PYRIDINE SUBSTITUTED TRIPHENYAMINES

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

of

Master of Science

by

DEEPALI ARORA

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Pyridine Substituted Triphenylamines** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from july, 2014 to june, 2015 under the supervision of Dr. Rajneesh Misra, Associate Professor, Discipline of Chemistry, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date
(DEEPALI ARORA)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor
M.Sc. thesis
(DR.RAJNEESH.MISRA)

DEEPALI ARORA has successfully given his/her M.Sc. Oral Examination held on **25.06.2015.**

Signature(s) of Supervisor(s) of MSc thesis
Date:

Convener, DPGC
Date:

Signature of PSPC Member #1
Date:

Signature of PSPC Member #2
Date:

Signature of PSPC Member #3
Date:

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Last but not the least; I would like to thank my family: my father Mr. Banwari Lal and my mother Mrs. Rajni Arora for her immense selfless love towards me and their support in every way, and guiding me spiritually throughout my life, above all others, for always going above and beyond in terms of their love and support.

.

I would like to dedicate this thesis

to my father

Mr. Banwari Lal

Abstract

The molecules were synthesized by attaching 2-ethynyl-pyridine and 3-ethynyl-pyridine groups to a triphenylamine backbone. Relative absorption and emission spectra were studied. We examined the donor ability of triphenylamine when functionalized with 2-ethyny-pyridine and 3-ethynyl-pyridine, it shows bathochromic shift. Further when it is attached to the acceptor it may be potentially used for efficient solar cell.

TABLE OF CONTENTS

LIST OF FIGURES

ACRONYMS

DSSC	Dye Sensitizer Solar Cell
TPA	Triphenylamine
CT	Charge Transfer
DCM	Dichloromethane
EtOAc	Ethyl Acetate
Hz	Hertz
HRMS	High Resolution Mass Spectra
NMR	Nuclear Magnetic Resonance
THF	Tetrahydrofuran
TLC	Thin-layer Chromatography
TMS	Tetramethylsilane
DMF	Dimethylformamide
CuI	Copper Iodide
Et_3N	Triethyl Amine
Tol	Toluene
OLED	Organic Light Emitting Diode
D-A	Donor-Acceptor

Chapter 1

Introduction

Triphenylamine

Triphenylamine and its derivative plays an important role in many fields such as pharmaceutical industries, OLED and Biosensors. It forms a stable aminium radical cation. Its donor strength makes it an eminent building block in systems such as DSSC. These compounds are used in sensing due to its high drift mobility and also possess charge transport characteristics in electro-photo-graphics and photoconductors.

Triphenylamine are generally the derivative of ammonia, in which all three hydrogens are replaced by phenyl group. Triphenylamine are generally found in solid state at room temperature with very low solubility in water. These aromatic amines are sensitive to oxidation. In most of the cases the organic sensitizers are made of a donor (D), a bridge (B, which are typically a π spacer), and an acceptor (A) moieties, the basic structure is (**D-π-A)**. In order to improve the efficiency and also to increase photo-induced intramolecular charge transfer (ICT) its properties can be tuned by applying the adequate structural modifications. Recently, it has been found that cyano-acetic acid and triphenylamine (TPA) are units of choice as electron acceptor and donor respectively [1]. According to the previous studies which show that the cyano group count has one of the strongest electron-withdrawing group as well as stronger electron-accepting effect when it is introduced with the conjugated system [2].

TPA derivatives show generally large CT-character electronic excitations. Due to the three phenyl rings present in TPA which causes large steric hindrance, it thus prevents unfavorable dye aggregation at the semiconductor surface. This can enhance the hole-transporting ability and reduce the crystallization propensity of the materials. Based on these types

of considerations, it is speculated that if AIE character can be explored with compound which possess donor–acceptor (D–A) behavior.

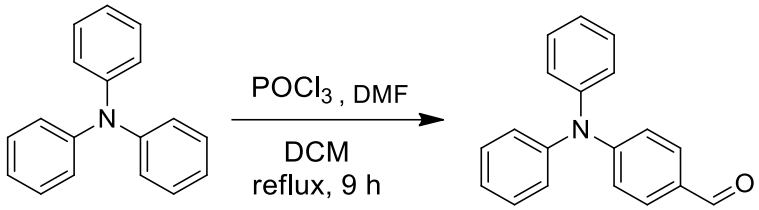
The reason behind choosing triphenylamine as a donor unit was that it has an electron rich nitrogen atom and it is commercially available in pure form.

Chapter 2

Literature

2.1. 4-(diphenylamino)benzaldehyde

Initially the mixture of $POCl_3$ and DMF stirred at 0 ºC for 2 h. Then the mixture of dry DCM and triphenylamine was added. After that the reaction mixture was refluxed for 9 h and after completion of the reaction the dry DCM was removed by rotary evaporator. The remaining crude product was poured into water and DCM and the yellow solid was collected by suction filtration. Product was obtained by recrystallization in ethanol (95% yield) [2].

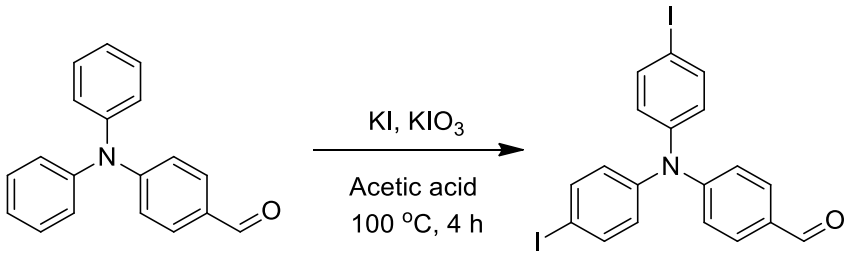


Scheme 1: Synthesis route of 4-Diphenylamino-benzaldehyde.

