SYNTHESIS OF DIAZIRINE-FUNCTIONALIZED ORGANIC SEMICONDUCTOR MATERIALS

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ABSTRACT

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Organic light-emitting diodes (OLEDs) could become the leading technology for fabrication of next generation displays and solid state lightening in the near future. To meet this goal, cheap and easy methods of OLEDs fabrication have to be developed. Modern OLEDs are generally prepared by multiple layer deposition. Vacuum deposition is the most common method of building such multilayer structure but it is costly and limited to vaporizable low molecular weight materials. By contrast, solution-processing technologies are much easier, less costly, and suitable for flexible display applications. A potential disadvantage of such techniques for fabricating multilayer devices is that preexisting layers could be partially dissolved by the solvent used in one of the following deposition steps. To overcome this problem, the cross-linking concept can be applied.

This thesis pursues investigation on diazirine-functionalized semiconductor materials, which can be transformed to insoluble layers by photo- or thermo-cross-linking. In particular, it focuses on its synthesis, optical and electrochemical characterization, polymerization, and first application in an OLED device. α-NPD, a commonly used hole-transport material, triphenylamine, diphenyl ether, bromo- and iodo-benzene were functionalized with diazirine groups within this work. Diazirine compounds undergo decomposition reaction (irreversible nitrogen loss) upon UV irradiation or pyrolysis forming highly reactive carbenes, which display high propensity for intermolecular bond insertions to form a polymer. Since the cross-linking is induced by UV light, the organic films become, not only insoluble, but can simultaneously be patterned as a negative photoresist using standard photolithography techniques. Photo patterning capability of diazirine-functionalized compounds may be advantageous for future OLEDs applications.
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CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION TO ORGANIC LIGHT-EMITTING DIODES

An organic light emitting diode (OLED) is a light emitting diode whose emissive electroluminescent layer is composed of a film of organic compounds. It is a solid-state semiconductor device with thickness no more than 200nm. OLED technologies currently are finding their way into commercial applications. Such systems can be used in television screens, computer monitors, small, portable system screens such as cell phones and PDAs, advertising, information, and indication.\(^1\) OLEDs can also be used in light sources for illumination and large-area light-emitting elements.\(^2\)

OLED materials have been discovered back in 1960, but only in the past 20 years researchers started to develop those technologies. For the past 20 years the progresses in this area improved significantly to the point to revolutionize the display industry. The potential importance of this technology is also obvious from the growth of the OLED market. In its latest Quarterly OLED Shipment and Forecast Report, DisplaySearch forecasts that the total OLED display market will grow from $0.6 billion in 2008 to $7.1 billion by 2016, with a Compound Annual Growth Rate (CAGR) of 36% (Figure 1.1).\(^3\) According to the forecast, OLEDs are the most promising technology for fabrication of full-color flat panel displays. It becomes workable due to the numerous advantages

Figure 1.1: OLED display revenue forecast\(^3\)
of OLED display over other display technologies like cathode ray tubes, liquid crystal displays, or plasma display panels. They provide very thin, light, flexible, energy efficient devices with wide viewing angles (close to 180°), fast response times, and improved range of colors and brightness compared to LCD and plasma displays. Along with their advantages, OLEDs have several disadvantages such as short operational lifetimes, water sensitivity, and high cost.

### 1.2 OLED WORKING PRINCIPLE

In the OLED, the light is generated by electroluminescence. The earliest report of electroluminescence (EL) from an organic material was made by Pope and later Helfrich and Schneider continued this study. In that work, electroluminescence was observed at high voltages from crystals of anthracene due to their big sizes. In 1987 Tang and co-workers, instead of applying a large voltage to a large crystal, used a thin film with a small applied voltage. This novel setup caused a growing interest in organic materials for LED research.

The EL phenomenon in OLEDs originates from the electron-hole recombination that occurs when a voltage is applied to an organic semiconductor materials sandwiched between two electrodes. The semiconductor materials are deposited in OLEDs as layers. Figure 1.2 shows the simplified OLED architecture.
**Figure 1.2:** Emission principle and device architecture of a triple layer OLED.\(^9\)

An OLED consists of a substrate, which can be made of either a glass or transparent plastic and it serves to support and protect the device. Indium tin oxide (ITO) deposited on the substrate is usually used as an anode. ITO is transparent, so the light can go through it easily. Hole transport layer (HTL), emissive layer (EML), and electron transport layer (ETL) – are layers made from organic small molecules or polymers. These layers form the organic electroluminescent film in OLED device. The cathode is typically made of metal alloys, for instance Li:Al and Mg:Ag.

