

## *N,N,N*-Tris-[4-(Naphthalen-1-yl-phenylamino)Phenyl]-*N,N,N*-Triphenylbenzene-1,3,5-Triamine을 이용한 Hole Transporting 재료의 합성

Siji Mathew and Karickal R. Haridas\*

School of Chemical Sciences, Kannur University, Payyanur Campus, Edat P.O. 670327, Kerala, India  
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## Synthesis and Characterisation of Hole Transporting Materials Based on *N,N,N*-Tris-[4-(Naphthalen-1-yl-phenylamino)Phenyl]-*N,N,N*-Triphenylbenzene-1,3,5-Triamine

Siji Mathew and Karickal R. Haridas\*

School of Chemical Sciences, Kannur University, Payyanur Campus, Edat P.O. 670327, Kerala, India

\*E-mail: krharidas2001@yahoo.com

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**요약.** Two derivatives of star shaped compounds based on naphthylamine benzene고리에 methoxy기와 ethoxy기가 치환기로 연결되어있는 naphthylamine 관련 화합물을 합성하였다. 합성한 화합물의 전자 및 열적특성을 cyclic voltametry (CV) 및 differential scanning calorimetry (DSC)를 이용하여 조사하였다.

**주제어:** 비결정성분자재료, 염료감응형 태양전지, Naphthyl amine

**ABSTRACT.** Two derivatives of star shaped compounds based on naphthylamine with symmetric trisubstituted benzene as core, methoxy and ethoxy as end substitutions are synthesized. The synthesized compounds are characterized by UV-visible, FT-IR and NMR spectrometric techniques. The electronic and thermal properties of the compounds are studied using cyclic voltametry (CV) and differential scanning calorimetry (DSC) respectively. The data's obtained have similarity with the arylamines that have been already used in optoelectronic devices. So these compounds are interesting materials for applications in such devices.

**Keywords:** Amorphous molecular material, Dye sensitized solar cell, Naphthyl amine

### INTRODUCTION

Organic star-burst materials are widely accepted as excellent candidate materials for applications in opto-electronic functional devices, such as solar cells, two-photon absorption (TPA), etc.<sup>1</sup> Excellent film-forming ability, stability, highly amorphous character and multi-branch concerted effects make them attractive in the above-mentioned fields. Triphenylamine-cored star-burst materials are extensively investigated for its easy modification, superior hole-transporting ability, propeller molecular conformation and so on.<sup>2</sup> Triphenyl amines were also used as the core to construct an opto-electronic functional star-burst material.<sup>3</sup> Triarylamine based compounds find increasing importance as hole transporting materials in various electro optical applications like photovoltaic, light emitting devices and photorefractive systems.

Triarylamine moiety fulfills the requirement of easy and reversible oxidation and therefore constitutes the building

block of many of the hole transporting compounds.<sup>4</sup> Various derivatives of triarylamines have been successfully applied in solid state dye sensitized TiO<sub>2</sub> solar cells.<sup>5</sup> Amorphous materials possessing high glass transition temperatures (*T<sub>g</sub>*) should have better opportunity for retaining the film morphology during device operation. A very simple concept for the formation of amorphous glass is non-planar molecular structure, because easy packing of molecules and hence ready crystallization can be retarded. Non-planar configuration has been achieved with the use of star shaped molecules or incorporation of bulky moieties in the molecules.<sup>6,7</sup>

In the present investigation, we focused on the synthesis of two derivatives of *N,N,N*-tris-[4-(naphthalen-1-yl-phenylamino)-phenyl]-*N,N,N*-triphenylbenzene-1,3,5-triamine, which are found to have thermal and electrochemical properties in good agreement with hole transporting materials used for fabricating solar cells. They are i) *N,N,N'*-Tris-{4-[(2-methoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-*N,N,N'*-triphenylbenzene-1,3,5-triamine (6a) and ii) *N,N,N'*-

Tris- {4-[(2-ethoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-*N,N,N'*-triphenylbenzene-1,3,5-triamine (6b). The synthesized compounds are characterized using FT-IR, UV-visible,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy. Thermal and electrochemical properties of these synthesized compounds were studied using Differential Scanning Calorimetry (DSC) and Cyclic Voltammetry (CV).

## EXPERIMENTAL

### Reagents

2-naphthol, 2-methoxynaphthalene, aniline, Mohr's salt (Merck, India), dichlorobenzene, 1-bromoethane, bromophenol, tetrabutylammoniumbromide (Loba Chemie) were purified before use as per common laboratory procedures. 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.

