

# Study of Optical and Electrical Properties of Imidazolin-5-one Molecules for Optoelectronic Applications

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**Abstract:** Optical and electrical properties of three new imidazolin-5-one molecules have been investigated. These molecules resemble the main chromophore responsible for high fluorescent properties of Green Fluorescent Proteins. They absorb in blue region (420-450nm) and show peak photoluminescence in green region (500-570 nm). Devices made from these molecules show current density-voltage (*J-V*) characteristics having rectifying behaviour with some devices giving 1.01 mA cm<sup>-2</sup> for 5 V forward bias. Preliminary results indicate that some of these molecules have potential for optoelectronic applications such as organic light emitting diodes (OLEDs) and organic solar cells.

**Keywords:** imidazolin-5-one; OLED; small molecule; absorption; photoluminescence; *J-V* characteristics

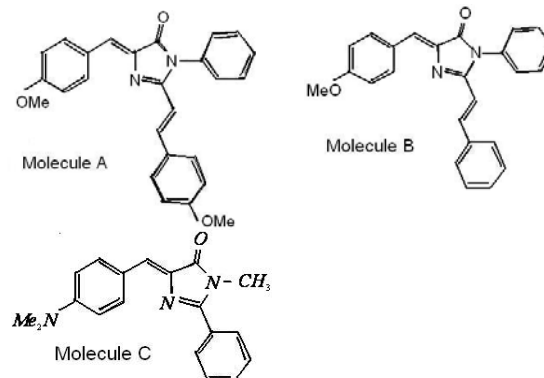
## I. Introduction

Organic Light Emitting Diodes (OLEDs) have gained considerable importance in recent times for their potential application in flat panel displays. This is due to their attractive characteristics such as simpler fabrication procedure, low cost, high brightness, high luminance efficiency, wide colour gamut and possibility of flexible displays [1-3]. Although significant progress has been made in last two decades since the development of bi-layer OLED using *Alq3* and diamine by Tang and Van Slyke [4], there are still many unsolved problems today which are topics of active research such as improved efficiency, reliability and stability [5-6]. There is a constant effort to identify new molecules that will help solve these problems. Some of these new materials being investigated for OLEDs may also be promising candidates for organic solar cells [7].

This paper investigates three imidazolin-5-one molecules for their viability in optoelectronic applications. Imidazolin-5-one is the main chromophore which is responsible for the high fluorescent property of Green Fluorescent Proteins (GFPs) discovered by Shimomura *et al.* in jellyfish [8-9]. GFPs are being routinely used in bio-engineering experimental studies. This chromophore, 4-(p-hydroxybenzylidene) imidazolin-5-one, is attached to the peptide backbone through 1 and 2 positions of the ring [10]. The GFP generally absorbs in UV region (395 nm) and emits in green visible region (508 nm). The imidazolin-5-one molecules investigated here have been designed to resemble the GFP chromophore, but are engineered to have an absorption and emission spectrum at higher wavelengths.

Luminescence studies of these new molecules have been performed to understand their optical characteristics. Absorption and photoluminescence (PL) spectra of the molecules in both thin film and solution have been carried out. Device structures have been fabricated and the current density-voltage (*J-V*) characteristics have been obtained. These characteristics were analyzed and parameters, such as, mobility were computed to gain better insight into the electrical properties of the molecules. Some preliminary reliability experiments on these molecules were also conducted.

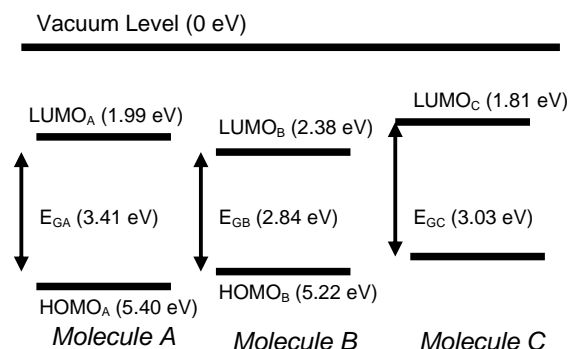
The paper is divided into six sections. Following the introduction (section I), the molecular structure and energy band diagram of the new molecules are given in section II. This is followed by a discussion of optical properties of the molecules in section III. In section IV, the device fabrication process is outlined while section V deals with electrical analysis of the devices. A summary of the work and suggestions for future work come under Section VI.



