Triphenylamine Derivatives: Synthesis, Electrochemical, Photophysical Properties and DFT Studies

M.Sc. Thesis

By AMIT LOCHAB



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2017

Triphenylamine Derivatives: Synthesis, Electrochemical, Photophysical Properties and DFT Studies

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by AMIT LOCHAB



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2017



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis **Triphenylamine Derivatives: Synthesis, Electrochemical, Photophysical Properties and DFT Studies** in the partial fulfillment 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 2016 to June 2017 under the supervision of Dr. Rajneesh Misra, Associate Professor, 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.

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

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Dedicated to my FAMILY....

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AMIT LOCHAB Discipline of chemistry IIT Indore

Abstract

In recent years a lot of work has been done in the field of dye-sensitized solar cells (DSSC). Dye-sensitized solar cell is a cost efficient way for light-energy conversion. Triphenylamine based organic dyes (with D-p-A structure) as sensitizer for dye-sensitized solar cells (DSSCs) attain considerable attention because of their structural versatility, low cost and high molar absorption coefficient. Two triphenylamine derivatives are synthesized by Sonogashira cross-coupling. Their electronics, photonics and computational studies reveal strong donor-acceptor interaction. The starting material 4,4'-((4-ethynylphenyl)azanediyl)dibenzaldehyde was synthesized by Sonogashira coupling reaction. The absorption spectra of the triphenylamine-derivatives were recorded in DMSO. The UV-visible absorption spectra were in the range of 380-480 nm. The electrochemical studies shows one oxidation peak corresponding to the oxidation of triphenylamine unit. The thermal stability of the Triphenylamine derivatives are reported, in which the melononitrile adduct show high thermal stability. The DFT calculation reveals the distribution of HOMOs over triphenylamine moieties with LUMOs over aldehyde and cyano moieties.

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NOMENCLATURE

λ	Wavelength
Å	Angstrom
δ	Chemical shift (NMR)
°C	Degree Centigrade
cm	Centiimeter
%	Percentage
g	gram
mol	Mole
mmol	Milimole
М	Molar
L	Litre
mL	Mililitre
π	pi
Κ	Kelvin
nm	Nanometer
0	Degree
rt	Room temperature
eV	Electron volt
V	Volt

ACRONYMS

D-A	Donor-Acceptor
OLED	Organic Light Emitting Diode
Ν	Nitrogen
0	Oxygen
С	Carbon
LUMO	Lower Unoccupied Molecular orbital
НОМО	Higher Occupied Molecular Orbital
NLO	Non-linear Optics
NMR	Nuclear magnetic resonance
Cu	Copper
DCM / (CH ₂ Cl ₂)	dichloromethane
CDCl ₃	Chloroform-d
CuI	Copper Iodide
$Pd(PPh_3)_2Cl_2$	Dichlorobis(triphenylphosphine) palladium(II)
TEA	Triethylamine
THF	Tetrahydrofuran
CHCl ₃	Chloroform
TMS	Tetramethylsilane
DFT	Density Function Theory
MeOH	Methanol
DMSO	dimethylsulphoxide
UV-vis	Ultraviolet-visible spectroscopy
KI	Potassium Iodide

CH ₃ CN	Acetonitrile
OFETs	Organic field effect transistors
AIE	Aggregation induced emission

CHAPTER ONE

INTRODUCTION

1.1 General Introduction:

Triphenylamines are organic non-planar nitrogen compounds that may be considered derivatives of ammonia with all the three hydrogen atoms replaced by aryl groups, these amines are referred as tertiary amines. Triphenylamine is a white solid at room temperature and slightly soluble in water. These aromatic amines are weakly basic in water. Triphenylamine have been synthesized conveniently by the Ullmann condensation of aryl halide with secondary amines, the nucleophilic substitution of aryl halide is promoted by copper compounds with addition of strong base like potassium hydroxide, potassium carbonate etc. . The general reactions for the synthesis are shown in Scheme 1. [1-3]

Triphenylamine is having excellent electron donor properties and widely used in organic photovoltaic functional materials. TPA prevents aggregation due to its non-planar structure, it also shows very good hole-transport properties. [4] Amino groups direct electrophilic aromatic substitution to the ortho and para positions of the phenyl ring but the geometry of triphenylamine is such that ortho substitution would be inhibited sterically and the most reactions are obtained that lead to the introduction of not more than three substituents, suggest that reaction occurs at three positions mainly at para. [5-7]

The photonic and electronic properties of the donor-acceptor systems can be tuned by changing or substituting the functional groups. The electron donating triphenylamine is an important building block in a variety of π conjugated D-A molecular systems.