### Instruments

Melting points were determined in open capillaries using melting point apparatus (JSGW, Gujarat). Infrared (IR) spectra were measured on a Shimadzu FTIR 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.  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded on a NMR-JEOL GSX-400 spectrometer with tetramethylsilane as the internal reference using  $\text{CDCl}_3$  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 ( $\text{TBAPF}_6$ ), in a three electrode cell and potentiostat assembly at room temperature. Differential Scanning Colorimetry studies were performed with a NETZSCH DSC 204 thermal analyzer under inert atmosphere. The sample were scanned from  $-50\text{ }^\circ\text{C}$  to  $150\text{ }^\circ\text{C}$  at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ .

**Synthesis of methoxynaphthylamine [2a]:** Conc.  $\text{H}_2\text{SO}_4$  (5.0 mL) and 2-methoxynaphthalene (0.01 mol, 1.58 g) were taken in a round bottom flask equipped with a condenser. It is cooled and temperature is maintained so that it does not exceed  $5\text{ }^\circ\text{C}$ . To this conc.  $\text{HNO}_3$  (4.0 mL) was added drop wise with stirring. The solution was stirred for one hour at  $0\text{ }^\circ\text{C}$ , one hour at room temperature and one hour at  $60\text{ }^\circ\text{C}$ . The contents of the flask were cooled and poured into ice,

neutralized with 40% NaOH. The yellow compound obtained is filtrated. The product (0.008 mol, 1.64 g), Mohr's salt (1.5 g), ethanol (20 mL), water (5 mL) and conc. HCl (0.5 mL) were heated in a round bottom flask on a stem bath for one hour. The product was extracted from the mixture by washing with hot ethanol and dried.

Appearance: Yellow solid; Yield: 75%; melting point:  $72\text{ }^\circ\text{C}$ ; IR (KBr,  $\nu\text{ cm}^{-1}$ ) 3467, 3379 ( $-\text{NH}_2$ ), 3083, 3029 (Ar-H), 2842, 1434 ( $-\text{OCH}_3$ ), 1218 (C-O-C), 1250 (C-N);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.9 (6H,  $-\text{OCH}_3$ ), 4.0 (2H,  $-\text{NH}_2$ ), 7.31-7.44 (6H, Ar);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , ppm): 56, 119.1, 119.5, 119.8, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2.

**Synthesis of (2-methoxynaphthalen-1-yl)-phenylamine [3a]:** 2a (0.0264 mol, 5 g), bromobenzene (0.0264 mol, 2.7 mL), CuCl (0.02 g, 0.0002 mol) and  $\text{K}_2\text{CO}_3$  (1.0 g, 0.007 mol) were refluxed together with dichlorobenzene (15 mL) for 10 hours at  $60\text{ }^\circ\text{C}$ . After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hours. Ethyl acetate (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water ( $100\text{ mL} \times 2$ ) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with ethanol.

Appearance: Yellow solid; Yield: 74%; melting point:  $102\text{ }^\circ\text{C}$ ; IR (KBr,  $\nu\text{ cm}^{-1}$ ) 3427 ( $-\text{NH}$ ), 3083, 3029 (Ar-H), 2842, 1435 ( $-\text{OCH}_3$ ), 1218 (C-O-C), 1250 (C-N);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.9 (3H,  $-\text{OCH}_3$ ), 4.0 (1H,  $-\text{NH}$ ), 7.31-7.44 (11H, Ar);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , ppm): 56, 117.9, 118, 119.1, 119.5, 119.8, 120.2, 123.4, 125.1, 128, 129.4, 141.2, 143.2.

**Synthesis of *N*-(2-methoxynaphthalen-1-yl)-*N*-phenylbenzene-1,4-diamine [4a]:** 3a (0.014 mol, 3.5 g), bromoaniline (0.014 mol, 2.4 g), CuCl (0.02 g, 0.0002 mol) and  $\text{K}_2\text{CO}_3$  (1.0 g, 0.007 mol) were refluxed together with 20 mL dichlorobenzene for 15 hours at  $60\text{ }^\circ\text{C}$ . After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hours. Diethyl ether (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water ( $100\text{ mL} \times 2$ ) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with ethyl acetate.