**Figure 1.** Molecular Structures of the three new imidazolin-5-one molecules fabricated based on the chromophore of green fluorescent protein.

## II. Organic Materials

The three imidazolin-5-one molecules investigated are:- (a) *Molecule A*: (4*Z*)-4-(4-Methoxybenzylidene)-2-((*E*)-4-methoxystyryl)-1-phenyl-1,4-dihydro-5H-imidazolin-5-one (b) *Molecule B*: (4*Z*)-4-(4-*N,N*-Dimethylaminobenzylidene)-1-methyl-2-phenyl-1,4-dihydro-5H-imidazolin-5-one (c) *Molecule C*: (4*Z*)-4-(4-Methoxybenzylidene)-2-((*E*)-styryl)-1-phenyl-1,4-dihydro-5H-imidazolin-5-one.



**Figure 2.** Energy Level Band Diagram of the three Molecules A, B and C denoting the HOMO-LUMO and the energy gap drawn with respect to the vacuum level

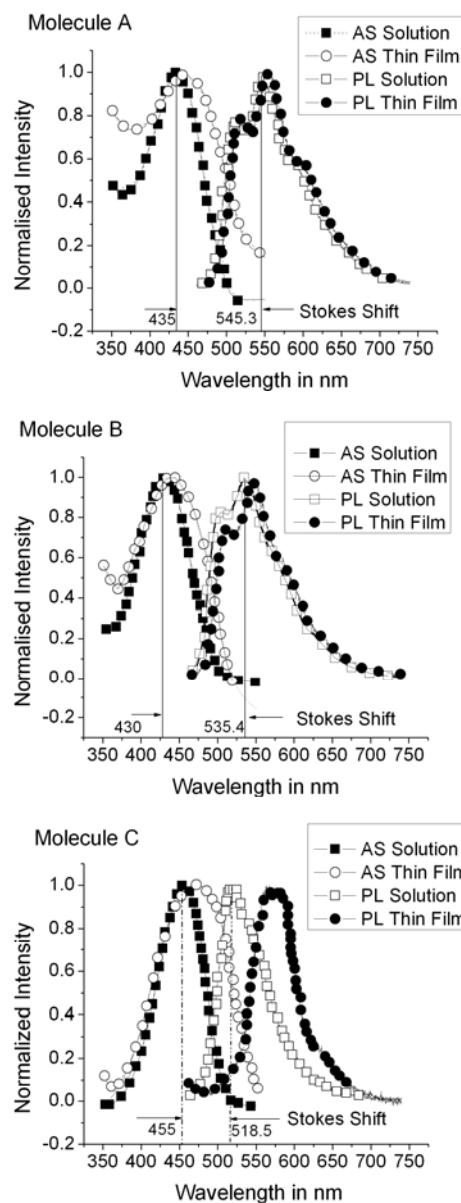
The structural formulae of these molecules are shown in figure 1 and their energy band diagrams are shown in figure 2. HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) values were estimated using simulation with the Gaussian 98 program [11] which makes use of the Time Dependent Density Functional Theory TDDFT (B3LYP) [12].

### III. Optical Properties

Absorption and photoluminescence studies of the three molecules were performed to understand their photo emission and absorption behaviour in solution and thin film form. Solutions of all three were prepared with chloroform as the solvent, while thin films were prepared by evaporating the molecules in high vacuum onto a glass substrate. All the samples show peak emission in the green-yellow region with absorption peaks lying in blue region. Stokes shift between absorption and emission spectrum can be clearly observed in figure 3 in both thin film and solution form. Broadening as well as the 'red shift' of absorption spectra in thin film compared to solution is also evident from the same figure. In thin film form, the molecules are very close to each other and intermolecular separations and mutual molecular orientations are random, causing overlap of orbitals which results in the splitting of HOMO and LUMO levels. The degree of overlap varies from molecule to molecule and results in a distribution of HOMO and LUMO levels which broadens the spectrum. Narrowing of the energy gap due to interaction of molecules and HOMO-LUMO splitting results in the 'red shift'. The extended tail structure caused by the distribution of HOMO and LUMO levels causes the band gap values obtained from the absorption spectra analysis to be less than those from theoretical calculations [13]. Table 1 compares the optical properties of all the molecules.