When a voltage is applied to the electrodes, electrons are injected from the cathode into the electron-transport layer (1), while holes are sent from the anode into the hole-transport layer (1). The electrons and holes are transported in the opposite direction until a recombination process occurs. The excited state is created in the emissive layer after recombination of electrons and holes (2) and light is emitted (3) when the exciton decays (Figure 1.3).

**Figure 1.3:** Electroluminescence process.
*Modified picture from reference 10.*
1.3 METHODS OF OLED FABRICATION

Despite the huge potential for OLEDs, they still do not have widespread use in the customer market. The reasons are the difficulties in fabrication of OLEDs as well as the short operational lifetimes of organic materials and general unfamiliarity with the new technology. The possible applications of the OLED display technology are numerous. As mentioned above, OLEDs are made from thin films of organic materials, which are deposited between an anode and cathode. A variety of organic materials can be used for fabrication of such films. There are two main classes of organic layers materials: small molecules or polymers. The method of fabrication will differ depending on this choice. There are a number of different methods that can be used for OLED fabrication and each technique brings its own challenges and advantages.

The most common methods of OLEDs fabrication are:

- Physical Vapor Deposition (PVD)
- Chemical Vapor Deposition (CVD)
- Inkjet Printing
- Spin Coating
- Roll-to-Roll Printing

Evaporative techniques (PVD) are usually used for small molecule layers. In a vacuum chamber, the organic molecules are heated (evaporated) and allowed to condense as thin films onto cooled substrates (Figure 1.4). It is usually carried out on a glass substrate. Multicolor displays are made using properly matched shadow masks for depositing RGB emitting materials.

**Figure 1.4:** PVD process.
This technology allows a very good control over layer thickness and uniformity, and it uses the generally available vacuum equipment that exists in the semiconductor industry. Less efficient use of materials, limited scale, not flexible substrates, and high costs are common disadvantages of this technique.

Another method is called chemical vapor deposition (CVD). CVD make use of reactive gases or precursors which are then reacted or decomposed to grow materials with efficient control over crystallinity, dispersion etc. but not uniformly.

When the organic layers in OLED consist of polymers, ink-jet technology is commonly used. In this method OLEDs are sprayed onto the substrates like ink sprayed on paper during usual ink-jet printing.

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Figure 1.5: Dimatix Materials Printer DMP-2800.

In ink-jet printing, the organic material is deposited as a solution in a suitable solvent. This technique allows OLEDs to be printed on large areas and on flexible substrates. The main disadvantages are stringent physico-chemical requirements for solvent, thickness, and potential phase separation.
Spin coating is used for polymers as well as for small molecules. A typical process involves depositing of organic material in solution form onto a substrate and then rotating the substrate at high speed (i.e. 3000 rpm) (Figure 1.6). The centrifugal force causes the liquid to spread and to form a thin layer as the solvent evaporates. Final thickness and other properties will depend on the nature of the compound (viscosity, drying rate, surface tension, etc.) and the parameters chosen for the spinning process.

Films produced in this way usually have inconsistent thickness as well as a poor surface smoothness compared to vapor deposition methods.

The OLED fabrication roadmap shown below represents the current and future technologies in the past few years and in the future (Figure 1.7). According to this forecast the most common OLEDs fabrication technology in next few years will be roll-to-toll printing.

**Figure 1.6: Spin Coating process**

**Figure 1.7: OLED fabrication roadmap.**
The roll-to-roll printing process is similar to color newspaper printing and it allows for low cost production, large scale, and high production efficiency. Furthermore, this fabrication method for OLEDs enables the use of flexible plastic or metal with transparent top electrode.

### 1.4 ROLL-TO-ROLL PRINTING AND CROSS-LINKING OF ORGANIC SEMICONDUCTORS

As stated above the most promising method for low cost production of flexible OLED-displays, organic solar cells, or organic field effect transistors is expected to be roll-to-roll printing, which allows for an efficient mass-production. It is considered to be the key technology for defined polymer deposition. Figure below demonstrates a possible cycle of production by roll-to-roll printing (Figure 1.8).

*Figure 1.8: Fabrication process using the roll-to-roll printing. Deposition of organic layer by roll-to-roll printing from the solution, removal of the solvent in vacuum, and cross-linking of organic film by photolysis (or pyrolysis) in order to make the fabricated film insoluble for the next layer deposition. The picture is reproduced from reference 7.*

Because the quality of roll-to-roll printed films depends on solvent and on phase separation during solvent drying, the roll-to-roll printing would enormously benefit from polymerizable
OLED “inks”, which is the subject matter of our research. The principle of our approach is based on conversion of soluble diazirine monomers into an insoluble polymer layer by intermolecular photo-cross-linking. The conversion of soluble monomers into an insoluble polymer would allow for all organic OLEDs to be printed from organic solvents and subsequently photo-polymerized, in as many cycles as there are organic layers in the device.