Appearance: yellow solid; Yield: 71%; melting point:  $82\text{ }^\circ\text{C}$ ; IR (KBr,  $\nu\text{ cm}^{-1}$ ) 3468, 3374 ( $-\text{NH}_2$ ), 3062, 3029 (Ar-H),

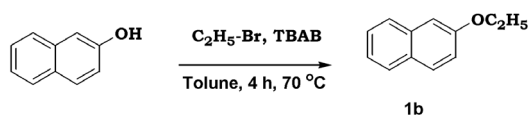
2842, 1434 (-OCH<sub>3</sub>), 1217 (C-O-C), 1267 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 3.9 (3H, -OCH<sub>3</sub>), 4.0 (2H, -NH<sub>2</sub>), 7.52-8.89 (15H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 56, 116, 119.1, 119.8, 120.2, 121.5, 122.3, 122.9, 123.4, 124.4, 128, 129.4, 129.9, 131.6, 141.1, 141.2, 141.6.

**Synthesis of *N,N,N'*-Tris-{4-[(2-methoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-benzene-1,3,5-triamine [5a]:** **4a** (0.007 mol, 2.4 g), tribromobenzene (0.002 mol, 0.77 g) CuCl (0.02 g, 0.0002 mol) and K<sub>2</sub>CO<sub>3</sub> (1.0 g, 0.007 mol.) were refluxed together with dichlorobenzene (25 mL) for 20 hours at 60 °C. After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hours. Diethyl ether (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water (100 mL × 2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with hexane.

Appearance: Yellow solid; Yield: 71%; melting point: 68 °C; IR (KBr, ν cm<sup>-1</sup>) 3469 (-NH), 3071, 3029 (Ar-H), 2838, 1435 (-OCH<sub>3</sub>), 1219 (C-O-C), 1250 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 3.9 (9H, -OCH<sub>3</sub>), 4.0 (1H, -NH), 7.35-8.22 (48H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 56, 96.8, 118.8, 119.1, 119.5, 120.2, 121.5, 122.4, 123.4, 124.4, 125.1, 128, 129.4, 131.1, 137.6, 141.2, 141.6, 145.

**Synthesis of *N,N,N'*-Tris-{4-[(2-methoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-*N,N,N'*-triphenylbenzene-1,3,5-triamine [6a]:** **5a** (0.0017 mol, 1.8 g), bromobenzene (0.0053 mol, 0.56 mL) CuCl (0.02 g, 0.0002 mol) and K<sub>2</sub>CO<sub>3</sub> (1.0 g, 0.007 mol) were heated together with dichlorobenzene (35 mL) for 22 hours at 60 °C. After removal of the solvent in vacuo, ammonia solution (50 mL) was added and the mixture was left to stand for 2 hours. Ethyl acetate (150 mL) and water (100 mL) were added. The organic phase was separated, washed with water (100 mL × 2) and brine solution (100 mL), dried over anhydrous sodium bisulphite, filtered and dried to remove the solvent. Purification with column chromatography using silica gel eluting with a mixture of ethyl acetate and hexane followed by recrystallization with hexane.

Appearance: yellow solid; Yield: 65%; melting point: 62 °C; IR (KBr, ν cm<sup>-1</sup>) 3083, 3029 (Ar-H), 2891, 1434 (-OCH<sub>3</sub>), 1218 (C-O-C), 1259 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 3.9 (9H, -OCH<sub>3</sub>), 7.19-7.52 (63H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 56, 108.9, 119.1, 119.5, 119.8, 120.2, 121.5, 122.4, 122.9, 123.4, 124.4, 125.1, 128, 129.4, 129.9, 136, 141.2, 141.6, 143.4.



**Scheme 1.** Synthetic procedure for 2-ethoxynaphthalene

**Synthesis of 2-ethoxynaphthalene [1b]:** Ethyl bromide (0.03 mol, 0.32 mL) in toluene (25 mL), 2-naphthol (0.03 mol, 4.32 g) in 40% NaOH (20 mL) and tetrabutylammoniumbromide (0.003 mol, 0.9 g) were refluxed at 70 °C for 4.0 hours. After the completion of the reaction which is monitored by TLC, the product is extracted using toluene-water system.<sup>8</sup> The obtained brown liquid was distilled under reduced pressure. The synthetic procedure for 2-ethoxynaphthalene is described in Scheme 1.

Appearance: Brown Liquid; Yield: 98%; boiling point: 250 °C; UV-vis. (ethanol, nm), 356, 361; IR (KBr, ν, cm<sup>-1</sup>) 3058, 3025.14 (Ar-H), 2879, 1379 (-OC<sub>2</sub>H<sub>5</sub>), 1217 (C-O-C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 6.97-7.64 (7H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 105.8, 118.8, 123.7, 126.4, 126.8, 127.7, 129.3, 129.5, 134.6, 157.7.

