

# SYNTHESIS AND CHARACTERIZATION OF A NOVEL CARBAZOLE BASED HOLE TRANSPORTING MATERIAL FOR APPLICATION IN SOLID STATE DYE SENSITIZED SOLAR CELL

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## ABSTRACT

The present work focuses on the synthesis of a novel carbazole based hole transporting material (HTM), 1,3,5-tris(3,6-dimethoxy-9-H-Carbazol-9-yl)benzene by Ullmann Coupling. During this, the intermediate compounds were synthesized by multi-step organic reactions. The synthesized compounds were characterized using UV-Visible, FT-IR and NMR spectroscopic techniques. By using the synthesized compound and a natural dye, solid state dye sensitized solar cell was fabricated and the performance analyzed.

**Keywords:** Carbazole; Hole-transporting material; Dye Sensitized Solar Cell; Ullmann coupling

## 1. Introduction

Nowadays the world is in huge demand of higher level technologies for providing inexhaustible energy. One of the main challenges is how to procure the hike in global energy demand without sacrificing our environment in future. The level of solar energy striking on the earth in an hour is much more than the overall energy utilized on the earth in one year. The solar energy gives a clean ample energy and one the best energy source for the future environment. The solar cells are the devices which transform light energy into electrical power. Looking at photovoltaic, dye sensitized solar cell is considered to be a lead candidate, they having long shelf life and are low cost renewable energy sources [1].

Carbazole based derivatives have attracted much attention because of their interesting photochemical properties [2]. Recent interest in the carbazole derivatives have been caused by its good charge transport function, which can be exploited in the molecular design of new types of HTMs in DSSCs. Another fascinating advantage is the versatility of the carbazole reactive sites that can be substituted with a wide variety of functional groups, allowing fine tuning of its optical and electrical properties. The carbazole derivatives generally possess good thermal stability and hole transport properties [3]. The combination of carbazole derivatives and triphenyl amine derivatives is expected to offer the improved thermal and morphological stabilities as well as their good hole transport properties [4]. Basic work in our laboratory include synthesis of hole transporting materials for the fabrication of solid state dye sensitized solar cells [5].

Molecules contain a  $\pi$ -rich heterocyclic or aromatic ring system functionalized with one or more electron donating substituents exhibits good hole transporting properties [6]. The most commonly encountered substituents are amino and alkoxy groups, which contain single bonded hetero atoms possessing sharable lone pairs [7]. The most widely used hole transport molecules are aromatic amines. Carbazole based derivatives have attracted much attention because of their interesting photochemical properties, good chemical and environmental stability provided by the fully aromatic unit, easy substitution of the nitrogen atom with a wide range of functional groups permitting a better solubility and a fine tuning of the electronic and optical properties [8,9].

Carbazole based material constitute a well-known class of hole conducting material. The charge carrier mobility and photo conductive properties of these materials have been studied by various groups. Hole-transporting materials based on the carbazole moiety have been the subject of an increasing number of investigations over the last decade [10-13]. Triphenylamine cored star-burst materials are extensively investigated for their easy modification, superior hole-transporting ability and propeller molecular conformation [14].

Triphenylamines were also used as the core to construct an opto-electronic functional star-burst material [15]. Triarylamine based compounds find increasing importance as hole transporting materials in various electro optical applications like photovoltaic, light emitting devices and photo refractive systems. Triarylamine moiety fulfills the requirement of easy and reversible oxidation and therefore constitutes the building block of many of the hole transporting compounds [16]. Various derivatives of triarylamine have been successfully applied in solid state dye sensitized TiO<sub>2</sub> solar cells [17].

In this paper, we mainly report the synthesis of a novel hole transporting material which is based on carbazole derivative by Ullmann coupling. By using the synthesized compound and a natural dye extracted from Red Sandal Wood, organic solid state dye sensitized solar cell was fabricated and performance analyzed.

