

Synthesis and properties of *N,N,N'*-tris-(2-ethoxy-naphthalenen-1-yl)-*N,N,N'* triphenylbenzene 1, 3, 5-triamine for dye sensitized solar cell

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Abstract. New starburst ethoxy naphthylamine is synthesized using multi-step organic reactions. The synthesized compound is characterized using UV-Visible, FT-IR and NMR spectrometric techniques. The thermal and electrochemical property of the compound was studied using DSC and cyclic voltammetry. Using this compound and a natural dye, organic dye sensitized solid state solar cell was fabricated and the performance analysed.

Keywords. Starburst molecule; triaminobenzene; hole transport material; Ullmann coupling; amorphous material.

1. Introduction

Organic solar cells, a relatively novel technology, are being studied extensively in universities, national laboratories and several companies around the world. Currently many solar cells are made from a refined, highly purified silicon crystal, similar to those used in the manufacture of integrated circuits and computer chips. The high cost of these silicon solar cells and a complex production process has generated interest in developing alternative photovoltaic technologies. Compared to silicon based devices, organic solar cells are light weight, disposable, inexpensive to fabricate, flexible, designable on a molecular level, and have little potential for environmental impact. Materials based on aryl amines have been extensively studied due to their interesting physical, photochemical, and electrochemical properties (Shirota 2000). Aryl amine based starburst compounds find increasing importance as hole transporting materials in various electro optical applications like photovoltaic, OLED and photorefractive systems (Masayoshi *et al* 2005). The arylamine moiety fulfills the requirements of easy and reversible oxidation and therefore, constitutes the building block of many of the hole transport compounds (Haridas *et al* 2001).

The general strategy to obtain amorphous compounds is to design either linear or hyperbranched oligomers with bulky aryl groups. Ishikawa *et al* (1992) have efficiently made use of this concept and have reported various dopable starburst compounds with different cores such as benzene, triphenylamine and 1, 3, 5-trisubstituted phenylbenzene. These compounds are found to have thermal and electrochemical properties which are in good agreement with hole transporting materials used for fabricating optoelectronic devices (Ostrauskaite *et al* 2002). A literature survey reveals that

1, 3, 5-triphenylamines are widely used as hole transporting compound in electroluminescent materials (Jun *et al* 2002). Benzene-1, 3, 5-triamine derivatives were recommended for enhancing the operation stability of electroluminescent devices because of their three dimensional expanded structure, high rigidity, excellent photo and thermal stability (Thelakkat *et al* 1999).

DSSCs are becoming popular because of their advantages of cost, easy to fabricate and higher shelf-life, in comparison with traditional solar cells (Ostrauskaite *et al* 2002). The materials that are needed for the fabrication of DSSC are nano and micro layers of nanocrystalline TiO₂ as semiconductor, indium tin oxide coated substrate and metal as electrodes, organic electronic compounds as hole transporting layers and dyes. The efficiency of the cells depends on the materials, thicknesses and mode of coating of all these layers.

In the present investigation, we focused on the synthesis of novel low molecular weight hole transporting compound *N,N,N'*-tris-(2-ethoxy-naphthalene-1-yl)-*N,N,N'*-triphenylbenzene 1,3,5-triamine (**D**). The synthesized compound is characterized using instrumental techniques such as FT-IR, UV-Visible, ¹H-NMR, ¹³C-NMR spectroscopy. Thermal and electrochemical properties of these synthesized compounds were studied using differential scanning calorimetry (DSC) and cyclic voltammetry (CV). Using this compound and a natural dye, organic dye sensitized solid state solar cell was fabricated and the performance analysed.

2. Experimental

2.1 Materials

2-Naphthol, aniline, Mohr's salt (Merck, India), 1-bromoethane, dichlorobenzene (Loba Chemie) and KI

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(Qualigens) were purified as per common laboratory procedure before use. Silica gel (60–120 mesh, SRL) and bromine (Merck) were used as such. The solvents were distilled before use according to procedures available in literature. Spectroscopic grade solvents (Merck) were used for UV-Visible spectrometric analysis.