**Synthesis of 2-ethoxynaphthylamine [2b]:** Synthetic procedure: same as **2a**; reaction time: 1 hour; Appearance: yellow solid; Yield: 77%; Melting point: 78 °C; UV-vis. (ethanol, nm), 322, 364; IR (KBr, ν, cm<sup>-1</sup>): 3511, 3425 (-NH<sub>2</sub>), 3075, 2985 (Ar-H), 2879, 1379 (-OC<sub>2</sub>H<sub>5</sub>), 1218 (C-O-C), 1250 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 4.0 (2H, -NH<sub>2</sub>), 6.87-7.59 (7H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 96.8, 119.1, 119.5, 119.8, 120.2, 123.4, 124.4, 125.1, 128, 129.9, 141.2, 145.

**Synthesis of (2-ethoxynaphthalen-1-yl)-phenylamine [3b]:** Synthetic procedure: same as **3a**; reaction time: 10 hour; Appearance: Light yellow solid; Yield: 75%; Melting point: 88 °C; IR (KBr, ν, cm<sup>-1</sup>): 3448 (-NH), 3074, 2985 (Ar-H), 2879, 1377 (-OC<sub>2</sub>H<sub>5</sub>), 1218 (C-O-C), 1255 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 4.0 (1H, -NH), 7.2-7.6 (11H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 117.9, 118, 119.1, 119.5, 120.2, 123.4, 124.4, 125.1, 129.4, 129.9, 141.2, 143.2.

**Synthesis of *N*-(2-ethoxynaphthalen-1-yl)-*N*-phenylbenzene-1,4-diamine [4b]:** Synthetic procedure: same as **4a**; reaction time: 15 hours; Appearance: Light yellow solid; Yield: 73%; Melting point: 65 °C; IR (KBr, ν, cm<sup>-1</sup>): 3450, 3346 (-NH<sub>2</sub>), 3074, 2985 (Ar-H), 2891, 1377 (-OC<sub>2</sub>H<sub>5</sub>), 1217 (C-O-C), 1255 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, δ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 4.0 (2H, -NH<sub>2</sub>), 7.2-7.6 (15H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 116, 119.1, 119.5, 119.8, 120.2,

121.5, 122.3, 123.4, 124.4, 128, 129.9, 131, 141, 141.6.

**Synthesis of *N,N,N'*-Tris-{4-[(2-ethoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-benzene-1,3,5-triamine [5b]:** Synthetic procedure: same as **5a**; reaction time: 20 hours; Appearance: Light yellow solid; Yield: 71%; Melting point: 60 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3595 (-NH), 3074, 2985 (Ar-H), 2891, 1377 (-OC<sub>2</sub>H<sub>5</sub>), 1217 (C-O-C), 1255 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 4.0 (1H, -NH), 7.2-7.92 (48H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 96.8, 118.8, 119.1, 119.5, 120, 121.5, 122.4, 123.4, 124.4, 125.1, 128, 129.4, 131.1, 137.6, 141.2, 141.6, 145.

**Synthesis of *N,N,N'*-Tris-{4-[(2-ethoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-*N,N,N'*-triphenylbenzene-1,3,5-triamine [6b]:** Synthetic procedure: same as **6a**; reaction time: 22 hours; Appearance: yellow needles; Yield: 63%; Melting point: 55 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3074, 2985 (Ar-H), 2891, 1377 (-OC<sub>2</sub>H<sub>5</sub>), 1217 (C-O-C), 1255 (C-N); <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.34-4.30 (-OC<sub>2</sub>H<sub>5</sub>), 7.2-7.93 (63H, Ar); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 14.3, 65.1, 108.9, 119.1, 119.5, 119.8, 120.2, 121.5, 122.4, 122.9, 123.4, 124.4, 125.1, 128, 129.4, 129.9, 136, 141.2, 143.4.

## RESULTS AND DISCUSSION

The synthetic strategy employed for *N,N,N'*-Tris-{4-[(2-alkoxynaphthalen-1-yl)-*N*-phenylamino]-phenyl}-*N,N,N'*-triphenylbenzene-1,3,5-triamine [**6a** & **6b**] involved the preparation of intermediates and their coupling with 1-bromobenzene to form the final compounds. The synthetic route for **6a** & **6b** are described in Scheme 2. Steric hindrance also has an important effect on Ullmann type condensation. With an increase in steric hindrance the reaction becomes more difficult.<sup>9</sup> Because of this yield of the products is decreased. The products **6a** & **6b** is soluble in common organic solvents like ethanol, ethyl acetate, tetrahydrofuran, dimethylsulphoxide. The products **6a** & **6b** are possessing similar nature (powdery solids) and colour.