## 2. Experimental Section

### 2.1 Materials and Measurements

The reagents Carbazole, Dimethyl formamide, N-bromo succinamide, Potassium carbonate, Copper powder, Copper(I)chloride, Methanol, 1,2-Dichlorobenzene, Sodium, Sodium nitrite, Aniline, Glacial acetic acid, Chloroform, Ethylacetate, 18-crown-6 were purchased from Merck. The solvents were distilled before use according to availing procedures in literature. Spectroscopic grade solvents (Merck) were used for UV-Visible spectroscopic measurements.

Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8400 S spectrometer as Potassium bromide (KBr) disc. Ultraviolet-Visible (UV-Vis) spectra of a dilute solution in spectroscopic grade chloroform were recorded on a UV-Vis Shimadzu 1700 using 1.0 cm length quartz tube. Nuclear magnetic resonance (NMR) spectra were recorded on a NMR-JEOL GSX-400 spectrometer with tetramethylsilane as the internal reference using CDCl<sub>3</sub> as solvent in all cases.

### 2.2 Methods

#### 2.2.1 Synthesis of 3, 6 – dibromocarbazole (A)

Carbazole 1.67g (0.01mol) was dissolved in 15ml DMF at 0°C with stirring followed by the addition of a solution of NBS 3.63g (0.02mol) in 10ml of DMF. The resulting mixture was stirred at room temp for 2 hr. and the solution then poured into 100ml of water, filtered and washed with water. The crude product was recrystallized from ethanol. Yield: 64%, Appearance: White crystalline solid, Melting point: 204°C.

The completion of the reaction is monitored by TLC.

UV-Visible spectra (Ethanol, nm): 363, 353, 338, 303, 267.

In UV-Visible spectra the  $\lambda_{\max}$  of 3,6-Dibromo carbazole is observed at 363nm. The parent compound carbazole shows  $\lambda_{\max}$  at 293 nm. The increase in  $\lambda_{\max}$  may be due to substitution of Br with lone pair of electron.

FT- IR Spectra (KBr, cm<sup>-1</sup>): 3406, 3068, 1471, 1284, 570

FT-IR gave characteristic peaks 3406cm<sup>-1</sup> indicated NH stretching frequency, 3068cm<sup>-1</sup> indicated the Ar C-H stretching, 1471 cm<sup>-1</sup> indicated the Ar C=C stretching, 1284 cm<sup>-1</sup> indicated the C-N stretching and 570 cm<sup>-1</sup> indicated the C-Br stretching.

#### 2.2.2 Synthesis of 3, 6 – dimethoxycarbazole (B)

Into a three necked flask fitted with a condenser, N<sub>2</sub> inlet, addition funnel and magnetic stirrer, was added 25ml of dry methanol. The entire was cooled 0°C with ice water before sodium 2.3g(0.1mol) was added gradually. The ice bath was removed and the mixture was stirred until all the sodium had reacted. To this sodium methoxide solution DMF 12.5ml, CuCl 3.8g(0.03mol), 3,6-dibromocarbazole 1.65g(0.005mol) and another 12.5ml of DMF were added. The resulting mixture was heated to reflux for 4 hrs under nitrogen. The precipitate was filtered while hot and the filtrate was diluted with 50ml of water and extracted with chloroform (30ml x 3). The combine organic layers were neutralized with 5% HCl followed by washing with water and brine, drying by passing through sodium sulphate and

concentrating in vacuum. The residue was recrystallized from methanol. Yield:60%, Appearance: White solid, Melting point: 104<sup>0</sup>C

UV-Visible spectra (Ethanol, nm): 350, 336, 303, 266

In UV-Visible spectra the  $\lambda_{\max}$  of 3, 6-Dimethoxy carbazole is observed at 350nm.

FT- IR Spectra (KBr, cm<sup>-1</sup>): 3409, 1326, 1053

FT-IR gave characteristic peaks at 3409cm<sup>-1</sup> indicated -NH stretching frequency, 1326cm<sup>-1</sup> indicated the Ar- C=C stretching and the peak at 1053cm<sup>-1</sup> is due to C-O stretch.