Recently organic compounds having π -conjugation have received a great attention as they are showing better optical, photophysical and charge-transporting properties, which can be used as potential materials for the application in the devices of organic electronics, such as organic light-emitting diodes, organic thin-film transistors, organic and dye sensitized solar cells.[8-15] The HOMO-LUMO gap of the triphenyl derivatives can be tuned either by altering the strength of D-A units or the π -bridge. However organic luminophores with highly π conjugated systems on phenylacetylene-based moieties have been developed remarkably quickly.[16] The elongated electronic pathways along π -extended conjugations in these molecules often present a bathochromic shift in the absorption and fluorescence spectra.[17] The linker connecting donor and acceptor is known to play a critical role in determining the electron transfer rate, because the electron transfer rate is affected by the properties of the linker such as the donor acceptor distance and the energy matching between the donor and linker components. [18]

1.2 Applications of Triphenylamine:

Metal free dyes can be synthesized simply and economically with this, they show high molar extinction coefficients due to intermolecular π - π *

transitions. In general organic dyes (use as sensitizer) contain D– π –A structure, where D is donor, π is linker/spacer and A is acceptor. When dye absorbs light, charge transfer occurs within the molecular due to this push-pull structure within donor-acceptor moieties, as charge transfer is essential for light harvesting. Moreover, it is easy to tune the absorption spectra as well as the HOMO and LUMO levels of the dyes by varying the donor and acceptor moieties. Among the metal-free organic dyes, the tripheylamine dyes are showing a very good efficiency rate. [19]

Triphenylamine dyes offer countless possibilities for improving a wide range of properties such as molecular structure and function, efficiency of light-harvesting ability in different parts of the light region, controlling molecular energy levels, charge generation and separation, and molecule interactions. There has been continuously growing research in triphenylamine derivatives due to their low oxidation potential (acting as an electron donor) and hole transport ability.

The scheme and synthesis of small molecule based donor-acceptor systems are monotonically increasing due to their applications in the field of Organic photovoltaics (OPVs), Organic field effect transistors (OFETs), Aggregation induced emission (AIE), Mechanochromism and Nonlinear optics (NLO). [20]

The linker connecting donor and acceptor is known to play a crucial role in determining the rate of electron transfer, because the electron transfer rate is affected by the properties of the linker such as the distance between donor and acceptor and the energy matching between the donor and linker components. [21] The extended electronic pathways along π -extended conjugations in these molecules often present a bathochromic shift in the absorption and fluorescence spectra. DSSC performance of these dyes decreases as the π -spacer length is increased which is probably due to elongated conjugation pathways which decreases the donor-

acceptor interaction. [22] Therefore we were interested to incorporate the two triphenylamine (TPA) donor with an acetylene spacer group in between having four aldehyde groups as acceptors at para position of the four unsubstituted phenyl rings.

1.3 Experimental Techniques in Electrochemical Studies

Voltammetry refers to the measurement of current that result from the application of potential. Unlike potentiometric measurements, which employ only two electrodes, voltammetric measurements utilise a three electrode electrochemical cell.

Cyclic Voltammetry (CV)

Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938 and described theoretically by Randies [23]. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes.

1.3.1 Basic principles of Cyclic Voltammetry

A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, E° , of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration. Charge flows between the working electrode and the auxiliary electrode.

1.3.2 Theory

The current measured during this process is often normalised to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material *[24-25]*.

To carry out an oxidation process, a positive potential ramp is applied and the electroactive species loses an electron at the electrode giving rise to an anodic peak current (i_{pa}) which usually gives an oxidation peak at a given potential (E_{pa}). Cathodic currents (i_{pc}) are observed when the potential is applied in the negative direction leading to a reduction process, typically giving a reduction peak at a given potential (E_{pc}). The CV is usually initiated at a potential where species are not electroactive.