2.2. 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde

In 2007, Zhijun Ning and his coworkers prepared this intermediate. They have funtionalised diphenylamine or carbazole as an electron donor while they used dicyanovinyl or aldehyde as the electron acceptor. They have emphasized on the quench phenomena caused by aggregation because of their charge transfer applications and they have described their applications in the field of OLEDs [4].

They have synthesized the compound shown above as an intermediate after they incorporated triphenylamine and carbazole group by using Ullmann reaction. To prepare this compound they stirred the mixture of 4-formyl triphenylamine and potassium iodide with acetic acid and water at 80 °C and heated it for 4 h.

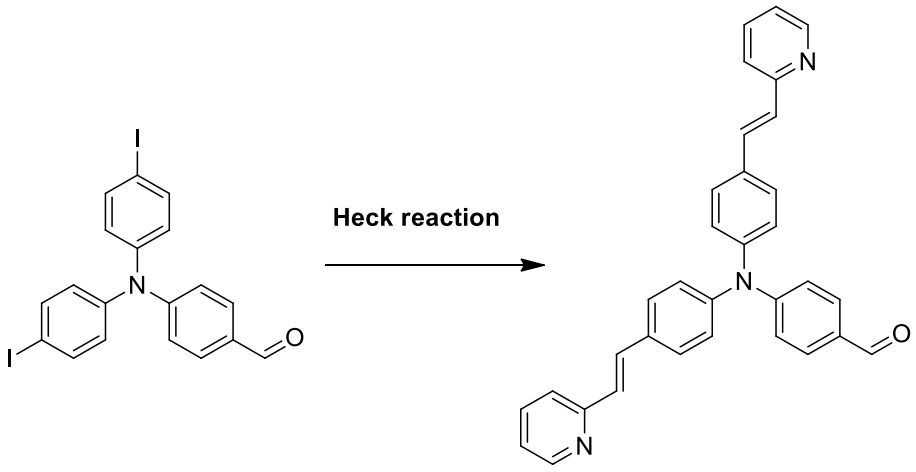


Scheme 2: Synthesis route of 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde.

After the reaction, most of the acetic acid was removed by rotary evaporation. The remaining crude product was dissolved in ethyl acetate solution and washed several times with the mixture of water and sodium bicarbonate solution. After drying the organic layer over $MgSO_4$, yellow solid was obtained [4].

2.3. 4-{Bis-[4-(2-pyridin-2-yl-vinyl)-phenyl]-amino}-benzaldehyde.

In 2014, Y. Qian and M. Luo prepared Pyridine triphenylamine conjugated chromophores by using palladium-catalyzed Heck reaction. They explain that the chromophores exhibit three-photon absorption and by increasing the length of conjugation charge transfer increase therefore increase the push pull units in D-A [3].

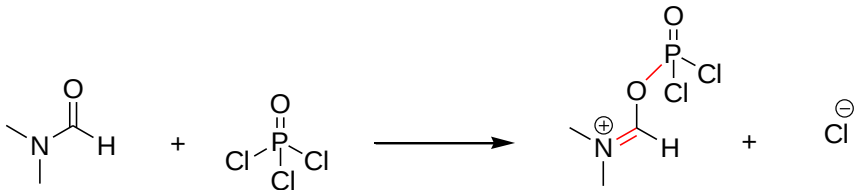


Scheme 3: Heck reaction of 4-{Bis-[4-(2-pyridin-2-yl-vinyl)-phenyl]-amino}-benzaldehyde.

They synthesized the desired compound by Heck coupling. They functionalized Iodo-triphenylamine with 2-vinylpyridine under a N_2 atmosphere. And they obtain crude product that was then recrystallized with methanol. To obtain high degree of purity they performed column chromatography. The final isolated yield was 57% [3].

2.2. Proposed mechanism of Vilsmeier reaction

Step 1:



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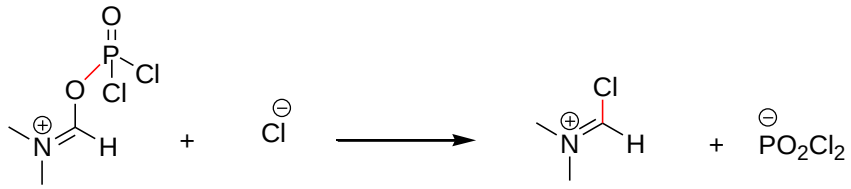

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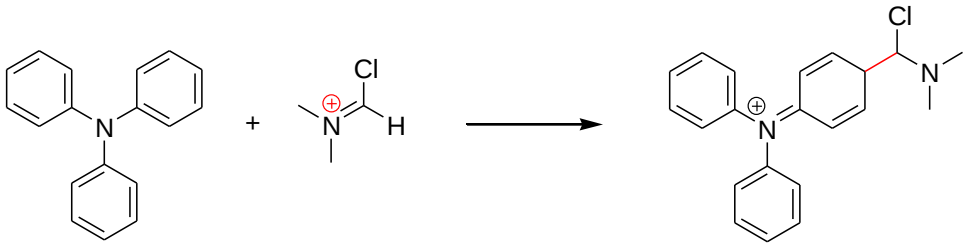

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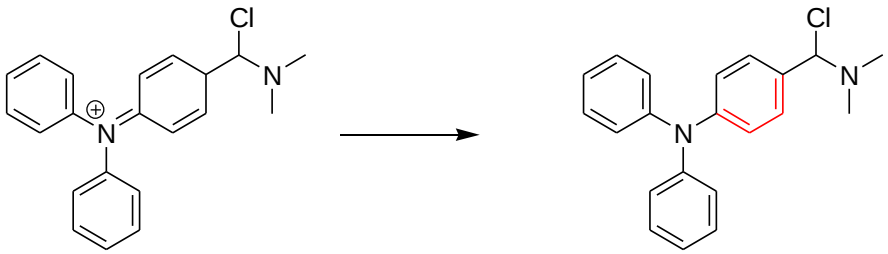