### 2.2.3 Synthesis of 1, 3, 5 – Tribromobenzene(C)

1,3,5-Tribromobenzene(C) was prepared from 1,3,5-Tribromoaniline according to available procedure of Vogel. Appearance: white solid, Melting point: 122<sup>0</sup>C

UV-Visible spectra (Ethanol,nm): 224, 210

In UV-Visible spectra the  $\lambda_{\max}$  of 1,3,5-tribromobenzene is observed at 224 nm.

FT- IR Spectra (KBr, cm<sup>-1</sup>): 3409, 1326, 1053

FT-IR gave characteristic peaks at 3409 indicated NH stretching frequency, 1326cm<sup>-1</sup> indicated the Ar C=C stretching and the peak at 1053cm<sup>-1</sup> is due to C-O stretch.

### 2.2.4 Synthesis of 1,3,5-tris(3,6-dimethoxy-9-H-Carbazol-9-yl)benzene (D)

3,6-Dimethoxycarbazole 1.25g (0.0075mol), 1,3,5-tribromobenzene 0.8g (0.0025mol), 2.65g (0.02mol) K<sub>2</sub>CO<sub>3</sub>, 1.8g (0.03mol) Copper powder and 200mg(0.00075mol) of 18-crown-6 were heated together in 50ml of orthodichlorobenzene under nitrogen atmosphere and the resulting mixture was refluxed for 24hrs at 170<sup>0</sup>C. The inorganic compounds were removed by filtration and the solvent orthodichlorobenzene was evaporated under vacuum. Then it was extracted using ethylacetate. The combined organic layers washed with brine, drying by passing through sodium sulphate and concentrating in vacuum to give brown residue and was purified by using chromatographic column.

Appearance: pale brown solid, Melting point: 160<sup>0</sup>C

UV-Visible spectra (Chloroform,nm): 354, 340

In UV-Visible spectra the  $\lambda_{\max}$  of coupling product is observed at 354 nm. This may indicate that the coupling reaction make the compound to bathochromic shift, when comparing to the individual compounds.

FT- IR Spectra (KBr, cm<sup>-1</sup>): 3070, 1326.

FT-IR gave characteristic peaks 3070cm<sup>-1</sup> indicated the Ar C-H stretching, 1326cm<sup>-1</sup> indicated the Ar C=C stretching. The peaks due to N-H stretch and C-Br stretch are absent, this confirms the formation of coupling product.

<sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, ppm): 7.1-7.9 (m, 21H), 3.48 (s, 18H)

The NMR spectra confirms the presence of aromatic ring at 7.1-7.9  $\delta$  and -OCH<sub>3</sub> group at 3.48 $\delta$

The structure of the synthesized compound 1,3,5-tris(3,6-dimethoxy-9-H-Carbazol-9-yl)benzene is confirmed from the spectral data.

### 2.2 .5 Dye extraction

Red sandalwood was commonly known as 'rakta chandan' (botanical name: '*Pterocarpus santalinus*', C<sub>14</sub>H<sub>14</sub>O<sub>7</sub>). Perkin and Everest have identified that there are at least two or more maroonish red colouring components in the red sandalwood, viz. santalin A, santalin B and deoxysantalin of which santalin A is considered as the main component. Red sandal wood is purchased commercially and made fine powder. It is steam distilled using ethanol. Ethanol extract contains Santalin A as the main component. The product is purified by chromatographic techniques and characterized using spectroscopic techniques. Santalin A is chemically,2,10-dihydroxy-6-(4-hydroxy-3-methoxy-benzyl)-5-(4-hydroxy-2-methoxy-phenyl)-1,3-dimethoxy-benzo[a]xanthen-9-one (Figure 1).

