

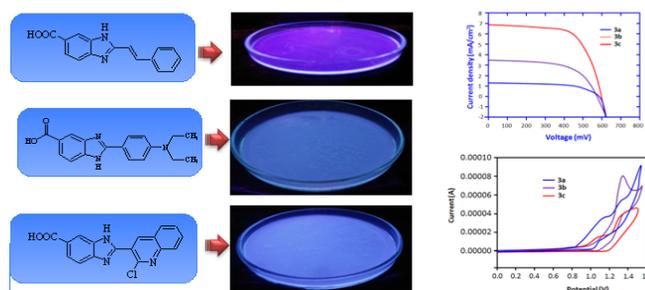
Synthesis of Blue Light emitting 5-Carboxylic acid-2-Aryl substituted Benzimidazoles as Photo-sensitizers for Dye-sensitized Solar Cells

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ABSTRACT



A series of 5-Carboxylic Acid-2-Aryl substituted Benzimidazoles **3a-c**, were synthesized and their Photo- physical, Electrochemical and DSSCs performance were studied. The UV-vis absorption and Photoluminescence (PL) Spectra of the compounds **3b** and **3c** exhibited intense deep-blue emissions with PL maximum at around 380, 382 and 400 nm (Fig. 3). Incidentally, their PL quantum yields (Φ_f) in solutions were found to be 0.36, 0.41 and 0.46 respectively. Thus, their emission spectrum displayed a broad FWHM feature extending to a longer-wavelength region, promoting the γ value of the CIE resulting in a sky-blue emission of the Dyes **3a-c**. Further, the good thermal stability and small FWHMs of the dyes **3a-c** indicates as promising compounds for deep-blue emitters in OLEDs. The Photovoltaic performances of the Solar Cells fabricated from the prepared Electrodes under AM1.5 Solar irradiation (85 mW/cm^2) are shown in Fig. 6. The Short-circuit Current Density (J_{SC}), Open-circuit Voltage (V_{OC}), Fill Factor (FF) and overall Conversion Efficiency (η) clearly reveals that the Dye **3c** shows higher efficiency (2.87 %) contributed by high value of J_{SC} , V_{OC} and FF.

Keywords: Dye solar cells, light harvesting, organic solar cells, heterocycles, fluorescence, phosphorescence.

INTRODUCTION

In the recent Organic Push-pull processes, Chromophores have been used as active components of Photovoltaic Cells, Organic Light-emitting Diodes (OLED), Optoelectronic devices, Semiconductors and as memory-storage devices.¹⁻³ The properties of Organic Chromophore system depends particularly on the

chemical structure of compounds possessing electronic behavior covering donors, acceptors and length of the π -conjugated linker.⁴ Recently, it is being reported that many Push-pull systems have been used as strong Intra-molecular Charge Transfer (ICT).⁸ Interestingly, in recent times it is found that various Benzimidazole derived Chromophores serve as Photo-sensitizers for Dye-sensitized Solar Cells.⁹⁻¹⁴ For instance, fused Phenanthroline Imidazole acceptor moiety, *N,N*-Dimethylamino donor, and Arylthienyl π -linker, are reported to function as CT chromophore.¹⁵ Further, Fluoreno[2,3-d]Imidazole cores, are said to have been used as strong blue emission molecules in OLEDs and Photoluminescence.^{16,17}

Recently, nitrogen-containing heterocycles are fundamental targets in the biological, medicinal and in materials science. Heterocycles have often been incorporated into the organic materials to take advantage of their known chemical, thermal and photochemical stabilities, as well as high quantum yields.^{18,19}