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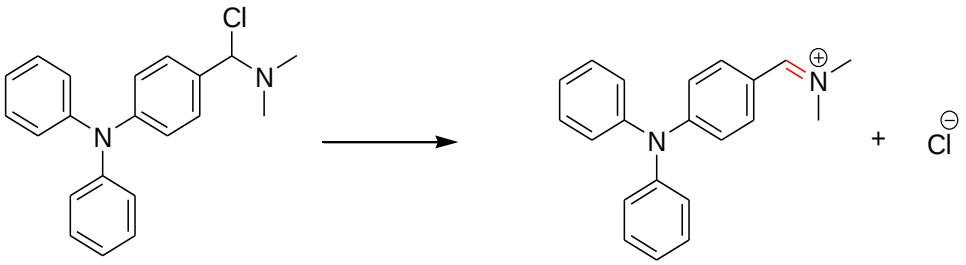

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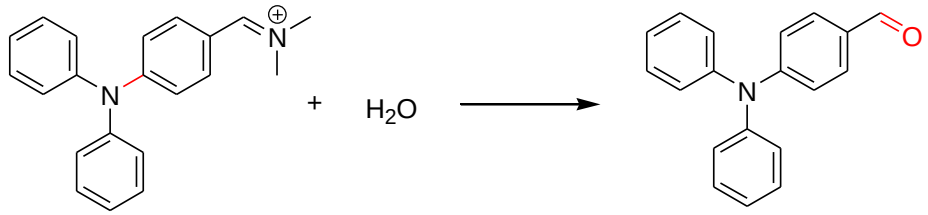
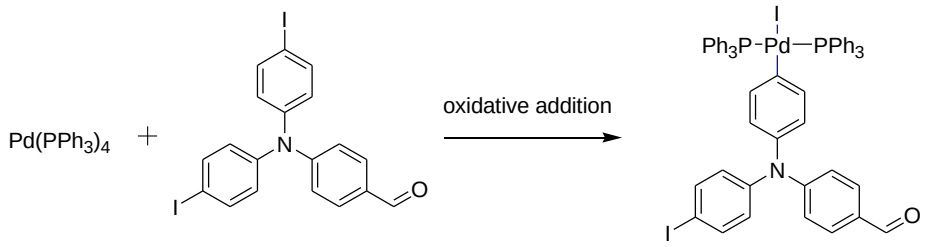


The Vilsmeier-Heck reaction is used to convert an electron rich aromatic ring to an aryl aldehyde using DMF, an acid chloride, and aqueous work-up. The first step of mechanism begins with the reaction of DMF with the acid chloride leads to form an iminium salt also known as the "Vilsmeier reagent". In the next step the electron rich aromatic ring then attacks the iminium ion with loss of aromaticity. A deprotonation from aromatic ring step restores aromaticity, which is followed by the release of a chloride ion to form another iminium intermediate. Final product obtain by aqueous work-up [5].

2.3. Mechanism of the Sonogashira Coupling

Step 1:



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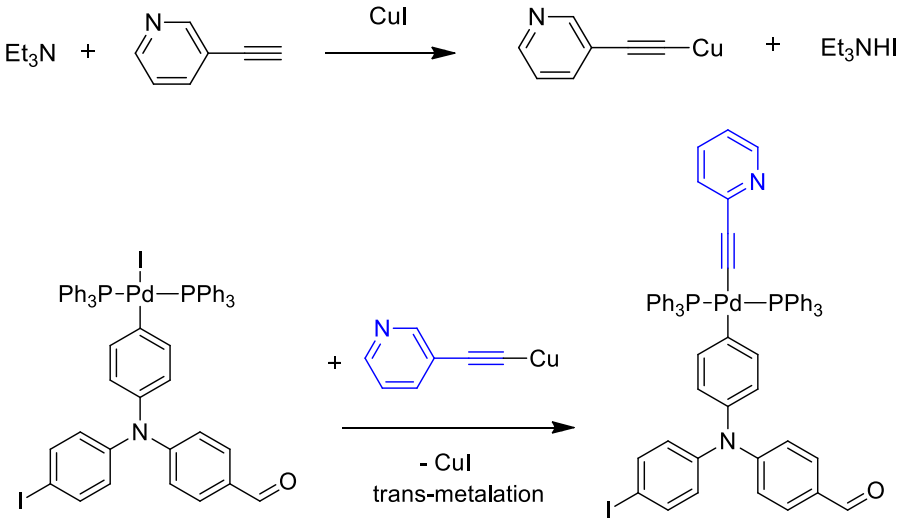

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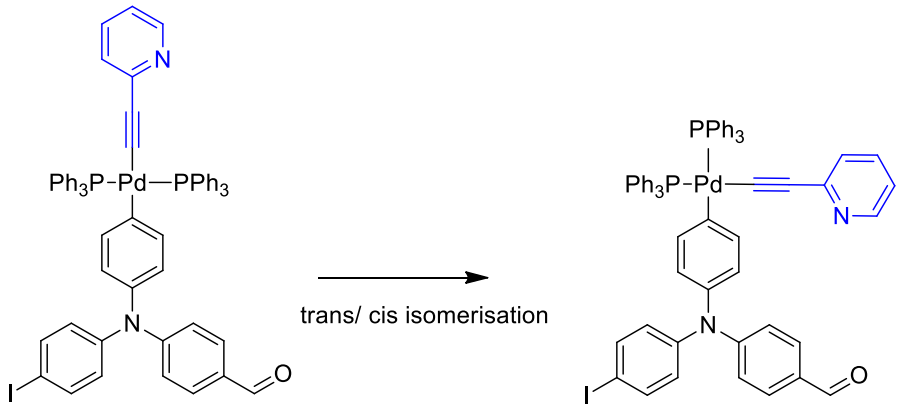