### Thermal properties

The glass forming properties and phase transition of compounds (**6a** & **6b**) are studied using DSC. The compounds are analyzed for heating and cooling thermograms (cyclic) in an inert atmosphere from -50 °C to 250 °C at a rate of 10 °C/min. The five compounds, **6a** & **6b** differ only in their substitutions at outer naphthalene rings. Due to these differences, we expect only a very few changes in thermal properties. Accordingly, the solubility and density of the com-

**Table 1.** melting temperature (T<sub>m</sub>), glass transition temperature (T<sub>g</sub>), crystallization temperature (T<sub>c</sub>) of **6a** & **6b**

Compound	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
<b>6a</b>	54	59	98
<b>6b</b>	55	60	95

pounds also may vary.

DSC scans for samples of **6a** and **6b** that was quenched from the melt. The T<sub>g</sub>, T<sub>c</sub> and T<sub>m</sub> values of synthesized compounds are listed in Table 1. T<sub>g</sub> value of **6a** is observed at 54 °C. The onset of crystallization is observed at about 59 °C and the onset of melting of **6a** is observed at about 98 °C. T<sub>g</sub> value of **6b** is observed at 55 °C. The crystallization and melting temperature of **6b** is observed at about 60 °C and 95 °C respectively. The melting endotherm is slightly larger than the crystallization exotherm indicating that the sample was not fully amorphous when quenched.

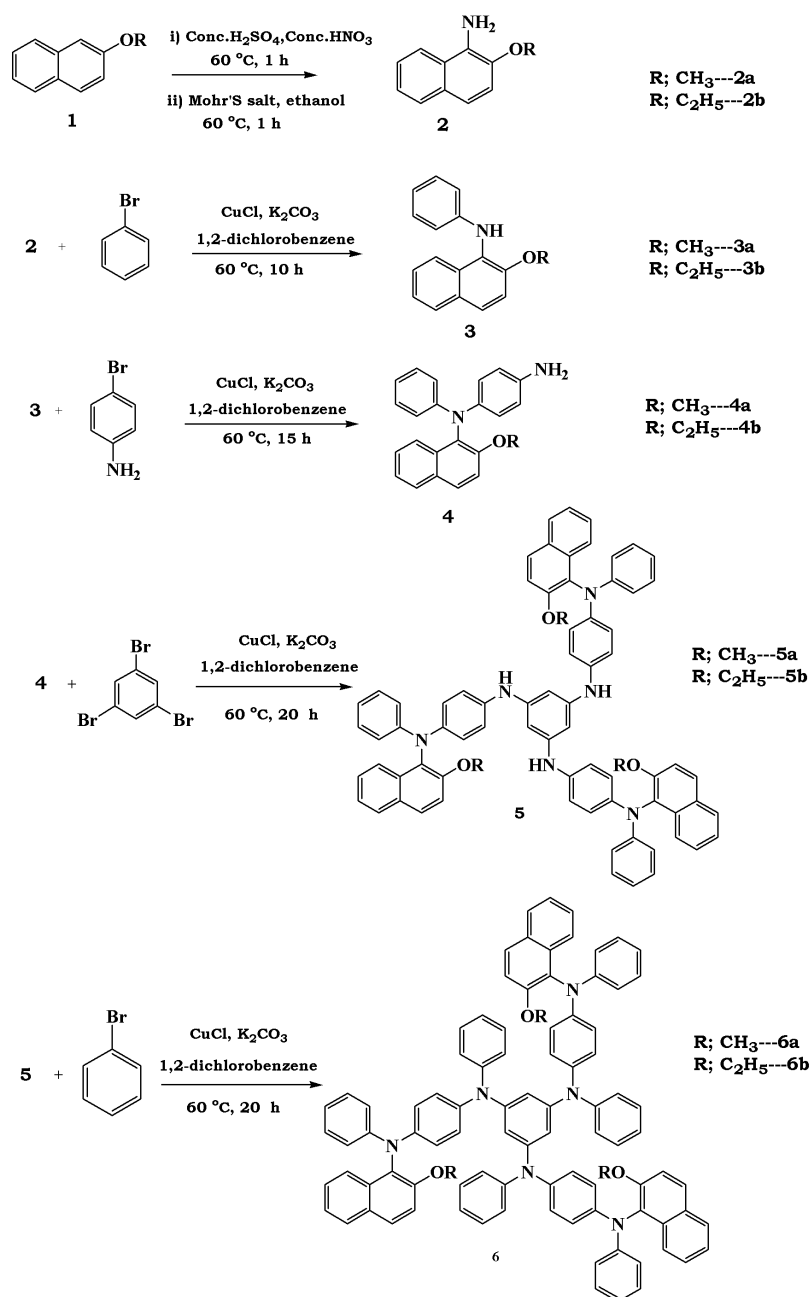
Generally for application of the compounds for optoelectronic device fabrication, the following thermal criteria are required: the low T<sub>g</sub> value, moderate melting point and stable upto 200 °C. We found that our starburst compounds fulfill all the required conditions. The lower T<sub>g</sub> 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 the HTM to intermix with the semiconductor (TiO<sub>2</sub>) in all its layers. The moderate melting point will also help the compounds to be in solid phase even after for a long time exposure of the cell.<sup>10</sup>