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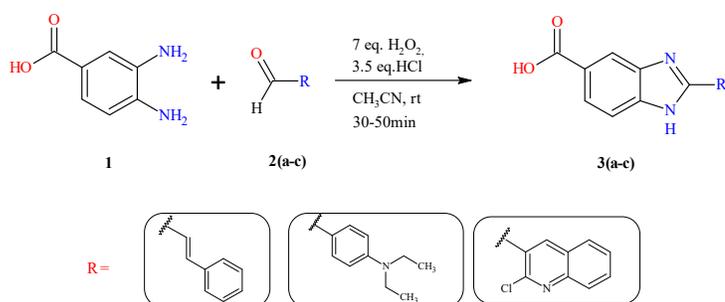
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Among π -conjugated molecules, benzimidazoles and their derivatives have attracted much interest due to their outstanding physiological and biological properties. Benzimidazoles are widely employed as acceptor moieties in various optoelectronic materials, because of their high electron-accepting character. More importantly, the five-membered heteroaromatic rings directly bonded to a donor facilitate maximal coplanarity between the donor and the acceptor subunits, which might be critical for the efficient charge transfer in those molecules.

In order to obtain highly efficient, thermally stable and a highly soluble active emissive material for OLEDs, the synthesis of 5-Carboxylic acid-2-Arylsubstituted Benzimidazoles (**3a-c**) and their Photo-luminescent properties are observed and reported. The synthesized compounds have also been explored for their forensic applications as Finger Print Developing Dyes. Apart from the excellent Photo-luminescent properties and Forensic applications of the synthesized compounds, the scope of the work includes mild reaction conditions and an easy better yield with One-pot Synthesis by using readily available 3,4-Diaminobenzoic acid, and 3-Phenylprop-2-Enal, 4-(diethylamino)Benzaldehyde, 2-Chloroquinoline-3-Carbaldehyde. The results of the carried work are described and given in detail in the experimental section.



Scheme 1. Synthesis of 5-Carboxylic acid-2-Arylsubstituted Benzimidazoles.

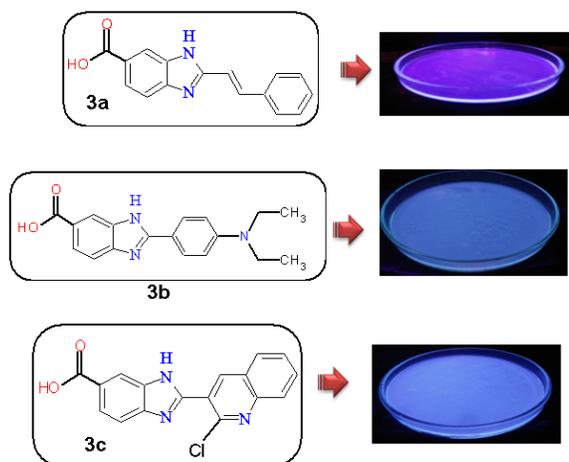


Figure 1. Colour emission images of 3a-c recorded in Ethanol under irradiation by UV light.

EXPERIMENTAL

MATERIALS AND INSTRUMENTS

Commercially available chemicals and reagents obtained from Sigma Aldrich were used for synthesis of new compounds 3a-c. All the solvents were of Reagent Grade and used without further purification. Melting points were determined by Electro-thermal apparatus in open capillaries and were uncorrected. The $^1\text{H-NMR}$ was recorded at 400 MHz in $\text{DMSO-}d_6$ as solvent and TMS as an internal standard. The FT-IR spectrum was recorded by scan method in the range of $4000\text{-}500\text{ cm}^{-1}$ using Agilent FT-IR spectrometer. Diffused reflectance spectrum was recorded using λ_{35} Perkin-Elmer UV-Visible Spectrometer. The Photoluminescence (PL) measurement was performed on a Jobin Yvon Spectro-fluorimeter Fluorolog-3 equipped with 450W Xenon lamp as an excitation source. Scanning electron microscopy (SEM) and EDAX measurements were performed on a TESCAN VEGA3LMU.