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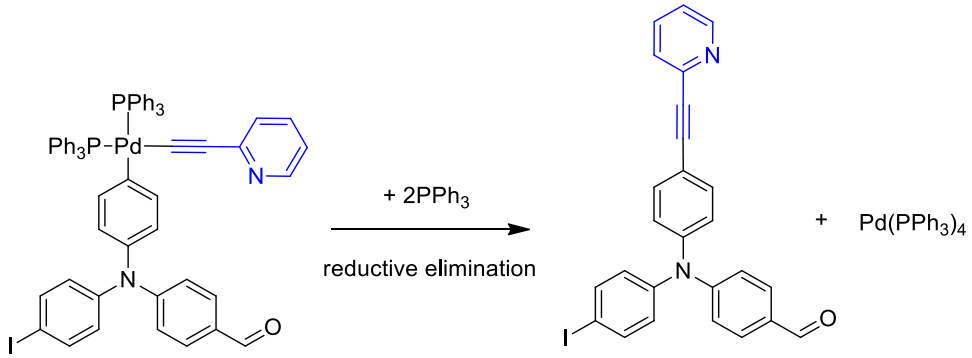


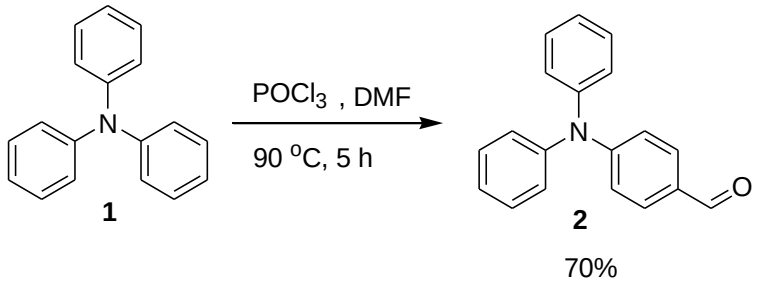
Sonogashira reaction is the cross-coupling between terminal alkyne and organohalide to give the coupled product by using a palladium catalyst, a copper catalyst, and base. In the first step, mechanism begins with oxidative addition of the organohalide to the Pd (0) then the copper replace iodide and from bond with the terminal alkyne. Then the alkynyl anion of copper replaces the halide on the palladium complex and reform the copper halide. Final coupled product obtain by Reductive elimination, regenerates the palladium catalyst, and the catalytic cycle can begin again [6].

Chapter 3

Results and Discussion

All the raw materials were used directly without any further purification. All the solvents as analytical reagent were purchased and were used without any purification. Throughout all experiments, water was used which is purified by the Millipore system. ^{1}H NMR spectra were performed by using a Bruker Avance 3 (400MHz) spectrometer (relative to tetramethylsilane). Mass spectra were obtained with Bruker's micrOTOF-Q II Mass spectrometer, and UV-vis spectra on a Cary 100 bio UV spectrophotometer. FL emission spectra were recorded on a Horiba Jobin Yvon floromax fluorescence spectrophotometer. DCM was used as a solvent.

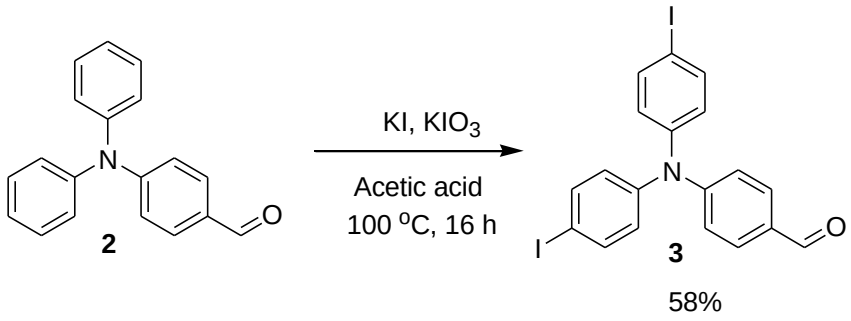
General procedure of 4-Diphenylamino-benzaldehyde (2): Initially the mixture of $POCl_3$ and DMF stirred at 0 ºC for 1 h. Then the mixture of dry DCM and triphenylamine was added. After that the reaction mixture was refluxed for 5 h and after the completion of reaction the dry DCM was removed by rotary evaporator. The remaining crude product was poured into water and DCM and the yellow solid was collected by suction filtration. Product was obtained by recrystallization in ethanol (70% yield).



Scheme 4: Synthetic route of 4-Diphenylamino-benzaldehyde (**2**).