2.2 Measurements

Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8400 S spectrometer as potassium bromide (KBr) disc. Ultraviolet-visible (UV-Vis) spectra were recorded as a diluted solution in spectroscopic grade ethanol on a UV-Vis Shimadzu 1700 using 1.0 cm length quartz tube. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a NMR-JEOL GSX-400 spectrometer with tetramethylsilane as the internal reference using CDCl_3 as solvent in all cases. The cyclic voltammetry (CV) measurements were carried out on a Autolab potentiostat PGSTAT 12 at a glassy carbon electrode using millimolar solutions in acetonitrile (ACN) containing 0.1 M of supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF_6), in a three electrode cell and potentiostat assembly at room temperature. Differential Scanning Colorimetry studies were performed with a NETZSCH DSC 204 thermal analyser under inert atmosphere. The sample was scanned from -50 – 150°C at a rate of $10^\circ\text{C min}^{-1}$.

2.3 2-Ethoxy naphthalene [A]

Ethyl bromide (0.32 ml, 0.03 mol) in toluene (25 ml), 2-naphthol (4.32 g, 0.03 mol) in 40% NaOH (20 ml) and tetrabutyl ammonium bromide (TBAB) (0.9 g, 0.003 mol) were refluxed at 70°C for 4 h. After the completion of the reaction which was monitored by TLC, the product was extracted using toluene–water system (Li *et al* 2004).

Appearance: brown liquid; yield: 98.1%; boiling point: 250°C ; UV-Vis (ethanol, nm): 356, 361; FT-IR (KBr, $\nu \text{ cm}^{-1}$): 3058, 3025.14 (Ar-H), 2879, 1379 ($-\text{OC}_2\text{H}_5$), 1217 (C–O–C); ^1H -NMR (CDCl_3 , δ): 1.33–4.08 ($-\text{OC}_2\text{H}_5$), 6.97–7.64 (7H, Ar); ^{13}C -NMR (CDCl_3 , ppm): 14.3, 65.1 (OC_2H_5) 105.8, 118.8, 123.7, 126.4, 126.8, 127.7, 129.3, 129.5, 134.6, 157.7 (Ar-C).

2.4 2-Ethoxy naphthalene-1-yl amine [B]

A (1.58 g, 0.01 mol) and conc. H_2SO_4 (5 ml) were taken in a round bottom flask equipped with a condenser. It was cooled and the temperature was maintained so that it did not exceed 5°C . To this, conc. HNO_3 (4 ml) was added drop wise with stirring. The solution was stirred for 1 h at 0°C , 1 h at room temperature and 1 h at 60°C . The contents of the flask were cooled and poured into ice and neutralized with 40% NaOH. The yellow compound obtained was filtered, washed, dried and recrystallized from ethanol. The product (1.64 g, 0.008 mol), ammonium ferrous sulphate (1.5 g, 0.003 mol),

ethanol (20 ml), water (5 ml) and conc. HCl (0.5 ml) were heated in a round bottom flask on a stem bath for 1 h. The product was extracted from the mixture by washing with hot ethanol, dried and recrystallized from ethanol.

Appearance: light yellow solid; yield: 76.8%; melting point: 78°C ; UV-Vis (ethanol, nm): 322, 364; FT-IR (KBr, $\nu \text{ cm}^{-1}$): 3511, 3425 ($-\text{NH}_2$), 3075, 2985 (Ar-H), 2879, 1379 ($-\text{OC}_2\text{H}_5$), 1218 (C–O–C), 1250 (C–N); ^1H -NMR (CDCl_3 , δ): 1.33–4.08 ($-\text{OC}_2\text{H}_5$), 6.87–7.59 (7H, Ar); ^{13}C -NMR (CDCl_3 , ppm): 14.3, 65.1 (OC_2H_5), 119.8 (C–NH $_2$) 119.1, 119.5, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2 (Ar-C).

