V, where as that for P3 is about 2.8 V. Additionally, the voltage at which the

FIG. 3. Current-voltage characteristics for ITO/PANI/PURET/Alq₃/Al and ITO/PANI/PURET:DCM/Alq₃/Al devices.

maximum EL power has been observed, decreases with the increase in dye content up to 1 wt%. This is a desirable feature for higher power efficiencies. It reduces both thermal heating as well as voltage driven electrochemical degradation in organic/metal thermal interfaces, thereby improving the lifetime of P-LEDs. Hence, it would be ideal to drive the device close to the turn-on voltage. For P3 the maximum EL has been obtained at about 5 V which is closer to the turn-on voltage. This indicates the enhancement of probability of electron-hole recombination by adding DCM dye in PURET. A maximum EL intensity of ~ 500 cd/m² was earlier reported by Cazeca *et al.*⁸ when 1 wt% Eu³⁺ complex was added to PURET. The forward bias was 9 V and the current was 190 mA. The luminance level decreases with the in-

FIG. 4. Luminance-voltage characteristics for ITO/PANI/PURET/Alq₃/Al and ITO/PANI/PURET:DCM/Alq₃/Al devices.

crease of dye concentration beyond 1 wt%. The maximum luminance levels of ~ 500 and 450 cd/m^2 have been obtained for P-LEDs having 2 and 5 wt% of DCM concentration, respectively. This may be due to the aggregation¹⁰ of dye, leading to extensive self-quenching in the dye aggregates and luminance losses. Higher doping levels, may involve the formation of nonemissive excimer states. For example, the exciton may be delocalized over two dye molecules such as $D^* + D \rightarrow D_2^*$, where D_2^* is non emissive. The other possibility which normally occurs¹⁰ at lower dye loading levels could be the formation of a dimer state between the dye and a segment molecule of host matrix.

It is possible to fit $I-V$ data according to the relationship, $I \propto \exp(eV/\eta k_B T)$, where k_B is the Boltzmann's constant and T is the temperature, but it yields an unreasonably high values of ideality factor ($\eta \sim 50$). A fit to a power law dependence according to the relation $I \propto V^{m+1}$, gives the value of $m \sim 0.3-0.7$ at low voltages and $m \sim 2.3-2.6$ at higher voltages for all the samples. The turnover between two regimes occurs in the region of EL onset. The barrier at hole transport layer is about 0.2 eV whereas that at electron transport layer is 1.1 eV. Therefore, the current at lower voltages seems to be determined by accumulated space charge at PANI/PURET interface. At higher voltages, sufficient numbers of electrons are injected from Alq_3 into PURET and recombine with trapped holes, thus giving rise to EL emission. This in turn reduces the positive space charge, which leads to the increase in the hole current. $m = 1$ is expected for the validity of space charge limited current model. The deviation is conjectured to the trap filling effects. However, for a three layer device it is complicated to describe $I-V$ characteristics by a simple model because the device has many more interfaces. Similar behavior has been observed by Suzuki *et al.*²¹ for the three layer device ITO: polymethyl phenyl silane:C6PS: Alq_3 : Al where C6PS is polystyrene matrix doped with coumarin 6 dye. The turn-on voltage was about 25 V.

The external quantum efficiencies have been calculated on the basis of amount of light captured by the photodiode from the face of the device. According to the calculations by Greenham *et al.*,²² for Lambertian emission, the total flux from a device is $F_0 = \int_0^{\pi/2} 2\pi L_0 \sin \theta \cos \theta d\theta = \pi L_0$ where L_0 is the flux per unit angle leaving the device. In our experiments, the light collected by the photodiode is within a cone of 27° and, hence, we obtain the measured flux $F_1 = 0.206F_0$. So we divide our measured power output (P) by this factor and the quantum efficiencies were calculated by the formula²³

$$\eta_{\text{ext}} = P/h\nu/Ie. \quad (1)$$

The maximum power efficiency for P3 at 5 V has been obtained $\sim 0.3\%$ whereas the quantum efficiency at the same voltage for P0 is 0.05%, for P1 and P2 is $\sim 0.2\%$, and for P4 and P5 is $\sim 0.1\%$. The increased quantum efficiencies may be due to good luminescence efficiency of the dye. The dye traps the excitons formed in the device and subsequently contributes to the emission.