Synthesis of 2-[2-phenylethenyl]-1H-benzimidazole-5-carboxylic acid (3a): A mixture of 3,4-Diaminobenzoic acid (1) (0.5g, 0.01 mmol) and 3-Phenylprop-2-Enal (2a) (0.43g, 0.01 mmol) was prepared in Acetonitrile solvent (4-5ml) followed by addition of aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) to the mixture. The reaction mixture was stirred at r.t for 40 minutes. The progress of the reaction was monitored by TLC (Ethyl Acetate: Hexane, 1:2v/v). After the completion of reaction, the reaction mixture was cooled and poured into ice cold water. The obtained solid was filtered and washed with water and subsequently it was dried and purified by re-crystallization from Ethanol to get pure product (3a). Similarly, the same procedure was used to synthesize the other compounds (3b-c).

Spectral Characterization of 3a-c

2-[(E)-2-Phenylethenyl]-1H-Benzimidazole-5-Carboxylic acid (**3a**): Pale dark brown solid. Yield 70%. M.P.= $228\text{-}230\text{ }^\circ\text{C}$. IR (KBr, cm^{-1}): 2971.82, 2538.00, 1674.05, 1284.07. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ ppm 5.38 (d, $J=4.80$ Hz, 1H), 6.35-6.51 (m, 2H), 7.22 (d, $J=6.80$ Hz, 1H), 7.32-7.38 (m, 1H), 7.43-7.47 (m, 1H), 7.61 (d, $J=5.60$ Hz, 1H), 7.72 (d, $J=7.20$ Hz, 1H), 7.95-7.97 (m, 1H), 8.02-8.06 (m, 1H), 8.32 (s, 1H), 12.94 (s, 1H). Mass (m/z) = $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$: 287 (M+Na)

2-[4-(Di-ethylamino)Phenyl]-1H-Benzimidazole-5-Carboxylic acid (**3b**): Pale dark brown solid. Yield 83%. M.P.= $246\text{-}248^\circ\text{C}$. IR (KBr, cm^{-1}): 2971.55, 2534.79, 1669.75, 1285.67. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ ppm 1.13 (t, $J=7.20$ Hz, 6H), 1.46 (d, $J=6.80$ Hz, 4H), 6.66 (d, $J=8.40$ Hz, 1H), 6.88 (d, $J=8.40$ Hz, 2H), 7.34 (d, $J=4.00$ Hz, 1H), 7.44 (s, 1H), 7.69 (d, $J=8.40$ Hz, 1H), 7.94 (d, $J=8.40$ Hz, 1H), 8.09 (s, 2H), 8.12-8.15 (m, 1H), 12.72 (s, 1H), mass (m/z) = $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2$: 332 (M+Na).

2-(2-Chloroquinolin-3-yl)-1H-Benzimidazole-5-Carboxylic acid (**3c**): Pale dark brown solid. Yield 74%. M.P.= $298\text{-}300\text{ }^\circ\text{C}$. IR (KBr, cm^{-1}): 2819.11, 2550.68, 1678.16, 1289.78, 691.32. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ ppm 5.51 (d, $J=5.60$ Hz, 1H), 7.06 (t, $J=7.60$ Hz, 1H), 7.24 (t, $J=4.40$ Hz, 1H), 7.34-7.36 (m, 1H), 7.69-7.71 (m, 1H), 7.84-7.87 (m, 2H), 8.34 (s, 1H), 8.39 (s, 1H),

8.54 (d, $J=8.00$ Hz, 1H), 9.41 (s, 1H), 12.75 (s, 1H), Mass (m/z) = $C_{17}H_{10}ClN_3O_2$: 346 (M+Na).

DEVICE FABRICATION AND PHOTOVOLTAIC MEASUREMENTS

The TiO_2 paste was coated onto the cleaned conducting glass substrate (Fluorine-doped SnO_2 (FTO; sheet resistance $10 \Omega \text{ sq.}^{-1}$)) according to the described procedure.²⁰⁻²³ After heating the TiO_2 thin film up to 80°C , the film was soaked in a DMF solution containing 0.3 mM sensitizers for 24 hours at room temperature for the Dye adsorb on the TiO_2 surfaces. The active area was $1 \times 1 \text{ cm}^2$. A platinized FTO was prepared by chemical deposition of 0.05 M Hexachloroplatinic acid in Isopropanol which acted as a counter electrode.²¹ After rinsing it with DMF, the Photo-anode was placed on top of the counter Electrode and tightly clipped to it to form a cell. The Electrolyte was composed of 0.5 M LiI, 0.05 M iodine (I_2) and 0.5 M 4-tert-butylpyridine (TBP) in 3-Methoxypropionitrile which was injected between the two electrodes.²²