These DSC results suggest that the compounds (**6a** & **6b**) are amorphous material with good film properties. From the result we can say that these compounds are good candidates as hole transporting material in solar cell.

### Electrochemical properties

The electrochemical stability is one of the other main conditions to be fulfilled by the materials to find application in various electro-optical devices. The CV measurements were carried out at a glassy carbon electrode using millimolar solutions in acetonitrile (ACN) containing 0.1 M of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), in a three electrode cell and potentiostat assembly at room temperature. The potentials were measured against platinum as reference electrode and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system.<sup>11</sup>

For a compound to be used in optoelectronic devices, its HOMO and LUMO values should be in accordance with that of the semiconductor. Arylamines are reported to have the same range and they are widely used. The HOMO and



**Scheme 2.** Synthetic route for the preparations of **6a** & **6b**

**Table 2.** Cyclic voltametry results and estimated HOMO-LUMO values, band gap ( $E_g$ ), ionization potential ( $P_i$ ), electron affinity ( $E_A$ ) of **6a** & **6b**

Compound	$E_{\text{ox}}$ vs Fc (v)	HOMO (eV)	$E_{\text{red}}$ vs Fc (v)	LUMO (eV)	$E_g$ (eV)	$P_i$ (eV)	$E_A$ (eV)
<b>6a</b>	-1.2	-6.0	1.1	-3.7	2.3	6.0	3.7
<b>6b</b>	-1.3	-6.1	0.8	-4.0	2.1	6.1	4.0

LUMO values of the compounds are calculated from the anodic oxidation potential using literature reported HOMO of ferrocene (4.8 eV) with respect to zero vacuum level as des-

cribed by Daub *et al* in the literature.<sup>12</sup>

The results of electrochemical studies are listed in Table 2. **6a** has a HOMO value of -6.0 eV and LUMO of -3.7 eV. The

compound **6b** exhibit a HOMO of -6.1 eV and LUMO of -4.0 eV. The electron affinity (EA), ionization potential (PI) and band gap of the compounds are calculated from the data. The values are in good agreement reported hole transporting material. The high-lying HOMO energy level and reversible electrochemical oxidation of **6a** & **6b** suggest that these compounds have high potential for hole transporting material.

## CONCLUSIONS

We describe the synthesis of two novel *N,N,N*-tris-[4-(naphthalen-1-yl-phenylamino)phenyl]-*N,N,N*-triphenylbenzene-1,3,5-triamine alkoxynaphthalenes based symmetric triaminobenzenes. They form a star shaped structure. The compounds are characterized by FT-IR and NMR techniques. We have also studied the thermal and electrochemical properties of the compounds. The melting endotherm is slightly larger than the crystallization exotherm indicating that the sample was not fully amorphous when quenched. From the thermal datas we can say that our starburst compounds fulfill all the required thermal conditions that are needed for hole transporting compounds in solar cells. From the CV diagram the HOMO and LUMO values are compactable with that of the semiconductor, TiO<sub>2</sub>. Based on thermal and electrochemical studies we can say that the synthesized compounds can be used as an efficient HTM for the fabrication of dye sensitized solid state organic solar cells. Fabrication of dye sensitized solar cell using these synthesized compounds are in progress.

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