At the anodic peak the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidised to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence results in an asymmetric peak shape.

1.3.3 Solvent

The solvent used for the electrochemical process must be a liquid at room temperature, it must have sufficient solubility for ionic substances to form conducting electrolyte, it must be able to dissolve the electroactive species of interest, it must have a wide enough potential region for the study of the redox process of interest, that is, solvent itself must not undergo oxidation or reduction in this potential region.

1.3.4 Supporting Electrolytes

These electrolytes impart conductivity to the solvent and hence enable continuous current flow in solution. The salient features of supporting electrolyte are, they must remain electroactive in the potential region of interest. They should not get adsorbed on the surface, in which case they can catalyse or inhibit other reactions. They should neither form ion pairs with anion radicals formed in the electrode process nor form complexes with the reactants or products.

1.3.5. Electrodes

1.3.5a Working Electrode

Working electrodes intended for general purpose work are usually made from a metal that is electrochemically inert over a wide range of potentials. The most widely used metals are mercury, platinum, gold, and various forms of carbon. Solid metals are typically fashioned into disks surrounded by a chemically inert shroud made from Teflon, glass, or epoxy.

1.3.5b Reference Electrode

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard, and that standard is the reference electrode. One of the most generally available reference electrodes for work in aqueous solutions is the saturated calomel electrode (SCE). The half reaction that occurs inside of an SCE reference is given below.

 $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$

At 25°C the formal potential for the SCE half reaction lies 0.2415 volts more positive than the SHE reference electrode.

1.3.5c. Auxiliary Electrode

In traditional two electrode cells that have only a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is made. If enough current flows through a reference electrode, its internal chemical composition may be significantly altered, causing its potential to drift away from the expected standard value. For this and other reasons, it is desirable to make electrochemical measurements without current flowing through the reference electrode. This auxiliary (or counter) electrode provides an alternate route for the current to follow, so that only a very small current flows through the reference electrode.

1.3.6 Reversible Electron Transfer Process

In an electrochemically reversible process the electron transfer is not rate limiting. For a chemically reversible process, both forms of redox couple (O for oxidized form and R for reduced form) are stable in the time scale of measurement. The rate of electron transfer is fast compared to the rate of mass transport and does not control the overall rate. In this process the rate of reaction is fast enough to maintain equal concentration of the oxidized and reduced species at the surface of electrode and follow Nernst equation.

1.3.7 Irreversible Electron Transfer Process

For an irreversible process, only forward oxidation or reduction peak is observed. This process is usually due to slow electron exchange or slow chemical reactions at the electrode surface. In an

irreversible electrode process, the mass transfer step is very fast as compared to the charge transfer step.

CHAPTER TWO

Experimental Section

2.1. Material and methods

All reagents were obtained from commercial sources, and used as received unless otherwise stated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. H NMR spectra were recorded using a Brukar AV 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard CDCl3, 7.26 ppm. C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard CDCl₃, 77.0 ppm. The H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet." The HRMS spectra of the compounds were recorded by using Bruker Daltonics MicroTOF-Q II mass spectrometer using chloroform and acetonitrile as solvent. Thermogravimetric analyses were performed on the Mettler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Cary-100 Bio UV-visible spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mVs⁻¹. A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH₂ prior to use.

2.2. General procedure for the preparation of the precursors:

The precursors 1a, 1b, 1c were synthesized as per reported procedure. [26-28]

2.2.1. Preparation of Precursor 1a.

In a two neck dry flask DMF (13.0 ml, 169 mmol) and POCl₃ (15 ml, 157 mmol) were stirred for one hour at room temperature. After that triphenylamine (5.0 g, 20 mmol) was added and the reaction mixture was refluxed for four hours at 84 °C in an argon atmosphere. Finally the reaction is quenched by cold water and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (silica gel, DCM: Hexane = 1:5 v/v) to give a solid yellow compound.