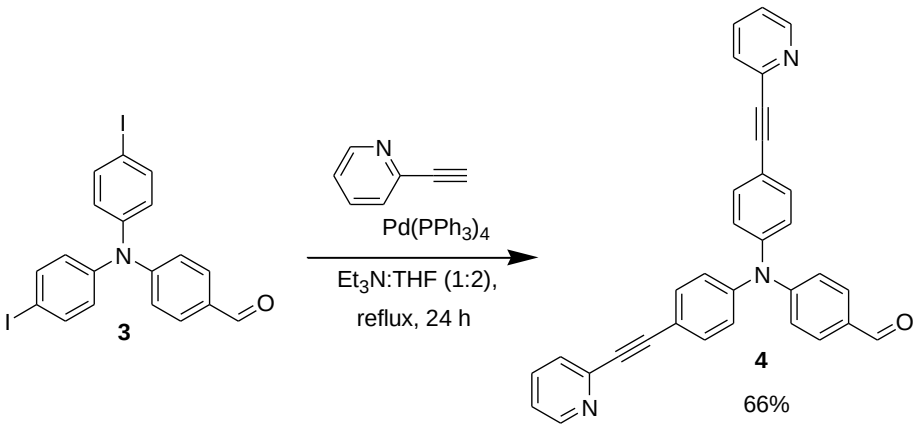
General procedure for of 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (3): We synthesized the compound shown in scheme 5. To prepare this compound, we stirred the of mixture of 4-formyl triphenylamine,

potassium iodide with acetic acid and water at 80 °C and heated it for 16 h. After the reaction, most of the acetic acid was removed by rotary evaporation. The remaining crude product was dissolved in ethyl acetate solution and washed several times with mixture of water and sodium bicarbonate solution. After drying the organic layer over Na_2SO_4, yellow solid was obtained (yield 58%).



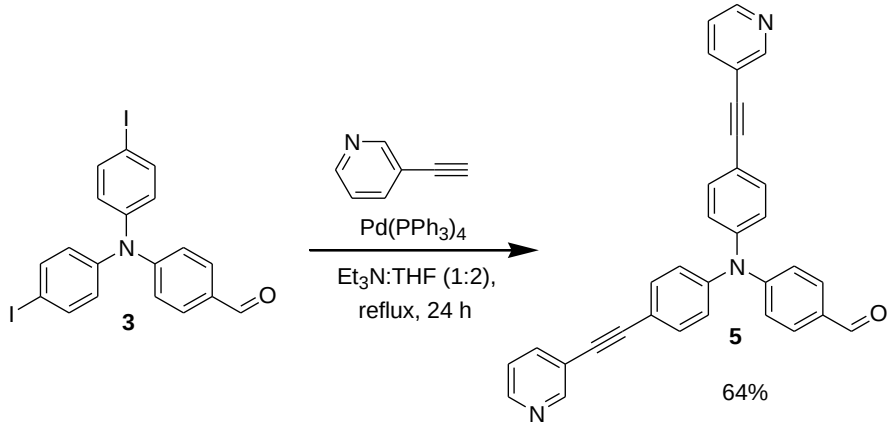
Scheme 5: Synthetic route of 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (**3**).

General procedure for 4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde: Under argon atmosphere the mixture of 2-ethynyl-pyridine (0.123 g, 1.19 mmol) and 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (0.250 g, 0.47 mmol) was dissolved in dry THF (30ml), added triethylamine (15 ml) and $Pd(PPh_3)_4$ (0.01 g, 0.008 mmol), stirred for 24 h in oven dried round bottom flask at 80 °C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by silica gel column chromatography, using Hexane: DCM (20:80), and obtained pure compound as a yellow solid (0.150 g, 66%).



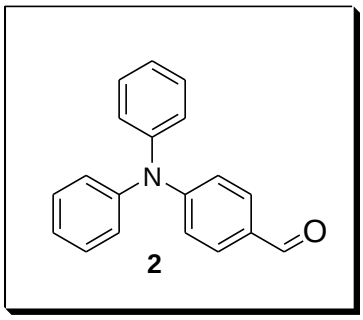
Scheme 6: Synthetic route of 4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde (**4**).

General procedure for 4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde: Under argon atmosphere the mixture of 3-ethynyl-pyridine (0.123 g, 1.19 mmol), 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (0.250 g, 0.47 mmol) was dissolved in dry THF (30ml), added triethylamine (15 ml), $Pd(PPh_3)_4$ (0.01 g, 0.008 mmol), stirred for 24 h in oven dried round bottom flask at 80 ^oC, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by silica gel column chromatography, using Hexane: DCM (20:80), and afforded pure compound as a yellow solid (0.148 g, 64%).



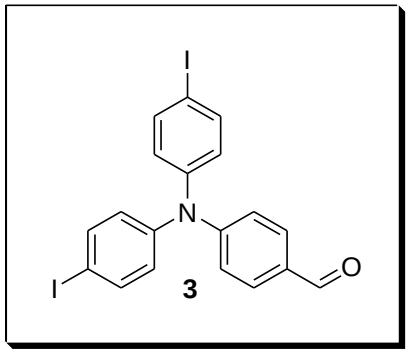
Scheme 7: Synthetic route of 4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde (**5**).

Characterization data



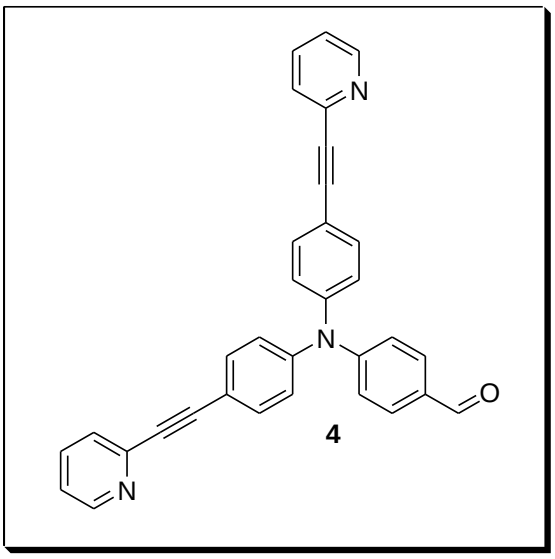
4-(diphenylamino)benzaldehyde (2)

Element analysis (%): calculated for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12; Found: C, 83.45; H, 5.49; N, 5.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (d, 2H), 7.30–7.36 (t, 4H), 7.15–7.18 (m, 6H), 7.67 (d, 2H), 9.79 (s, 1H).