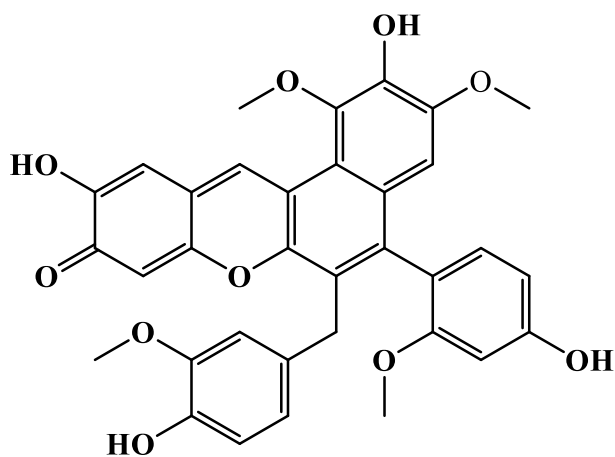


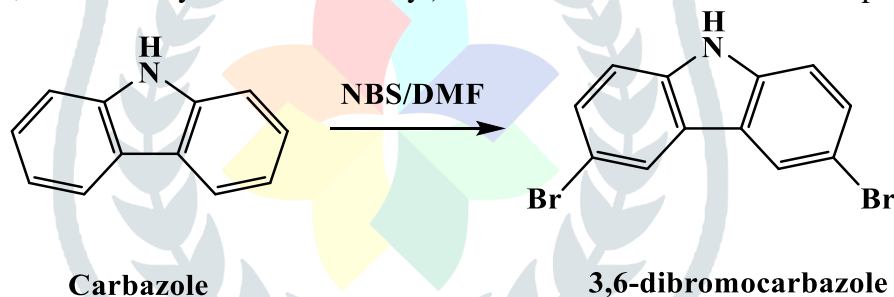
Figure 1: Structure of Santalin A

UV-Visible (ethanol, nm): 506.5,474.5,310.5

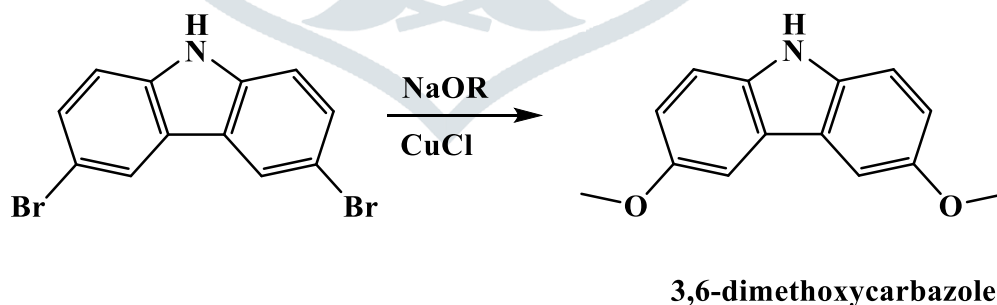
<sup>1</sup>H NMR Spectra (CDCl<sub>3</sub>, ppm):3.73(12H,s, methoxy), 3.92(2H,s, methylene), 4.78(4H,s, Hydroxyl), 6.11-7.20(10H, m, Aromatic).

### 3. Results and Discussions

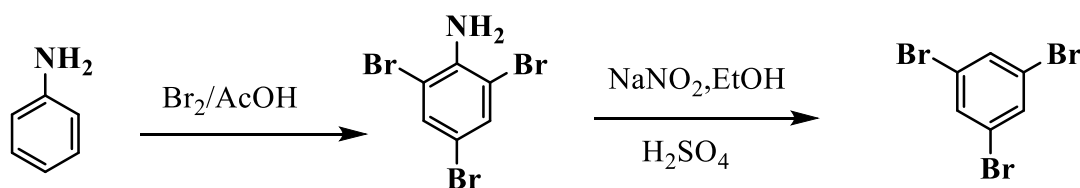
The synthetic strategy employed for the synthesis of various intermediate compounds and the hole transporting material are described in scheme 1-4. The synthesis of the final compound involves multistep organic reactions. The compound synthesized in every step was subjected to purification process. The purity of the compound is checked by TLC. The synthesized compounds were characterized by UV-Visible, FT-IR, NMR and Mass spectroscopic techniques. The structure of the synthesized compound 1,3,5-tris(3,6-dimethoxy-9H-Carbazol-9-yl) benzene is confirmed from the spectral data.