RESULTS AND DISCUSSION

Chemistry

The 5-Carboxylic acid-2-Arylsubstituted Benzimidazole (**3a-c**) derivatives were prepared by equivalent mole of 3,4-Diaminobenzoic acid (**1**) and Aryl Aldehydes (**2a-c**) taken in aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) mixture. Then the reaction mixture was stirred at room temperature in Acetonitrile as solvent to afford moderate to good yields of the products **3a-c**. The reaction sequence for the synthesis of 5-Carboxylic acid-2-Arylsubstituted Benzimidazoles **3a-c** are depicted in **Scheme-1**. The dye compounds **3a-c** was confirmed by IR, ^1H NMR and LC-MS spectral analysis.

Photo-physical Properties

As shown in Figure 2 and 3, the Dyes **3a-c** displays similar UV-vis absorption and Photoluminescence (PL) Spectra. According to the Absorption Spectra assignment, the strong absorption band peaking at around 280 nm of some reported Benzimidazole-5-Carboxylic acid, which have a similar conjugated π system to the molecules in this study,²³ can be attributed to the Quinoline ring. The longer-wavelength absorption bands in the range of 330 to 360 nm can be assigned to the delocalized $\pi \rightarrow \pi^*$ transition from the 2-substituted Quinoline to the Benzimidazole-5-Carboxylic acid ring (Fig. 2).

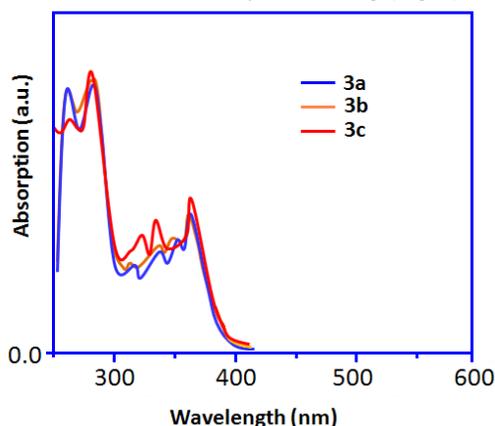


Figure 2. UV-vis absorption of **3a-c**.

The two dyes **3b** and **3c** exhibit intense deep-blue emissions with PL maximum at around 380, 382, 400 nm respectively in both solutions and vacuum-evaporated thin-film states (Fig. 3). Their PL quantum yields (Φ_f) in solution were determined to be 0.36, 0.41 and 0.46. Thus, the fluorescence efficiencies of dye compounds **3a-c** are comparable and the FWHM value is very crucial for the color purity of deep-blue emitters. Generally, the blue emitters may have an emission maximum at around 430 nm, which is short enough for blue light. However, their emission spectra display a broad FWHM feature and extend to the longer-wavelength region, which can promote the y value of the CIE resulting in a sky-blue emission. Due to good thermal stability and small FWHM, values indicate that the Dye Compounds **3a-c** are promising elements/candidates for deep-blue emitters in OLEDs.

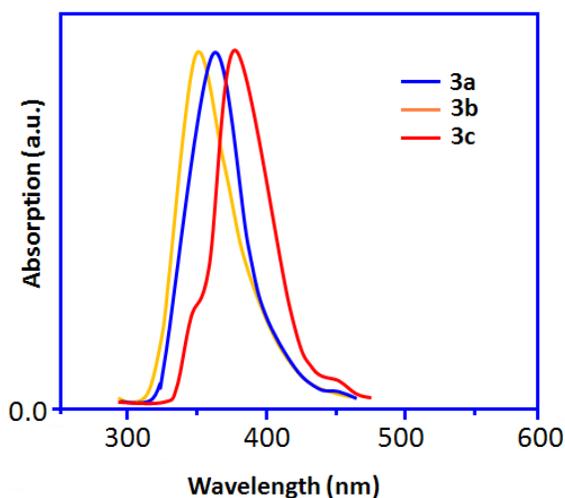


Figure 3. Photoluminescence (PL) spectra of **3a-c**.