2.2.2. Preparation of Precursor 1b.

In a flask compound (1a) (1.73 g, 5.74 mmol) and KI (1.28g, 7.71 mmol) were dissolved in 30 ml of acetic acid which was kept for stirring for one hour at 80°C using condenser with empty balloon. Then reaction mixture was allowed to cool to room temperature with further addition of KIO₃ (1.23g, 5.7 mmol) and further stirred for four hours at 80°C. Then the reaction mixture was allowed to cool and work up was done by sodium bicarbonate and sodium thiosulphate to quench excess acetic acid and iodine respectively, using ethyl acetate as an organic layer to give a gel like yellow solid.

2.2.3. Preparation of Precursor 1c.

In a dry flask compound 1b (2.8 g, 5.4 mmol), THF (50 mL), Pd(PPh₃)₂Cl₂ (33.8 mg, 0.048 mmol), CuI (18.3 mg, 0.096 mmol) and dry TEA (10 mL) were mixed followed by the addition of trimethylsilylacetylene (1.07 g, 10.9 mmol) and stirred under argon atmosphere for 16 hours at 70°C. Then the reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (silica gel, DCM:Hexane 1:5 v/v) to give as a yellow gel like compound. The obtained product (2g, 5 mmol) was then dissolved in dry methanol (30 ml), THF (5 ml) and K₂CO₃ (2 g, 14 mmol) was added and mixture was stirred for 3 hours at room temperature. The product was purified by using CH₂Cl₂ and water work up. The product was purified by using silica gel column chromatography using DCM: Hexane (1:5 v/v) finally a pale yellow colour solid was obtained.

2.2.3. Preparation of triphenylamine-derivative TPA1.

In the presence of argon atmosphere a mixture of (0.7g, 1.6mmol), 4,4'-((4-iodophenyl)azanediyl)dibenzaldehyde (1b), Pd(PPh₃)₂Cl₂(33.8 mg, 0.048 mmol) and CuI (18.3 mg, 0.096 mmol) were dissolved in THF (20 ml) and TEA (10)addition of ml) by later 4,4'-((4 ethynylphenyl)azanediyl)dibenzaldehyde (1c) (0.6 g, 2.13 mmol) . Then the reaction mixture was stirred for 16 hours at 70 °C after completion of the reaction, it was concentrated under reduced pressure. The crude compound was purified by column chromatography on silica gel, using DCM :Hexane (3:7 v/v) to get a yellow solid with 35% yield.

¹H NMR (400 MHz, CDCl₃, δ in ppm): δ = 9.92 (s, 4H, CHO), 7.80 (d, 8H, CH), 7.52 (d, 4H, CH), 7.22 (d, 8H, CH); ¹³C NMR (100 MHz, CDCl3, δ in ppm): 190.34, 151.60, 145.58, 133.25, 131.81, 131.40, 126.11, 123.39, 120.27, 89.47; HRMS (ESI-TOF): m/z calculated for

$$\begin{split} C_{42}H_{28}N_2O_4 ~ 624.2044 ~ [M]^+ ~ found ~ 624.2048; ~ UV/vis ~ (DMSO: \lambda_{max} = 408 \\ nm~(\epsilon = 65307 ~ [M^{-1}cm^{-1}]). \end{split}$$

2.2.4. Preparation of triphenylamine-derivative TPA2.

In condenser only TPA 1 (0.1g, 0.16 mmol), melononitrile (0.1 g, 1.5 mmol) and ammonium acetate (0.15g,1.9 mmol) were dissolved in dry DCM (10 ml) and mixture was stirred for 5 hrs at 70°C. Then reaction mixture was concentrated under reduced pressure, the pure compound was crystallised by DCM and ethanol to get a red solid with 50% yield.

¹H NMR (400 MHz, CDCl3, δ in ppm) δ =7.86 (d, 8H, CH2), 7.64 (s, 4H, CH), 7.20 (d, 6H, CH2), 7.16 (d, 6H, CH2); ¹³C NMR (100 MHz, CDCl3, δ in ppm): 158.88, 151.08, 145.13, 133.39, 132.79, 131.64, 127.05, 126.67, 123.47, 121.00, 120.92, 119.34, 114.86, 114.45, 113.530, 89.48; HRMS (ESI-TOF): m/z calculated for C54H28N10 817.2571 [M + nH] found 817.2509 ; UV/vis (DMSO: λ_{max} = 408 nm (ε = 65307 [M⁻¹cm⁻¹]).