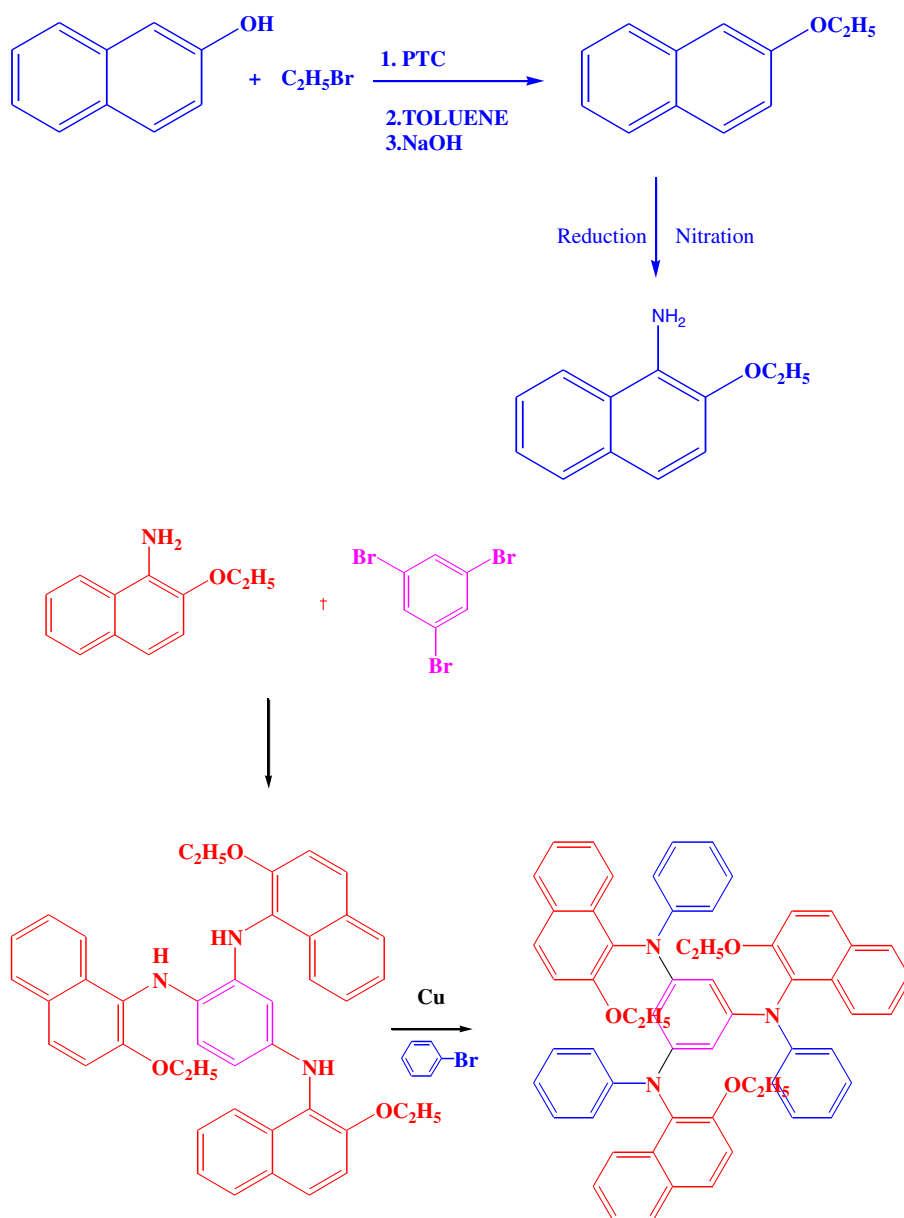
2.5 N, N, N'-tris-(1-ethoxynaphthalene-2-yl)-benzene-1, 3, 5-triamine [C]

B (5.67 g, 0.03 mol), tribromobenzene (3.30 g, 0.01 mol), CuCl (0.02 g, 0.0002 mol) and K_2CO_3 (1.0 g, 0.007 mol) (dried at 110°C) were refluxed together with 20 ml acetone for 12 h at 60°C . The completion of the reaction was monitored by TLC. After removal of the solvent by vacuum, ammonia solution (50 ml) was added and the mixture was left to stand for 2 h. Ethyl acetate (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml \times 2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, and concentrated *in vacuo* to give yellow residue which was purified by chromatographic column using ethyl acetate–hexane (4:1) as the eluent to obtain yellow solid which was recrystallized from ethanol.

Appearance: light yellow solid; yield: 42.4%; melting point: 65°C ; UV-Vis (ethanol, nm): 351, 318; FT-IR (KBr, $\nu \text{ cm}^{-1}$): 3478 (N–H), 3073, 2984 (Ar–H), 2870, 1379 ($-\text{OC}_2\text{H}_5$), 1217 (C–O–C) 1254 (C–N); ^1H -NMR (CDCl_3 , δ): 1.33–4.08 (15H, $-\text{OC}_2\text{H}_5$), 4.0 (3H, –NH), 5.02–7.59 (21H, Ar); ^{13}C -NMR (CDCl_3 , ppm): 14.3, 65.1 (OC_2H_5), 96.8 (12, 14, 16 C), 145 (11, 13, 15 C) 119.1, 119.5, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.3 (Ar–C).