### IV. Fabrication of Devices

The structure of the devices fabricated consists of the following layers (figure 4):- ITO/PEDOT:PSS/Organic Layer/Aluminium. Indium Tin Oxide (ITO) coated glass substrates were first patterned using photolithography to obtain ITO strips of 2mm width. The patterned substrates were RCA cleaned and vacuum dried for 1hr at 120°C to remove any moisture content. These substrate were

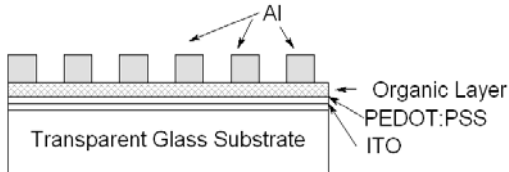


**Figure 3.** Absorption (AS) and PL Spectra of the three molecules in solution and thin film form. Broadening and red shift in the spectrum for thin film is due to splitting of energy levels when the molecules come closer.

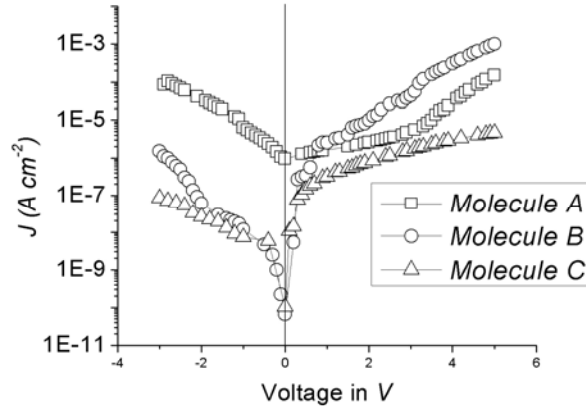
further exposed to ozone gas at high temperature for 10 minutes to improve the ITO work function. Concentrated PEDOT:PSS solution was then spin coated onto these substrates at 1000 rpm for 60 seconds and the substrates were again dried at 120°C for 1 hour. Organic material was deposited on these substrates by vacuum evaporation at a pressure of  $6 \times 10^{-6}$  mbar at an average rate of  $0.5 \text{ \AA s}^{-1}$ . A layer of thickness 200Å was obtained by this process. Aluminium was then deposited onto the substrates using vacuum evaporation at  $7 \times 10^{-6}$  mbar pressure to obtain the cathode having a thickness of 200nm. The deposition rate was initially kept low at  $0.2 \text{ \AA s}^{-1}$  to ensure good contact of metal with organic molecule film and then increased to  $2 \text{ \AA s}^{-1}$  average rate beyond 100Å thickness. Deposition

**Table 1.** Comparison of optical properties of *Molecules A, B and C*

	<i>Molecule A</i>	<i>Molecule B</i>	<i>Molecule C</i>
<b>Absorption Peak (Soln)</b>	435 nm	430 nm	455 nm
<b>Absorption Peak (Thin Film)</b>	444.5 nm	436 nm	471 nm
<b>PL Peak (Soln)</b>	545.3 nm	535.4 nm	518.5 nm
<b>PL Peak (Thin Film)</b>	554.9 nm	547.4 nm	566.7 nm
<b>Stokes Shift (Soln)</b>	0.577 eV	0.568 eV	0.333 eV
<b>Stokes Shift (Thin Film)</b>	0.555 eV	0.579 eV	0.445 eV
<b>FWHM PL (Soln)</b>	0.427 eV	0.423 eV	0.296 eV
<b>E<sub>g</sub> (from AS of Soln)</b>	2.50 eV	2.56 eV	2.41 eV

**Figure 4.** Schematic cross-section of the fabricated device structure. The organic layer was formed with *Molecules A, B and C* in the three different types of devices.

was done through a shadow mask with aluminium metal deposited orthogonal to the ITO strips to obtain devices of 2mm × 2mm dimensions. The devices were then encapsulated in a thick glass to reduce the degradation rate.