Scheme 1: Synthesis of compound A

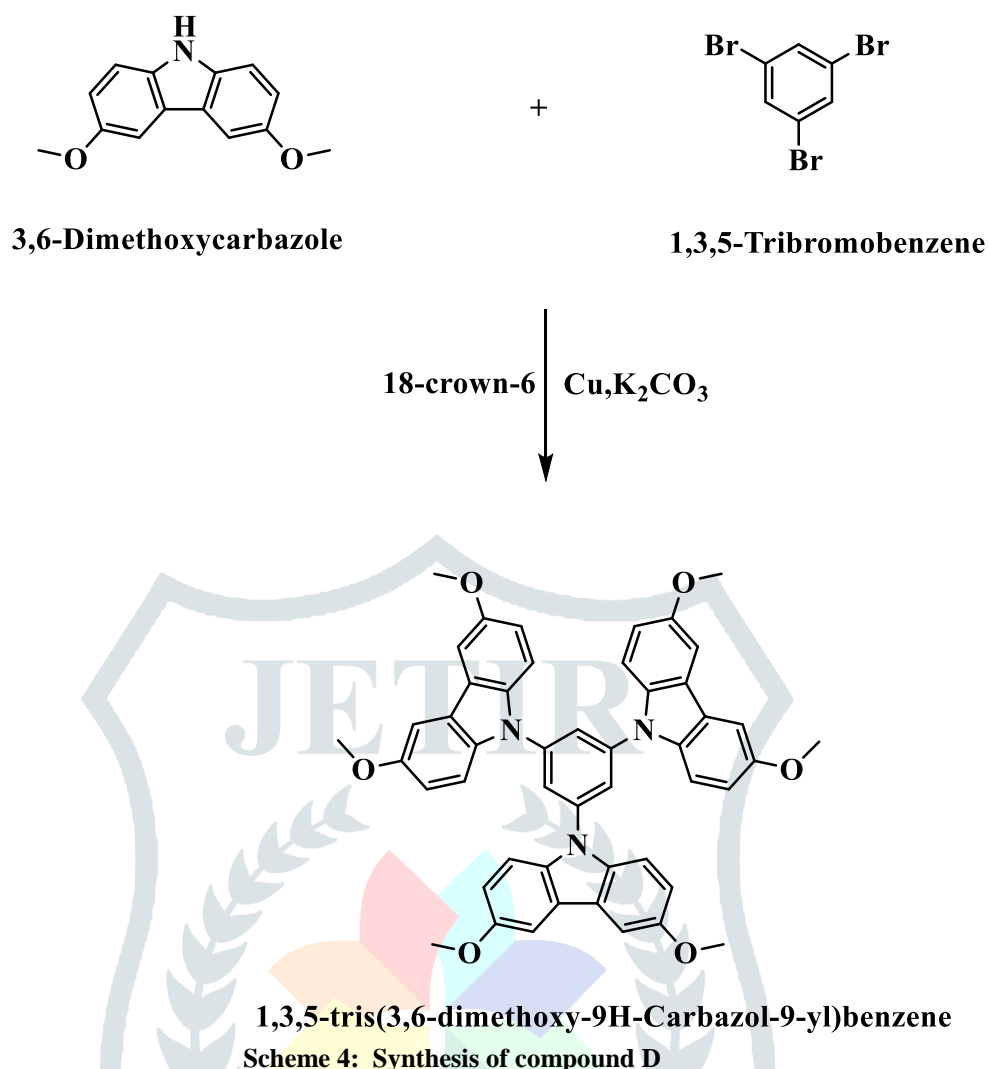


Scheme 2: Synthesis of compound B



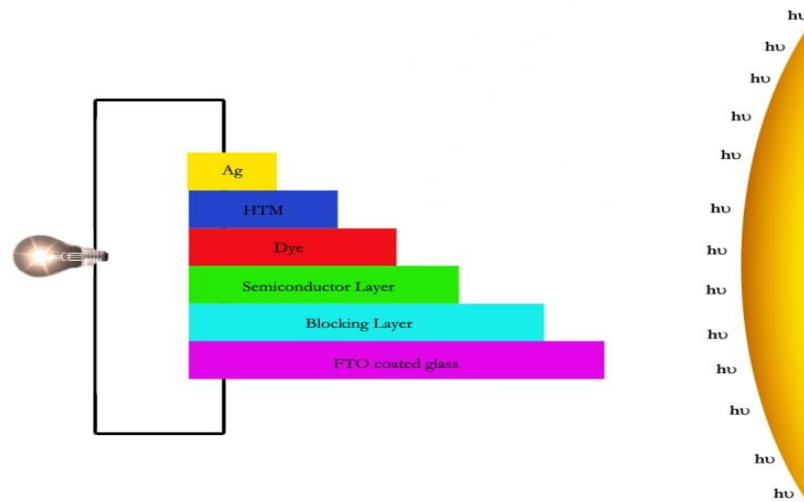
Scheme 3: Synthesis of compound C





### Device Fabrication

DSSC device comprised of a transparent conducting oxide (TCO) glass electrode coated with porous nano crystalline titania (TiO<sub>2</sub>), dye molecule attached to the surface of the nano crystalline titania, hole transporting material and a counter electrode. Fluorinated tin oxide (FTO) coated transparent glass strips (25mm x 25mm) with resistance of 30μohms were used for the device fabrication. The structuring of the TCO is done using a chemical etching method. Zinc granulates are spread out on the glass (20 mg/cm<sup>2</sup>). Scotch tape is used to mask the TCO area needed for the back contact. The fast reaction between HCl and Zinc powder leads to the removal of the SnO<sub>2</sub>. After two treatments of 3 minute reaction time, the SnO<sub>2</sub> is completely removed. The structured glass is then cleaned by ultra-sonication in various solvents such as acetone, ethanol and water, for 10 min in each solvent. Compact TiO<sub>2</sub> (30nm) were deposited on FTO glass by spin coating that acts as a blocking layer. The FTO is placed in a chamber for 1 min and accelerated at a speed of 1000 rpm. 150μl of TiO<sub>2</sub> solution is applied onto the substrate. The substrate is spun up to a speed of 1000 rpm for 30 second with an acceleration of 200 rpm/s. The samples were dried