CHAPTER THREE

Results and Discussion

3.1 Synthesis and characterization:

The precursor (1a) 4,4'-(phenylazanediyl)dibenzaldehyde and (1b) (4,4'-((4-iodophenyl)azanediyl)dibenzaldehyde was synthesized by applying Vilsmeier-Haak Reaction on triphenylamine followed by iodination respectively(Scheme 2). And the precursor (1c) 4,4'-((4 ethynylphenyl)azanediyl)dibenzaldehyde was synthesized by the Pd-Cu catalyzed Sonogashira coupling reaction of precursor (1a) with trimethylsilylacetylene followed by base catalyzed deprotection (Scheme 3).





The triphenylamine derivative **TPA1** was synthesized by the Pd/Cucatalyzed Sonogashira coupling reaction. The Sonogashira cross–coupling reaction of 4,4'-((4ethynylphenyl) azanediyl)dibenzaldehyde (**1c**) with 4,4'-((4-iodophenyl) azanediyl)dibenzaldehyde (**1b**) resulted in TPA1 as a product with 35% yield (Scheme4). The Knoevenagel Condensation of 4,4',4'',4'''-((ethyne-1,2-diylbis(4,1phenylene))bis(azanetriyl))tetrabenzaldehyde (TPA1) with Malononitrile resulted in 50% yield of TPA2 (Scheme5). *[29]*



In TPA1 singlet peak at $\delta = 10$ corresponds to aldehyde due to anisotropic effect causing more de-shielding and down field shift. The doublet peaks of δ values between 7-8 correspond to aromatic protons having one proton on its adjacent carbon atom that too due to anisotropic de-shielding effect. There are solvent peaks at $\delta = 7.26$ for CDCl₃ and 5.28 for DCM.

In TPA2 missing of aldehyde singlet peak at $\delta = 10$ confirms the condensation reaction of aldehyde with melonitrile and the converted proton shows a singlet for four protons at $\delta = 7.64$ in addition to aromatic doublet peaks.

3.2 Photophysical properties:

The electronic absorption spectra of the triphenylamine-derivatives TPA1 and TPA2 were recorded in DMSO at room temperature and the data are listed in Table 1. The triphenylamine-derivatives **TPA1** and **TPA2** exhibit a strong absorption corresponding to $\pi \rightarrow \pi^*$. The **TPA2** exhibit a significant red shift due to more extended conjugation by eight cyano groups, conjugation increases the energy level of the HOMO and depresses the energy level of the LUMO, so less energy is required for an electronic transition in a more conjugated system. [30]

The triphenylamine-derivatives **TPA1** and **TPA2** are showing maximum absorption band at 380 and 470 nm corresponding to the π - π * transition. The optical band gap (Eop) calculated from the onset absorption wavelength for triphenylamine-derivatives **TPA1** and **TPA2** are 2.91 and 2.35 eV respectively. Fluorescence emission behaviour with increasing length of the conjugated backbone causes red shift. [31-33]



Figure 1. UV-visible spectra of **TPA1 and TPA2** in 10^{-5} M DMSO solution



Figure 2. Fluorescence spectra of **TPA1** and **TPA2** in 10^{-5} M DMSO solution

3.3 Thermal properties:

The thermal properties of the **TPA1** and **TPA2** were investigated by the thermogravimetric analysis under nitrogen atmosphere and their thermograms are shown in Figure 4. The **TPA1** and **TPA2** exhibit good thermal stability upto 400 °C at 10% weight loss under nitrogen atmosphere. The decomposition temperature for 10% weight loss in **TPA1** and **TPA2** were found to be 380 and 449 °C respectively. This shows that incorporation of malononitrile makes **TPA2** more thermally stable which is due to increase in resonating chain length. There is no weight loss up to 80°C indicates that solid have no water molecules. [34]