**Figure 5.** Current Density-Voltage characteristics for typical devices fabricated using the three molecules.

## V. Electrical Properties

The current-voltage characteristics of all the three devices were measured using the Keithley 4200 Analyzer. From the measurements,  $J$ - $V$  plots were determined which are shown in figure 5. Analysis of the plots was performed to fit the  $J = A \times V^m$  relation to all the curves. Here  $A$  and  $m$  are fitting parameters. The fitted curves showed a very good match with the actual measured curves and the values of  $m$  are mentioned in Table 2 below. The barrier for hole injection is very small for all the devices fabricated (figure 6) and hence we can safely assume the current to be bulk limited. Thus we can compute the values of mobility [14] using space charge limited (SCL) current given by

$$J_{SCLC} = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3} \quad (1)$$

and trap limited current model given by

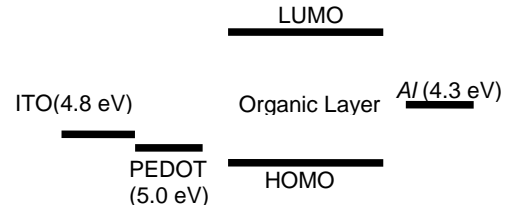
$$J_{TRAP} = \frac{q \mu N_v V}{d} \left[ \{f(l)\}^{-1} \frac{\epsilon_0 \epsilon_r V}{q d^2 N_{total}} \right]^l \quad (2)$$

where

$$f(l) = \left( \frac{2l+1}{l+1} \right)^{-(l/l)} \frac{(l+1)^2}{l(2l+1)} \quad (3)$$

$$N_{total} = \frac{\epsilon_0 \epsilon_r V_{TFL}}{f(l) q d^2} \quad (4)$$

$q$  is the electronic charge,  $\epsilon_0$  and  $\epsilon_r$  are the permittivity of the free space and material,  $\mu$  is the mobility,  $J$  is the current density,  $V$  is the voltage applied,  $d$  is the thickness of the device,  $N_v$  is the density of states,  $l$  is  $(m-1)$  where  $m$  is the slope of  $J$ - $V$  curve in the trap filling region and  $V_{TFL}$  is the voltage at which all the traps are filled.

**Figure 6.** Energy Band Structure of the device fabricated with organic layer replaced with *Molecules A, B and C*

*Molecule A* has a molecular weight of 410 g mol<sup>-1</sup> and a density of 1.1 g cm<sup>-3</sup>. Thus, assuming one HOMO and LUMO state per molecule, *Molecule A* should have the density of states  $N_v$  as 1.62 × 10<sup>21</sup> cm<sup>-3</sup>. Similarly,  $N_v$  for other molecules was computed [15].

For *Molecules A* and *B*, the field effect mobility  $\mu_{FE}$  is then computed. This is a pessimistic estimate of the mobility, assuming  $V_{TFL}$  to be 10 V, which is the maximum voltage of measurement of the devices. The actual  $V_{TFL}$  is more than this value and therefore, the mobility values will be better than those determined. *Molecule C*, however, showed SCL current and hence, the mobility values were computed directly using (1). The mobility values obtained are shown in Table II. It is seen that the conservative estimates of mobility for *molecules A* and *B* are still better than the mobility for *molecule C*.

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Although the devices were encapsulated, all of them showed degradation in their electrical behaviour, especially under voltage bias stress. Voltage stress studies on *Molecule A* show strong dependence of degradation on the amount of charge flowing through the device [16]. Further reliability and stability studies are needed to understand the degradation mechanisms of these molecules.

**Table 2.** Comparison of Electrical Properties of Molecules A, B, C

Molecule	A	B	C
$J_{on}$ at 5V(A cm <sup>-2</sup> )	$1.51 \times 10^{-4}$	$1.01 \times 10^{-3}$	$4.60 \times 10^{-6}$
$I_{ON} : I_{OFF}^*$	<1	~100	~10
$m$ (J=A×V <sup>m</sup> )	7.6	5.6	2
$N_v$ in cm <sup>-3</sup>	$1.62 \times 10^{21}$	$1.74 \times 10^{21}$	$2.17 \times 10^{21}$
$\mu$ in cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	<sup>#</sup> $2.4 \times 10^{-11}$	<sup>#</sup> $3.6 \times 10^{-11}$	$5.7 \times 10^{-12}$