4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (3)

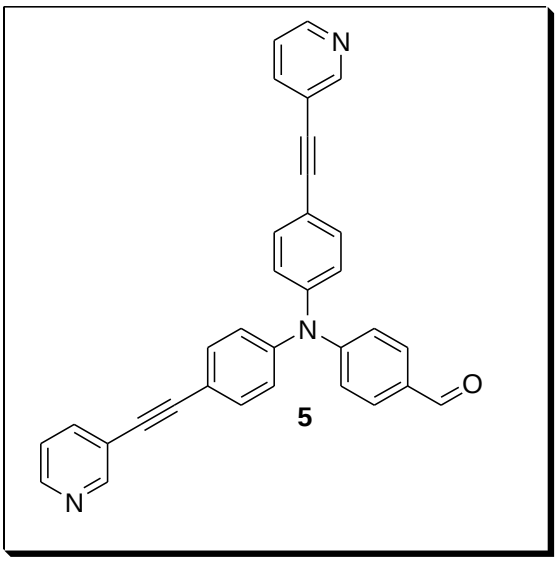
^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.85 (1H, s, CHO), 7.71 (2H, d, Ar), 7.63 (4H, d, Ar), 7.05 (2H, d, Ar), 6.89 (4H, d, Ar).



4

4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde (4)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 8.63 (d, 1H), 7.78 (d, 2H), 7.69 (m, 3H), 7.57 (m, 7H), 7.26 (m, 2H), 7.15 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.52 , 152.07, 149.88, 146.53, 143.17, 136.44, 133.57, 131.39, 130.92, 127.19, 125.16, 122.15, 118.30, 89.19, 88.86 ppm; HRMS (ESI): calculated for $C_{33}H_{21}N_3O$ 476.1757 [M^+]; found 476.1758.



5

4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde (5)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1H), 8.66 (s, 1H), 8.44 (d, 1H), 7.70 (m, 7H), 7.39 (m, 7H), 7.10 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.38, 151.61, 144.75, 131.97, 130.27, 128.90, 127.43, 125.52, 123.76, 119.78, ppm; HRMS (ESI): calculated for $C_{33}H_{21}N_3O$ 476.1757 [M^+]; found 476.1759.

Synthesis of the targeted molecules is shown in scheme 6 and 7. As illustrated, the third steps for compound **4**, **5** formation involve a simple Sonogashira Coupling followed by iodination to give 4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde (yield 66%) and 4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde (yield 63%).

The first step in the synthesis procedure was the formation of 4-Diphenylamino-benzaldehyde (yield 70%) which was prepared by Vilsmeier Reaction. The second step was the iodination the desire product was 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde (yield 58%).

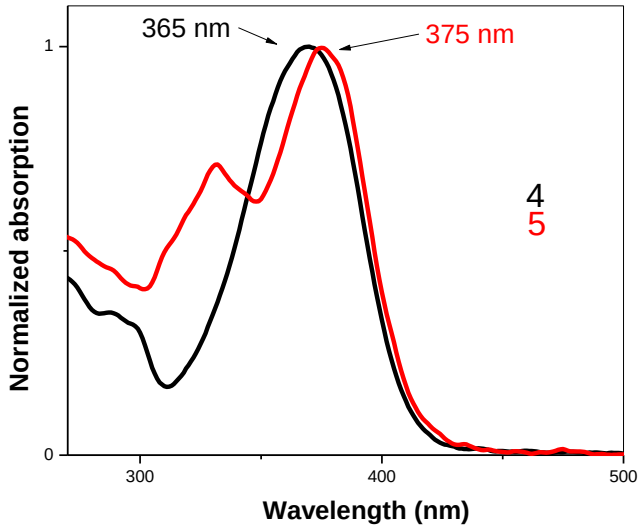


Figure 1: Normalized electronic absorption spectra of the compounds **4**, **5** in CH_2Cl_2 (1.0×10^{-4} M).

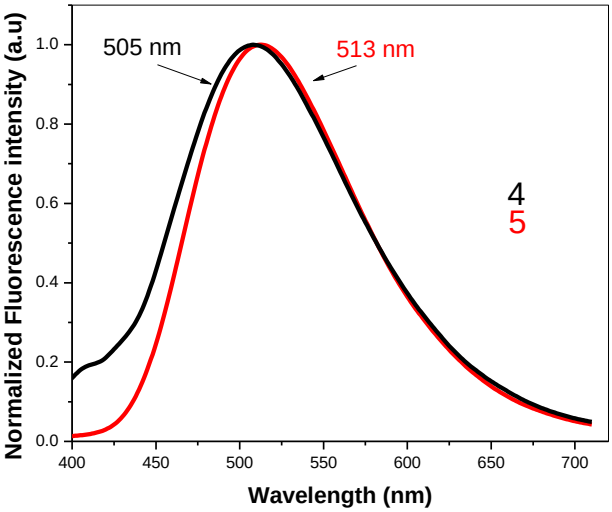


Figure 2: Fluorescence spectra of the compounds **4**, **5** in CH_2Cl_2.

By analyzing UV and Florescence data, we conclude that in both absorption and emission spectra the position of the main peak in shows a bathochromic shift, therefore little more charge density involving in conjugation in compound 4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde (**5**) than the compound 4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde (**4**).

Chapter 5

Conclusion and scope for work in future

Finally, we have synthesised target molecules by novel Pd (II) catalysed efficient Sonogashira Coupling. 4-[Bis-(4-iodo-phenyl)-amino]-benzaldehyde lead to the synthesis of 4-[Bis-(4-pyridin-2-ylethynyl-phenyl)-amino]-benzaldehyde (**4**) and 4-[Bis-(4-pyridin-3-ylethynyl-phenyl)-amino]-benzaldehyde (**5**) and are well characterised by ^{1}H NMR, ^{13}C NMR and HRMS. The absorption and emission spectra shows bathochromic shift.