Figure 3: Thermogravimetric analysis of **TPA1** and **TPA2** measured at a scanning rate of 10°C/min under nitrogen atmosphere

3.3 Electrochemical properties:

The electrochemical behaviour of triphenylamine-derivatives TPA1 and TPA2 were studied by the cyclic voltammetric (CV) in dichloromethane solution using tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. The electrochemical data are listed in Table 1. and cyclic curve representations are shown in Figure 5 and 6. The triphenylamine-derivatives exhibit one reversible oxidation wave the oxidation of triphenylamine donor unit. The corresponding to oxidation peak for TPA1 and TPA2 observed at 1.02 and 0.824 eV respectively. [34]



Figure 4. Cyclic voltammogram of **TPA1** in 10^{-5} M DCM solution



Figure 5. Cyclic voltammogram of **TPA2** in 10^{-5} M DCM solution

Table 1. Photophysical, electrochemical, and thermal properties of the triphenylamine derivatives.

Compounds	$\lambda_{max}[nm]$	Eoxid	Stoke	Eop	T _d
	(E[Lmol-cm ⁻¹])	(V)	Shift	(eV)	(°€)
			(nm)		
TPA1	380 (54930)	1.02	153	2.91	380
TPA2	469 (83551)	0.82	158	2.35	449

Absorbance measured in DMSO at 10^{-5} M; $\lambda_{abs}(max)$: absorption wavelength; ϵ : molar extinction coefficient; E_{oxid} is oxidation potential; E_{op} is the optical band gap estimated by using the onset oxidation potential; T_d : is the ten % weight loss

3.4 Theoretical Calculations:

To explore the electronic structure of the triphenylamine-derivatives **TPA 1** and **2**, density functional theory (DFT) calculation were performed at the B3LYP/6-31G**.[35] The contours of the HOMO and LUMO of TPA**1** and TPA **2** are shown in Table 2. The HOMO is delocalized on the full stretch of the molecule and partly localized close to the attachment group. The LUMO is mainly on the acceptor part, which is far away from the attaching group, beneficial for a p-type DSSC. [36] The distribution of electrons in between the HOMO and LUMO shows a intramolecular charge separation after excitation The HOMO–LUMO energy gap for triphenylamine-derivative **TPA1** and **TPA2** are 2.7 and 2.37 eV respecitvely.

Compound s	HOMO (eV)	LUMO (eV)
TPA1	-5.35	-2.03
TPA2	-5.59	-2.96

Table 2. HOMO and LUMO orbitals of triphenylamine-derivative **TPA1**and **TPA2** at the B3LYP/6-31G** level for C, N, O and H

CHAPTER FOUR

Conclusions:

The donor-acceptor systems (D-A) based on triphenylamine were synthesized by Pd/Cu catalyzed Sonogashira cross coupling reaction and Knoevenagel Condensation. The characterization of triphenylamine-derivatives **TPA1** and **TPA2** was done by different techniques such as ¹H NMR, ¹³C NMR and mass spectroscopy. The optical and electrochemical properties of these compounds were studied. The UV/vis spectra shows absorption due to the $\pi - \pi^*$ transitions. The electrochemical studies shows that there is one peak in the cyclic voltammograms of the triphenylamine-derivative **TPA1** and **TPA2** corresponding to the oxidation of donor triphenylamine unit. The DFT calculations reveal distribution of HOMO and LUMO energy levels. HOMOs are mainly localized over triphenylamine moiety while LUMOs over aldehyde and cyano moieties in **TPA1** and **TPA2** respectively.

APPENDIX-A





Figure 6. 400 MHz 1 H NMR spectrum of compound **TPA1** in

CDCl₃



Figure 7. 400 MHz H NMR spectrum of **TPA2** in CDCl₃



Figure 8. 100 MHz ¹³C NMR spectrum of **TPA1** in CDCl₃



Figure 9. 100 MHz 13 C NMR spectrum of **TPA2** in CDCl₃



Figure 10. HRMS spectrum of **TPA2** in CH₃CN and CHCl₃



Figure 11. HRMS spectrum of **TPA1** in CH₃CN and CHCl₃

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