To further explore the issue of mechanism of conduction, the impedance spectra in low frequency regime (20

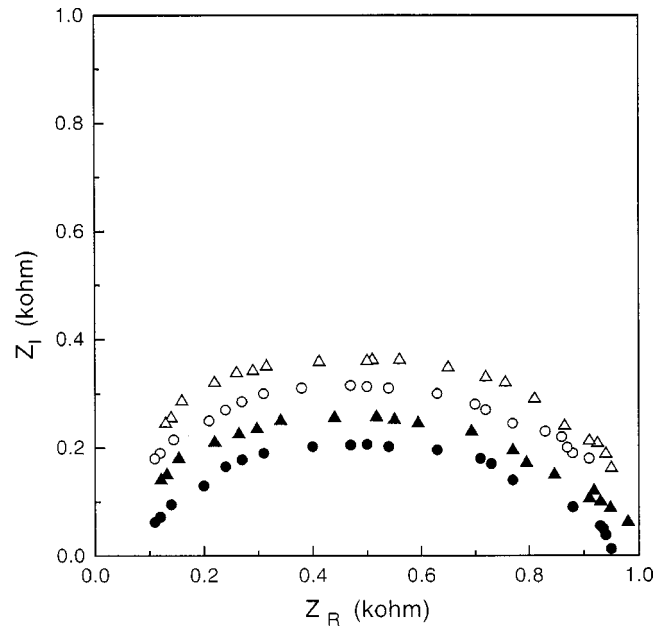


FIG. 5. Cole-Cole plot of the impedance of the device P3 for various forward bias voltages viz. 0 V (Δ), 1 V (\circ), 2 V (\blacktriangle), and 3 V (\bullet).

Hz–10 MHz) were recorded at different applied bias voltages. An alternating current modulation of 50 mV was applied to measure the complex impedance. The real (Z_R) and imaginary (Z_I) parts have been plotted in a complex plane and are shown in Fig. 5. The total impedance is given by

$$Z = \frac{dV}{dI} = Z_R + Z_I. \quad (2)$$

According to Schokley relation for diodes²⁴

$$I(V) = I_0 \left\{ \left[\frac{\exp(qV - IR_b)}{\eta k_B T} \right] - 1 \right\}. \quad (3)$$

At lower frequencies

$$Z_R(\omega \rightarrow 0) = \frac{dV}{dI} = R_f, \quad (4)$$

$$\frac{dV}{dI} = \frac{\eta k_B T}{I_0 q} \exp \left[\frac{-(qV - IR_b)}{\eta k_B T} \right] + R_b. \quad (5)$$

Therefore,

$$\frac{dV}{dI} = R_j + R_b, \quad (6)$$

where R_j is the bias dependent junction resistance and R_b is bias independent bulk resistance. In this case, two semicircles should be obtained on the plot of Z_I vs Z_R , one representing the bias dependent junction resistance and the other representing the bias independent bulk resistance.²⁵ The Cole-Cole plots of the impedance of the device P3 at zero and small forward bias have been shown in Fig. 5. It is evident from Fig. 5 that only one semicircle with its center displaced from the axis has been obtained for each bias voltage. So the equivalent circuit of the device consists of a single parallel RC. The diameter of these semicircles correspond to the bulk resistance while the corresponding RC time