for 30 min. After deposition, the prepared TCO/ TiO<sub>2</sub> were annealed at 200°C for 1 hour in air with a hot plate to achieve complete pyrolysis of organic species. Then nanoporous TiO<sub>2</sub> (~2.5μm) was coated by doctor blading. The layers were sintered for 30 min at 350 °C to consume the organic additives and to obtain mechanically stable samples. Then the sample is cooled down slowly to 80 °C and placed into alcoholic solution of red sandal dye overnight. After the dip coating, HTM in THF deposited on the cell by spin coating method. The cells were kept overnight to allow maximum penetration of HTM in TiO<sub>2</sub>. The metal electrode silver (200 nm) is coated on HTM of DSSC by thermal evaporation. Different layers of DSSC are represented in figure 2.



**Figure 2: Different layers of DSSC**

The current-Voltage (I-V) characteristics is monitored and measured by using a Keithley 276 source measurement unit. Photocurrent-Voltage (I-V) characteristics of DSSC based on D as HTM is measured using I-V characteristic curve plotted in figure 3. The result for photocurrent density ( $I_{sc}$ ), open-current voltage ( $V_{oc}$ ), fill factor (FF) and corresponding photo-energy conversion efficiency ( $\eta$ ) are summarized in table 1. The low conversion efficiency may be due to the following reasons: (i) instead of the ruthenium dye, which is commonly used for DSSC s, we used a natural dye, the red pigment of red sandal and (ii) instead of gold as back electrode we applied silver.