2.6 N, N, N'-tris-(2-ethoxy-naphthalene-1-yl)-N, N, N' triphenylbenzene 1, 3, 5-triamine (D)

C (4.2 g, 0.0071 mol), bromobenzene (2.2 ml, 0.0213 mol), CuCl (0.02 g, 0.0002 mol) and K_2CO_3 (1.0 g, 0.007 mol) (dried at 110°C) were mixed together with dichlorobenzene (20 ml) for 15 h at 170°C . The completion of the reaction was monitored by TLC. After removal of the solvent *in vacuo*, ammonia solution (50 ml) was added and the mixture was left to stand for 2 h. Ethyl acetate (150 ml) and water (100 ml) were added. The organic phase was separated, washed with water (100 ml \times 2) and brine solution (100 ml), dried over anhydrous sodium bisulphite, filtered and the solvent was removed in vacuum. The product was purified with column chromatography using ethyl acetate–hexane as eluent to obtain yellow solid which was recrystallized from hexane.



Scheme 1. Synthetic route for starburst tertiary amine.

Appearance: Light yellow solid; yield: 39.5%; melting point: 105°C ; UV-Vis (ethanol, nm) 394, 319; IR (KBr, ν cm^{-1}): 2870, 1353 ($-\text{OC}_2\text{H}_5$), 1218 (C–O–C), 1254 (C–N); ^1H NMR (CDCl_3 , δ): 1.02–4.33 (OC_2H_5), 7.18–8.73 (36H, Ar); ^{13}C -NMR (CDCl_3 , ppm): 14.6, 65.9 ($\text{O C}_2\text{H}_5$), 106.5 (12,14,16 C), 143.5 (11,13,15 C) 114.2, 119.9, 120.4, 121.2, 124.5, 125.0, 126.9, 127.7, 127.9, 128.9, 131.4, 131.9, 137.8, 147.9 (2–10C and 17–22C).

2.7 Dye extraction

Red sandalwood was commonly known as ‘rakta chadan’ (botanical name: ‘*Pterocarpus santalinus*’, $\text{C}_{14}\text{H}_{14}\text{O}_7$). 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 was extracted according to the literature (Samanta *et al* 2006).

3. Results and discussion

The synthetic strategy employed for *N, N, N'*-tris-(2-ethoxy-naphthalen-1-yl)-*N, N, N'* triphenylbenzene-1, 3, 5-triamines involved the preparation of star shaped intermediate and their coupling with bromobenzene to form the final compounds (scheme 1). Steric hindrance also has an

important effect on Ullmann type condensation. With an increase in steric hindrance the reaction becomes more difficult (Jun *et al* 2002). Due to the same reason, we found a decrease in yields of the products.

3.1 Thermal properties

The glass forming properties and phase transition of compound (**D**) is studied using DSC. The compounds are analysed for heating and cooling thermograms (cyclic) in inert atmosphere from -50 – 250°C at a rate of $10^\circ\text{C min}^{-1}$. The T_g and T_m values of synthesized compound is listed in table 1.

Generally for application of compounds for optoelectronic device fabrication, the following thermal criteria are required: low T_g value, moderate melting point and stable up to 200°C . The compound **D** shows one sharp decomposition along with T_g . The T_g value is found to be 80°C . The sharp phase transition occurred at temperature 105°C (T_m). **D** is stable up to 200°C .

We found that our starburst compound fulfils all the required conditions. The lower T_g values made the compounds to become glass at low temperature. This also will enable the compounds to have high penetrating ability, which is required for HTM to intermix with the semiconductor (TiO_2) in all its layers. The moderate melting point will also help the compounds to be in solid phase even after a long time of exposure of the cell. Since the decomposition occurred only above 200°C , they will be stable in the device structure once fabricated (Jager *et al* 2001).

The DSC results suggest that the compound (**D**) is an amorphous material with good film properties. From the result we can say that this compound is a good candidate as hole transporting material in solar cell.

3.2 Electrochemical properties

The CV measurements were carried out at a glassy carbon electrode using millimolar solutions in acetonitrile (ACN) containing 0.1 M of supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF_6), in a three-electrode cell and potentiostat assembly at room temperature. The

Table 1. Phase transition temperature for **D**.

Compound	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)
D	80	105

Table 2. Cyclic voltammetric data and HOMO–LUMO values of **D**.