There are many groups that we can substitute on triphenylamine core and study how they affect its donor ability.

APPENDIX

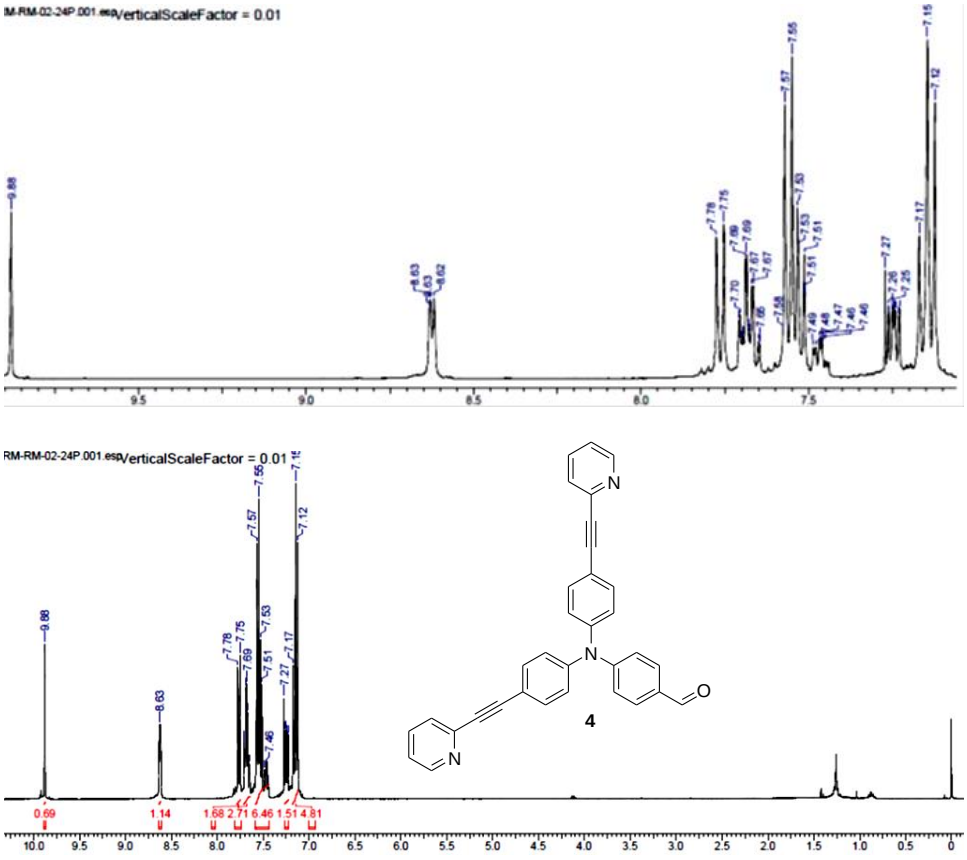


Figure 3: ^{1}H NMR spectra of compound **4**.

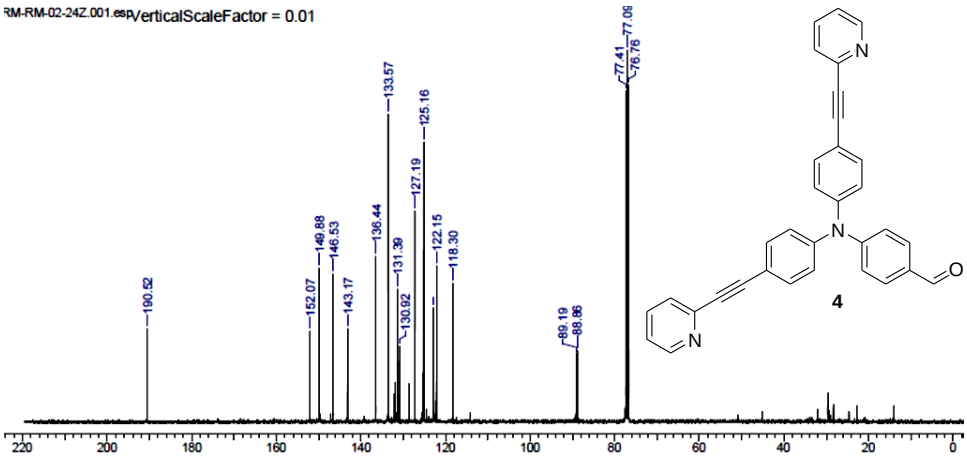


Figure 4: ^{13}C NMR spectra of compound **4**.

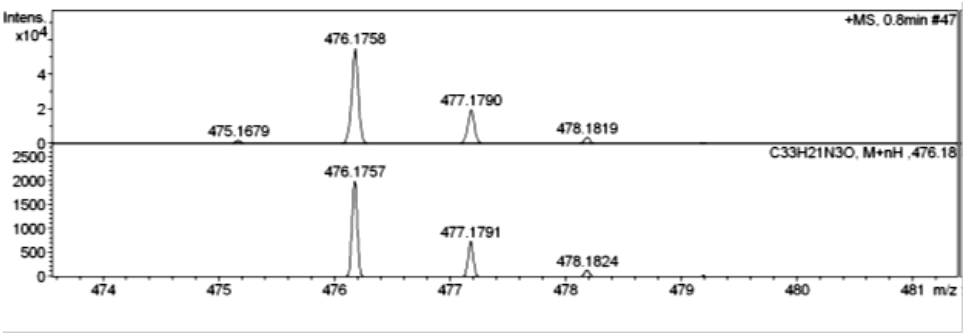


Figure 5: 400 MHz HRMS Spectra of compound **4 i**n $CDCl_3$.