1.5 CROSS-LINKABLE ORGANIC SEMICONDUCTORS

The preparation of OLEDs by solution processing techniques, such as spin coating, inkjet printing or roll-to-roll printing is beneficial because it combines the advantages of ease of fabrication and low cost production. Moreover these technologies are more suitable for flexible display applications. As mentioned above, modern OLEDs are prepared by multiple layer deposition of various materials (HTL, EML, ETL). One of the main difficulties to use solution processable OLEDs are that preexisting layers could be partially dissolved by the solvent used in one of the following deposition steps. Even if so-called “orthogonal” solvents are used (in which the fabricated layers are insoluble), the interface mixing/erosion remains a severe problem.

In order to make the low-cost solution processing technologies suitable for the fabrication of multilayer OLEDs the cross-linking concept was proposed. This concept deals with low molecular weight compounds with polymerizable units. Such compounds can be deposited to the substrate and then transformed into an insoluble polymeric network by irradiation with UV light or thermal treatment.

A number of efforts were made in order to develop organic semiconductor materials that can provide solvent resistance after thermo- or photo-cross-linking (Figure 1.9). Functionalization of
traditional semiconductor materials with cross-linkable functional groups such as oxetane\textsuperscript{20}, siloxane\textsuperscript{21}, styrene\textsuperscript{22}, acrylate\textsuperscript{23} is the most common way.

\textbf{Figure 1.9:} Examples of cross-linkable organic semiconductor materials.

Among these functionalized materials, the oxetane-based compounds can be cross-linked by UV light irradiation in the presence of a photoacid initiator, while the styrene-based materials can be cross-linked by heating with no initiators. The chlorosylil-functionalized compounds in the presence of moisture hydrolyze and undergo condensation reaction.
1.6 INVESTIGATION SCOPE AND MOTIVATION

Recently in our group was developed the idea of utilizing diazirine-functionalized compounds as a cross-linkable materials for OLED application.\(^9\) The key advantage of this approach is that under the thermal treatment or UV light exposure with no photoinitiators, diazirines form a carbene.

9,9-Dialkylfluorene based polymers are common emitting polymers for LEDs. The UV light can be used to drive the photopolymerization process of fluorene derivatives. The figure below represents an approach to the synthesis of a bisphenyl-fluorene derivative (Scheme 1.1) and its photopolymerization.\(^9\)

![Scheme 1.1: Coupling, diazirination, and UV-light photo-cross-linking of the diazirine-functionalized fluorene derivative.](image)

The high reactivity of bis-phenylfluorene dicarbene derivative after UV irradiation and the reasonable stability of the corresponding diazirine precursor make those materials particularly attractive. Preliminary photolysis experiments demonstrate that nitrogen loss increases quantum...
yield of diazirine bearing compound. The new diazirine-functionalized material can be used in OLED fabrication according to the following scheme (Figure 1.10).

![Diagram showing the process](image)

**Figure 1.10:** Applied sequence for the new diazirine-based organic materials for use in organic electronics. Picture is reproduced from reference 7.

Preliminary tests on fluorene derivatives in a multi-layer architecture of OLEDs\(^9\) suggested that the diazirine photo-cross-linking approach could also be applied for electron (ETL) and hole transporting materials (HTL) as well.

The main goal of this work is the synthesis and testing of photo-polymerizable HTL materials and their use in OLED fabrication. The Scheme 1.2 for a \(N,N'\)-bis(1-naphtyl)-\(N,N'\)-diphenyl-1,1'-biphenyl-4,4'-diamine (α-NPD) derivative represents the approach described in this work for the synthesis of a suitable material.
Scheme 1.2: *Diazirination and cross-linking of the diazirine-functionalized α-NPD derivative.*

Triarylamines have proven to be well-suited materials for the hole-transport layers in OLEDs due to their ability to undergo p-doping, as a result of having HOMO-energies around 5 eV, and the ability to form smooth amorphous layers.\(^{24}\) Typical materials are \(N,N’\)-bis-(3-methylphenyl)-\(N,N’\)-diphenyl-benzidine (TPD), \(N,N,N’,N’\)-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD), α-NPD, di-NPD etc. (Figure 1.11).