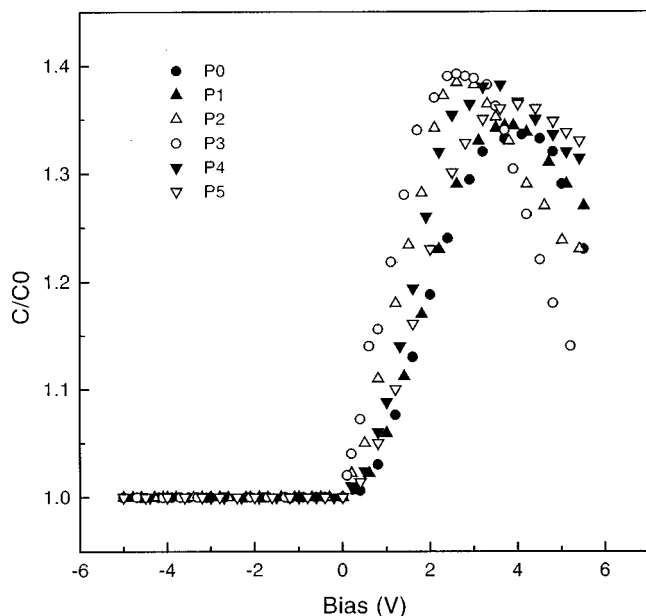


FIG. 6. Reverse and forward bias $C-V$ characteristics for ITO/PANI/PURET/Alq₃/Al and ITO/PANI/PURET:DCM/Alq₃/Al devices. C_0 is the capacitance of the device at zero bias.

constants are given by reciprocal of angular frequency at the apex of each semicircle.²⁶ The diameter of all the semicircles are constant with their apexes displaced. The semicircle for various reverse bias voltages coincided, which indicates that R_b and C are constants. This is indicative of a fully depleted bulk layer.

The capacitance versus voltage ($C-V$) plots at 1 kHz for P0, P1, P2, P3, P4, and P5 have been shown in Fig. 6. The capacitance is essentially constant under the reverse bias conditions. An increase in the capacitance with a maximum just before significant injection has been observed in the forward bias $C-V$ characteristics. This behavior is similar to those obtained by Campbell and his co-workers²⁷ for MEH-PPV LEDs. The behavior is qualitatively different from Schottky and $p-n$ junction diodes as P-LEDs are metal-semiconducting polymer-metal structures and not completely analogous to conventional inorganic diodes. According to the model proposed by Campbell *et al.*,^{27,28} for the bias conditions under which strong electrical injection does not occur (reverse, zero, or forward bias) the increase in the capacitance is due to charge trapping by impurity states or intrinsic states of the polymer. Energetically, deeper traps have a larger effect on the capacitance voltage results than shallow traps before significant injection starts. It is evident from Fig. 6 that the slope of the curves is increasing with the dye content up to 1 wt % of dye and is maximum for P3. This indicates that the charging of traps is maximum for P3. Thus, our P-LEDs may be modeled as resistor and capacitor in parallel for the frequency range of 20 Hz–10 MHz. Under reverse bias the polymer layer is fully depleted and shows characteristics independent of bias. At small values of forward bias charge trapping occurs and the capacitance increases. These traps are neutralized at higher bias with significant carrier injection which in turn decreases the capacitance. The traps are enhanced by addition of DCM

upto the concentration of 1 wt %, which subsequently enhances the EL emission from PURET.

IV. CONCLUSION

By the addition of DCM dye up to 1 wt % a significant enhancement in the EL output and quantum efficiencies of PURET has been observed. This is attributed to the trapping of excitons and enhanced probability of electron-hole recombination in the EL layer. The device can be modeled as a parallel RC circuit in which the polymer layer is fully depleted in the reverse bias. Prior to the significant injection, traps are charged which increases the capacitance. The traps are neutralized at higher voltages with significant carrier injection. DCM dye can be considered as a good match for PURET. Additionally, the maximum EL emission has been observed, closer to the turn-on voltage. The fabricated P-LEDs are stable under atmospheric conditions. These results establish PURET, a derivative of polythiophene family of polymers as a good candidate for display devices. Further opportunity in structural modification of this class of polymers to obtain color tunability and other dye dopant combination for further emission enhancement are under investigations.

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