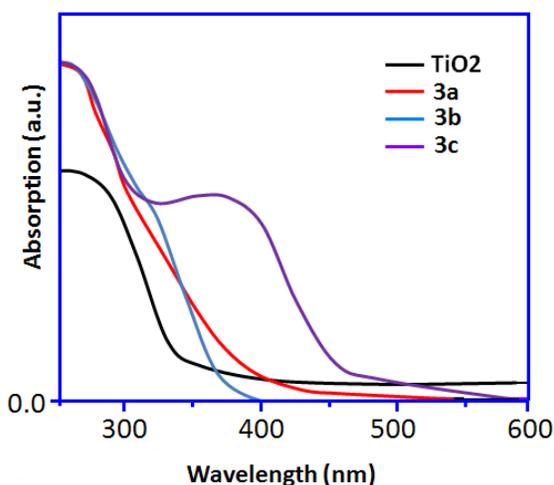


Figure 4. Absorption Spectra of synthesized Dyes adsorbed on a transparent TiO_2 films.

The Absorption Spectra of the synthesized Dyes adsorbed onto the TiO_2 films are shown in Figure 4. Compared with the absorption spectra in solution, the absorption spectra of the Dyes attached to TiO_2 film exhibit a significant red-shift which can be

attributed to the formation of a J-aggregation or dye-TiO₂ interaction. In addition, a broadened absorption peak was observed and this may be significantly due to the strong interaction between anchoring group i.e. -COOH of the Dye and TiO₂ surface. Such broadening of the absorption in the visible region is desirable for fabrication of light harvesting device which leads to a large photocurrent. From the Photo-physical studies, it is apparent that the 3c Dye could be a good sensitizer when compared to the other Dyes (3a and 3b) for DSSC applications.

Electrochemical measurements

The geometry of the DSSCs was a conventional sandwich configuration that consists of a working electrode and a counter electrode, and the space between the electrodes was filled with an electrolyte solution.

In CV, voltage sweep rate was fixed at 100 mV/s with a sensitivity of 0.001 A/V. The voltammograms of the various dyes in solution form were recorded using platinum as a working electrode as well as a counter electrode. KCl was used as a supporting electrolyte during the analysis. While analyzing the photo anode, the stacked structure glass/FTO/TiO₂/dye was made as the working electrode, while reference and counter electrode remained the same.

In order to rule out the effect of scan rate on oxidation potential, the experiment was repeated for various scan rates for each sample. For scanning performed in the potential range of 0 to 1.6 V, it was observed that variation in oxidation potential was less than 0.05 V when the scan rate was varied between 50 and 200 mV/S. The anodic current shows a gradual increase with increase in scan rate, but there is no significant deviation in peak value of oxidation potential. The first oxidation peak of dye coated on TiO₂ corresponds to modified HOMO energy level of the dye-TiO₂ complex. All the dyes show significant oxidation peaks in the positive potential region in the Ag/AgCl reference scale.

To elucidate the Thermodynamic feasibility of Electron injection to the TiO₂ Electrode and Dye regeneration through Electrolyte, the Cyclic Voltammetry (CV) experiment was carried out in a solution of 0.1 M TBAP in DMF medium and the representative Cyclic Voltammograms are shown in Fig. 5.

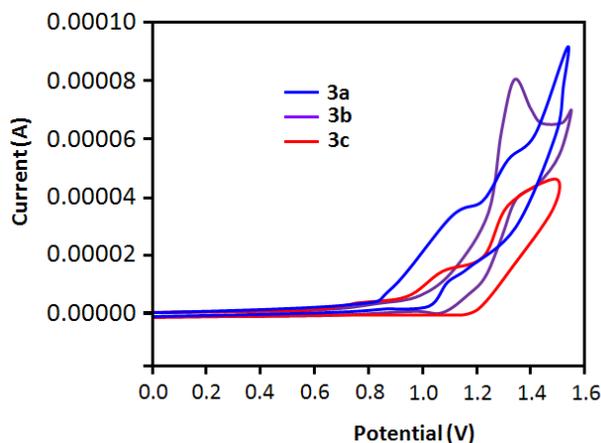


Figure 5. Cyclic voltammograms curves of 3a-c.