\* $I_{ON}$  is the current value at 5V and  $I_{OFF}$  is the value at -5V

<sup>#</sup>Field Effect Mobility

## VI. Conclusion

Three imidazolin-5-one molecules have been compared in terms of their optical and electrical characteristics. Although all of these molecules are potential candidates for optoelectronic device applications, *Molecule B* shows the most promise. Its smaller band gap is attractive for solar cell application as its absorption has a better coverage of the solar spectrum. Its photoluminescence characteristics show potential for OLED applications. It has well placed HOMO-LUMO levels with respect to work functions of typically used electrodes allowing easy charge injection when forward biased. In the devices fabricated with the molecule, the higher current value in forward bias region also indicates its better current carrying capability and better carrier mobility. For the same forward bias current, the device also shows better rectification behaviour with low conduction in the reverse bias compared to the devices fabricated with the other two molecules.

Blends and bi-layers of these molecules, especially *Molecule B*, with other organic material including carbon nanotubes and C<sub>60</sub> are worth exploring to achieve even higher carrier mobility. Other cathode metals could also be looked into for improving electron injection. Novel device structures could be explored to improve the functionality of the device, especially to achieve useful optoelectronic phenomena such as electroluminescence and photovoltaic effect.

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## References

1. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns & A.B.

Holmes, "Light-emitting diodes based on conjugated polymers", *Nature*, vol.347, pp.539-541, 1990

2. F. Wang, Su Liu, J Zhou, Shuo Sun, Bingli Qi, Guping Ou, "Bright green organic light-emitting devices having a composite electron transport layer", *Microelectronics Journal*, 2006, 916-918
3. Ullrich Mitschke and Peter Bauerle, "The electroluminescence of organic materials", *J.Mater.Chem*, 2000, 10, 1471-1507
4. C.W. Tang & S.A. VanSlyke, "Organic Electroluminescent Diodes", *J. Appl. Phys.* 85(9)
5. Young Kook Kim, Seok-Hwan Hwang, "Highly efficient organic light-emitting diodes using novel hole-transporting materials", *Synthetic Metals* (2006), doi:10.1016/j.synthmet.2006.06.025.
6. L.S.Hung, C.H.Chen, "Recent progress of molecular organic electroluminescent materials and devices", *Materials Science and Engg R39* (2002) 143–222
7. S.S. Sun and N.S. Sariciftci, "Organic Photovoltaics – Mechanisms, Materials and Devices", *CRC Press*, 2005.
8. RY Tsien, "The Green Fluorescent Protein", *Ann. Rev. Biochem.*, 1998, 67, 500
9. M. Zimmer, "Green Fluorescent Protein (GFP): Applications, Structure, and Related Photophysical Behavior", *Chem. Review*, 2002, 102, 759
10. Gitalee Bhattacharjya, Arun Tej, SSK Iyer, Gurunath Ramanathan, "Imidazolin-5-ones in organic semiconducting diodes", *Proceedings of International Conference On Molecules To Materials*, 2006, 8-12.
11. Frisch *et al.*, "Gaussian 98", Revision A.11.1 Gaussian, Inc, Pittsburgh PA, 2001
12. (a) J.B. Foresman, M. Head-Gordin, J.A. Pople and M.J. Frisch, "Towards a Systematic Molecular Orbital Theory for Excited States", *J. Phys. Chem.*, 1992, 96, 135. (b) M.E. Casida, C. Jamorski, K.C. Casido and D.R. Salahub, "Molecular Excitation Energies to High Lying Bound States from Time Dependent Density Functional Response Theory: Characterization and Correction of the Time Dependent Local Density Approximation Ionization Threshold", *J. Phys. Chem.* 1998, 108, 4439
13. Martin Pope and Charle E. Swenberg, "Electronic Processes in Organic Crystals and Polymers", *Oxford University Press*, 1999
14. Z. Chiguvare and V. Dyakonov, "Trap-limited hole mobility in semiconducting poly(3-hexylthiophene)", *Physical Review B* 70, 235207 (2004)
15. A. J. Campbell, D. D. C. Bradley, and D. G. Lidzey, "Space-charge limited conduction with traps in poly phenylene vinylene light emitting diodes", *J. Appl. Phys.* **82** (12), 15 December 1997
16. Munish Jassi, "Electrical and Photo-degradation Study of Organic Semiconductor Devices", *BTech Project Report*, IIT Kanpur, 2006