Compound	E_{ox} vs Fc (v)	HOMO (eV)	E_{red} vs Fc (v)	LUMO (eV)	E_g (eV)	P_1 (eV)	E_A (eV)
D	0.9	-5.7	-1.1	-3.7	2.0	5.7	3.7

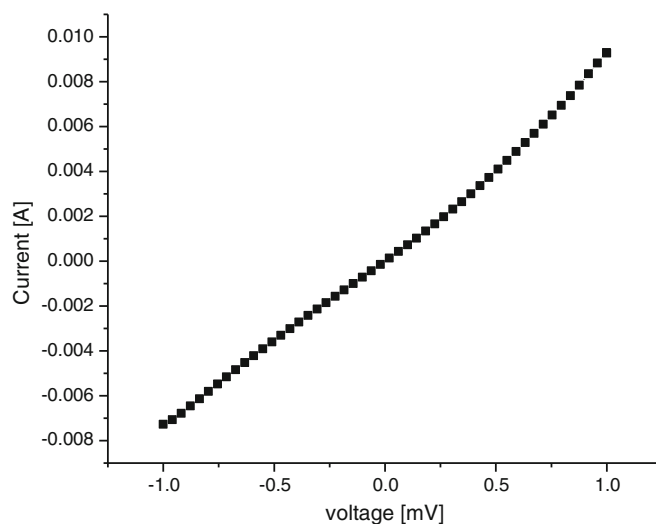


Figure 1. I – V curve of DSSC prepared using **D** as HTM.

potentials were measured against platinum as reference electrode and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system (Gritzner and Kuta 1984). For a compound to be used in an optoelectronic device its HOMO and LUMO values should be in accordance with that of the semiconductor. The HOMO and LUMO values of these compounds are calculated from the anodic oxidation potential using HOMO of ferrocene (4.8 eV) with respect to zero vacuum level as described by Daub *et al* (Jorn *et al* 1995).

The results of electrochemical studies are listed in table 2. HOMO level of the compound **D** is -5.7 eV . The electron affinity (E_A), ionization potential (P_1) and bandgap of the compounds are calculated from the data. The values are in good agreement with the reported value of hole transporting material (Thelakkat and Schmidt 1998). The high-lying HOMO energy level and reversible electrochemical oxidation of **D** suggest that this compound has high potential for hole transporting material.

3.3 Device fabrication

Blocking layer, nanoparticle layer of titanium dioxide, HTM and dye are fabricated on indium tin oxide glass substrate according to available literature. The efficiency of the cell is determined. Fluorinated tin oxide (FTO) coated transparent glass strips ($25 \times 25\text{ mm}$) with a resistance of $30\mu\text{ ohm}$ are used for device fabrication. Blocking layer is coated

Table 3. I – V characteristics of DSSC prepared using **D** as HTM.

Hole conductor	V_{OC} [V]	I_{SC} [A/cm ²]	V_{MAX} [V]	I_{MAX} [A/cm ²]	FF [%]	η [%]
ENTT	0.25	0.9	2	1	8.8	0.39

(~30 nm) on FTO. Then the nanoporous TiO₂ layer of thickness 3–4 μ m is coated by screen printing. The layers were sintered for 30 min at 350°C to burn out the organic additives and to get mechanically rugged samples. Then the sample was cooled down slowly to 80°C and poured into alcoholic solution of red sandal dye overnight. After dip coating of HTM using a suitable solvent, the cells were kept overnight to allow maximum penetration of HTM in TiO₂. 150 Å Thick silver electrode was vacuum evaporated as back electrodes (Jager *et al* 2001) and the measurements were carried out at normal light intensity of 1000 W/m².

Photocurrent–voltage (I – V) characteristics of DSSC based on **D** as HTM is measured using I – V characteristic curve plotted in figure 1. The result for photocurrent density (I_{SC}), open-current voltage (V_{OC}), fill factor (FF) and corresponding photo-energy conversion efficiency (η) are summarized in table 3.

The low conversion efficiency may be due to the following reasons: (i) instead of the ruthenium dye, which is commonly used for DSS cells, we used a natural dye, the red pigment of red sandal and (ii) instead of gold as back electrode we applied silver. In the meantime 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 advancement to mankind.

4. Conclusions

We have synthesized amorphous naphthylamine based starburst compound with good yield. The compound exhibits excellent electrochemical and high thermal stability with low T_g . Efficiency of the dye sensitized solar cell is measured using current–voltage characterization. Efficiency is minimum due to the presence of natural dye. Further studies

are being carried out for the synthesis of various other starburst compounds and improve the efficiency of DSSC using different dyes.

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