Photovoltaic performance

The synthesized Dyes 3a-c was tested as a sensitizer in Dye-sensitized Solar Cells. The effective light exposure area of the DSSCs was maintained typically at 1 cm², 0.05 M I₂/0.5 M LiI/0.5 M, in which 4-tert-Butylpyridine in 3-Methoxypropionitrile solution was used as a liquid Electrolyte. The Photovoltaic performances of the Solar Cells fabricated from the prepared Electrodes under AM1.5 Solar irradiation (85 mW/cm²) are shown in Fig. 6. The detailed parameters such as Short-circuit Current Density (J_{sc}), Open-circuit Voltage (V_{oc}), Fill Factor (FF) and overall Conversion Efficiency (η) are summarized in Table 1. Fig. 6, clearly shows that the efficiency of the fabricated device is found to decrease in the order of 3c > 3b > 3a respectively. Among the synthesized Dyes, the Quinoline ring donor based dye 3c show higher efficiency of 2.87 % contributed by high value of J_{sc} , V_{oc} and FF compared to *N,N*-Diethyl Amine donor based Dye 3b (ECB and EB) (See Table 1). In the donor segment, Phenyl rings appear more twisted than the Ethyl groups, as it separates the Dye Molecules in the TiO₂ surface which may be the reason for higher efficiency of 3c Dye in Solar Cells.

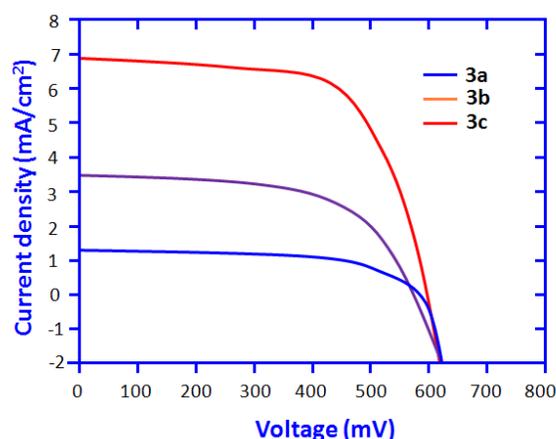


Figure 6. Photocurrent-voltage Spectra of DSSC based on 3a-c Dyes.

Table 1. DSSC Performance Parameters of the synthesized Dyes 3a-c.

Dye	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	Efficiency (η) (%)
3a	0.326	510	0.5982	0.22
3b	2.187	518	0.5993	1.43
3c	5.612	579	0.6014	2.87

CONCLUSION

In sum, the experimental inference reveals the successful synthesis of three different 5-Carboxylic acid-2-Aryl Benzimidazoles 3a-c by One-pot reaction. The Photo-physical, Electrochemical and DSSCs performance of the synthesized Dyes were observed. Among 3a-d Dyes, the 3c Dye containing Quinoline as a donor and Benzimidazole Carboxylic acid as an

acceptor shows higher efficiency of 2.87%. The improved J_{sc} , V_{oc} and overall efficiency may be attributed to the reduced band gap, broadened absorption bands in the visible region, longer recombination resistance and high Electron lifetime in 3c Dye. Thus, from the Photo-physical studies, it can be clearly inferred that the 3c Dye could serve as a good sensitizer compared to the other Dyes 3a and 3b in the process of DSSC application.

CONFLICT OF INTEREST: Authors declare no conflict of interest.

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SUPPORTING INFORMATION

The spectra data (NMR and Mass) of all new compounds is provided as supporting information file and can be downloaded from journal site.

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