**Figure 1.11:** *Representative structures of triphenylamines.*
The work presented here focuses on synthesis, optical characterization, polymerization, and photo-patterning of diazirine-functionalized α-NPD derivative.

Likewise another concept of organic semiconductor cross-linkable materials is studied in the current thesis. The main idea of this approach is the developing of internal diazirine-bearing cross-linkers that will form an insoluble polymer by reaction with the traditional semiconductor materials. The compounds shown below (Scheme 1.3) may serve as co-monomers and carbene-producing precursors for the intermolecular bond insertions, to form a polymeric film with the semiconductor material upon UV irradiation or thermal activation.

\[ \text{Scheme 1.3: Cross-linking with traditional organic semiconductor molecules.} \]

The worth of this concept was recently proved by Man-kit Leung and co-workers who used 4,4',4'-tris(acetoxymethylene)triphenylamine as an efficient cross-linker for producing polyvinylcarbazole-containing material (PVK).\(^{25}\)
Scheme 1.4: Photoinduced cross-linking reaction of 4′,4′′-tris(acetoxymethylene)triphenylamine with PVK. The picture is reproduced from reference 26.

In the reported example it was shown that utilizing triphenylamine derivative as a cross-linker largely improved hole injection and transport performance, as well as the resistance to the solvent.

The last concept, covered in this work, is the synthesis of so-called diazirine modifiers that can be used to functionalize traditional organic molecules. The key point of this approach is the development of universal diazirine-containing simple precursors, that can be attached to a variety of molecules by using well-established protocols and significantly decrease the synthetic efforts.

The structure and principle of those modifiers is shown in Scheme 1.5.

Scheme 1.5: The concept of diazirine modifiers.
CHAPTER 2: RESULTS AND DISCUSSION

2.1 GENERAL SYNTHETIC APPROACH

Trifluoromethyl diazirines are reasonably stable reagents used in photolabeling by carbene generation.\textsuperscript{26,27} The commonly used approach to the synthesis of trifluoromethyl diazirines involves the transformation of a trifluoromethyl carbonyl compound into a diaziridine in three steps, followed by final oxidation to the corresponding diazirine.\textsuperscript{28}

Within the investigations on diazirines in this work, diazirine-functionalized derivatives of α-NPD (16), diphenyl ether (20), triphenylamine (27) and diaziridine-functionalized derivatives of iodophenyl (32), and bromophenyl (37) were synthesized (Figure 2.1).

\textbf{Figure 2.1:} Representative structures of synthesized compounds.
The general method of introduction of all diazirine groups is described in the Scheme 2.1

Scheme 2.1: General pathway for synthesis diazirines.

Trifluoromethyl ketones were used as a starting material. They were converted to oxime, to the corresponding tosyloxy-derivative, diaziridine, and finally they were oxidized to the diazirine. Diaziridine can be successfully dehydrogenated to the corresponding diazirine using tert-butyl hypochlorite ($\text{t-BuOCl}$), iodine/triethylamine, or silver oxide ($\text{Ag}_2\text{O}$) as the oxidants. According to the literature oxidation by $\text{I}_2$/Et$_3$N is the most suitable way, which resulted in higher yields and shorter reaction time.

2.1.1 Synthesis of $N,N'$-bis(1-naphtyl)-$N,N'$-di(4-((3-trifluoromethyl)-3-phenyl)-3$H$-diazirine))-1,1’-biphenyl-4,4’-diamin

The target molecule for OLED applications $N,N'$-bis(1-naphtyl)-$N,N'$-di(4-((3-trifluoromethyl)-3-phenyl)-3$H$-diazirine))-1,1’-biphenyl-4,4’-diamine was synthesized according to the general
procedure (scheme 2.2) for introduction of diazirine group. For this purpose the corresponding trifloromethyl-ketone (4) was synthesized according to Scheme 2.2.

**Scheme 2.2:** Synthetic route for \(N,N'\)-bis(1-naphtyl)-\(N,N'\)-di(4-((3-trifluoromethyl)-3-phenyl)-3\(H\)-diazirine))-1,1'-'biphenyl-4,4'-diamine.

The first step is Buchwald-Hartwig\(^{32}\) Pd-catalyzed C-N coupling between 4,4'-dibromobiphenyl and 1-naphtylamine using \textit{in situ} prepared catalyst from tris(dibenzylideneacetone)dipalladium(0) (Pd\(_2\)(dba)_3) and 1,1'-bis(diphenylphosphino)-ferrocene (DPPF).\(^{33}\) It gives \(N,N'\)-bis(1-naphtyl)-\(N,N'\)-biphenyl-4,4'-diamine (1) with yields up to 90%.