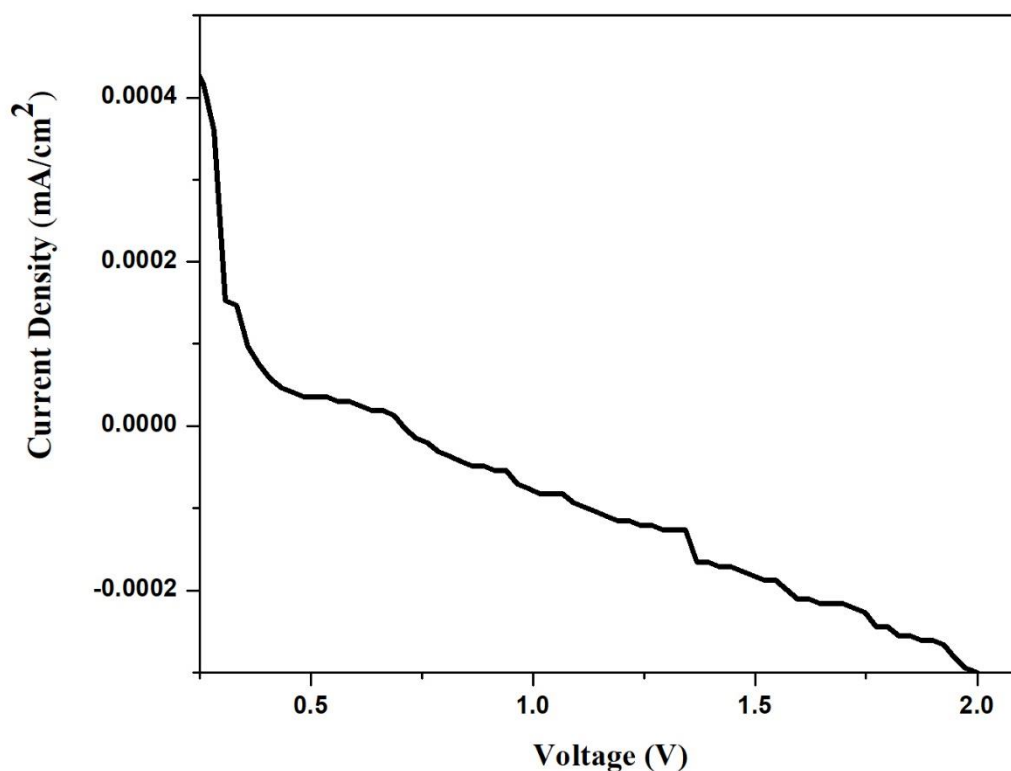


Figure 3: I-V curve of DSSC using D as HTM

Table 1: I-V characteristics

Compound	Voc (V)	Isc (mA)	Jsc (mA/cm <sup>2</sup> )	Vmax	FF	η (%)
D	1.571	0.0046	0.155	1.495	2.91	0.71

#### 4. Conclusion

The solar power is presently a rapidly growing but often relatively expensive renewable energy form. One of the key elements in DSSC is HTM, which is responsible for the regeneration of the oxidized sensitizer after electron injection into the semiconductor and for the transport of positive charge to the counter electrode. Carbazole based hole transporting materials find increasing applications in various electro optical devices like organic photovoltaic cells.

Here we have synthesized a novel carbazole based starburst HTM, 1,3,5-tris(3, 6-dimethoxy-9H-Carbazol-9-yl) benzene. The synthesized compounds were characterized using UV-Visible, FT-IR and NMR spectroscopic techniques. Efficiency of the dye sensitized solar cell is measured using current-voltage (I-V) characterization. Efficiency is minimum due to the presence of natural dye. We would like to highlight the total cost effect of the cell, which will be down to nearly 30-40% of a similar type of fabricated cell. The conversion of the non-conventional energy, even if for very low percentage is amelioration to mankind.

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