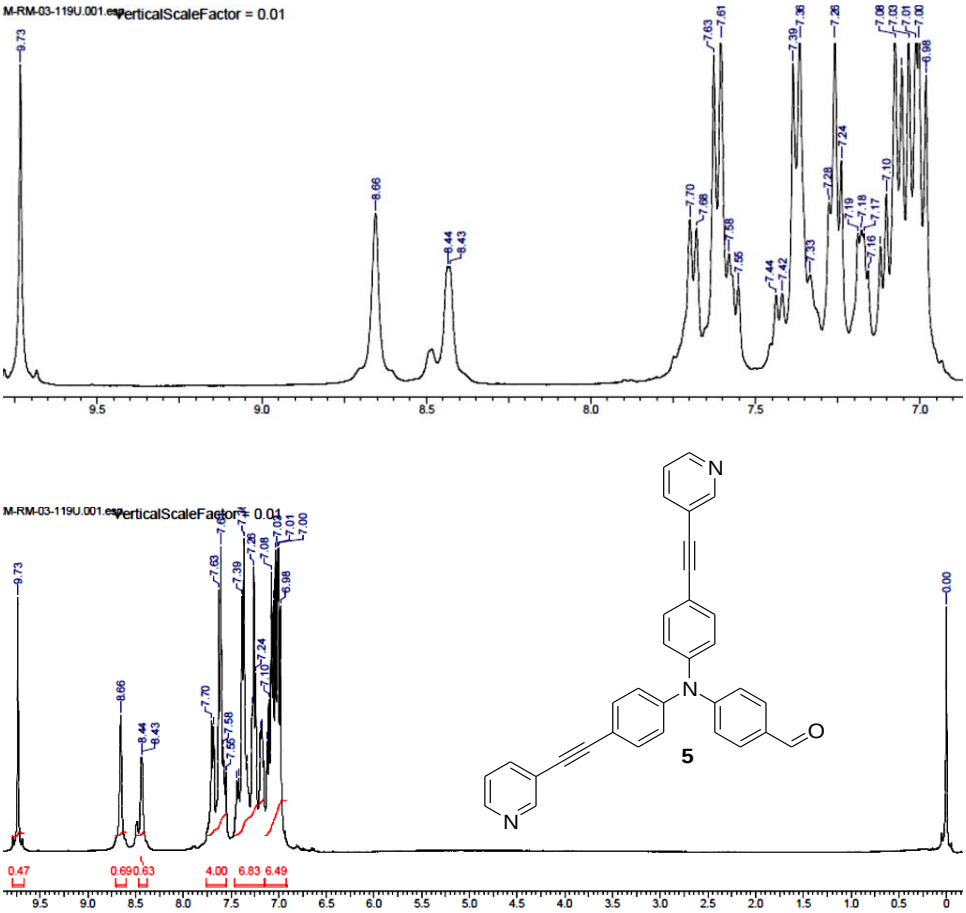


Figure 6: ^{1}H NMR spectra of compound **5**.

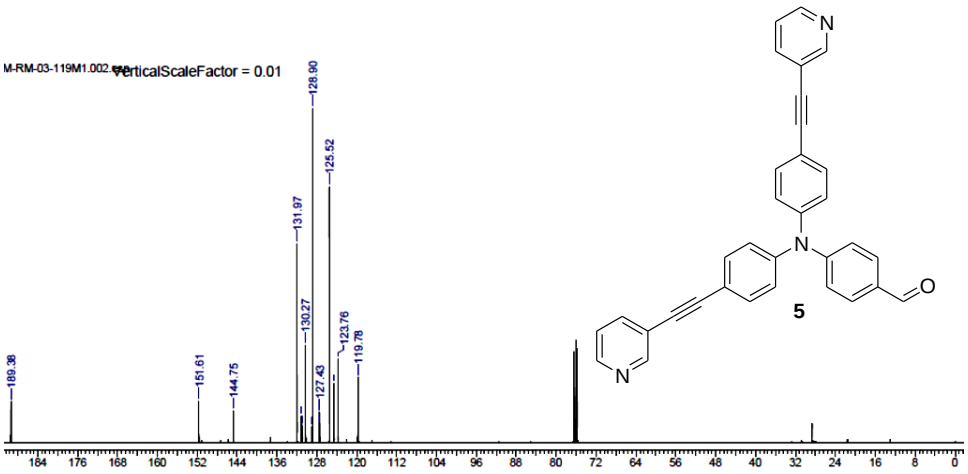


Figure 7: ^{13}C NMR spectra of compound **4**.

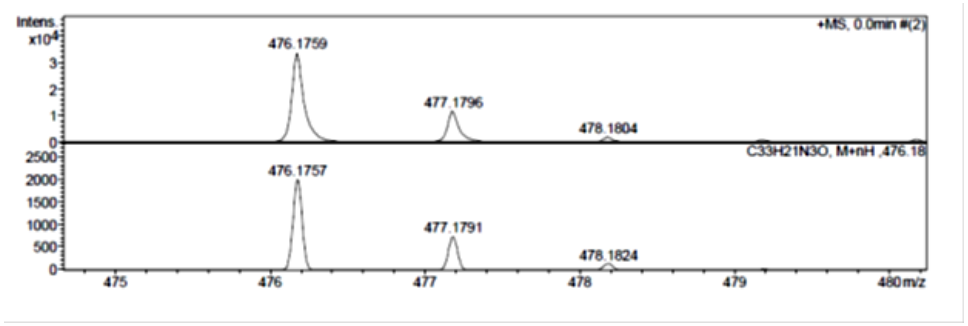


Figure 8: 400 MHz HRMS Spectra of compound **5 i**n $CDCl_3$.

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