The diamine (1) is reacted under Ullman conditions with an excess of aryl halides in the presence
of a stoichiometric amount of copper affording the corresponding triphenylamines (2 and 3).\textsuperscript{34} Ullman reactions require high temperatures, long reaction times and provide moderate yields (40-60\%). According to the literature the Pd catalyzed C-N coupling works with some aryl iodides or bromides and forms triphenylamines.\textsuperscript{35,36} A different approach to ketone (4) is shown in Scheme 2.3.

![Scheme 2.3: Alternative route for the synthesis of ketone 4.](image)

The reactions afforded no products. Other reaction conditions were tested using different Pd catalyst systems but according to GCMS and TLC analysis the results were also negative (Scheme 2.4).

![Scheme 2.4: Buchwald-Hartwig reaction of diphenylamine.](image)

The alternative strategy based on introduction of trifluoroacetyl groups to pre-synthesized dihalogenated α-NPD derivative was devised. Then, lithium-halogen exchange reaction followed by addition of stoichiometric amount of ethyl trifluoroacetate (ETFA)\textsuperscript{37} yielded 52\% of diketone
(4) and 36% of monoketone (5). The optimal time for the reaction was 30 minutes, increasing the reaction time formed mono- and di-alcohols (10, 11, 12) in total yield up to 60% (Scheme 2.5).

**Scheme 2.5:** Lithium-halogen exchange reaction.

Scheme 2.6 can explain the formation of alcohols (10, 11, 12). The proposed mechanism was adopted from the literature where similar results were observed in the reaction with Grignard reagents.

**Scheme 2.6:** Possible reaction mechanism for alcohols formation (10, 11, and 12).

The target molecule $N,N'$-bis(1-naphthyl)-$N,N'$-di(4-((3-trifluoromethyl)-3-phenyl)-$3H$-diazirine))-1,1’-biphenyl-4,4’-diamin (16) was synthesized according to the common procedure. Scheme 2.7 shows the preparation of diazirine 16 in four steps, with an overall yield of 37%.

**Scheme 2.7** shows the preparation of diazirine 16 in four steps, with an overall yield of 37%.
Scheme 2.7: Synthetic route for diazirine 16.

Molecules based on 3-trifluoromethyl-3-phenyldiazirine (TFMPA) are known to be reasonably stable at room temperature and even under light exposure in the visible spectrum. However, diazirine 16 is unstable under the conditions described above and it needs to be stored in a freezer in the dark. At room temperature it may partially polymerize and react with oxygen from the atmosphere. Decomposition products were found by TLC after 1 hour at room temperature and exposure to light.
2.1.2 Synthesis of 1,1’-(4,4’-((3-trifluoromethyl)-3-phenyl)-3H-diazirine))ether

The second target molecule was 1,1’-(4,4’-((3-trifluoromethyl)-3-phenyl)-3H-diazirine))ether (20). The ketone (7) was prepared by lithium-halogen exchange reaction followed by the addition of ethyl trifluoroacetate (ETFA). In order to introduce the diazirine group, ketone (7) is converted to oxime (17), tosylated (18), and treatment the tosylated species with liquid ammonia in an autoclave yielded diaziridine (19). Diaziridine (19) was then oxidized with iodine/triethylamine to form the desired diazirine (20) with overall yield of 46%. The synthetic route described above is shown in Scheme 2.8.

Scheme 2.8: Synthetic route for diazirine 20.
2.1.3 Synthesis of tris-(4-(((3-trifluoromethyl)-3-phenyl)-3H-diazirine))amine

In order to make triphenylamine-based cross-linker, ketone (23) had to be synthesized. The synthetic route started from bromination of triphenylamine (TPA) according to the procedure described by Walter and co-workers.\(^{42}\) Lithium-halogen exchange reaction followed by the addition of ETFA resulted in ketone (23). Diazirine (27) was synthesized following the general protocol applied for all diazirinations within this work as shown in Scheme 2.9.

Scheme 2.9: Synthetic route for cross-linker 27.
2.1.4 Synthesis of 3-(4-iodophenyl)-3-(trifluoromethyl)diaziridine and 3-(4-bromophenyl)-3-(trifluoromethyl)diaziridine

Previously described 3-(4-Iodophenyl)-3-(trifluoromethyl)diaziridine\textsuperscript{43} and 3-(4-bromophenyl)-3-(trifluoromethyl)diaziridine\textsuperscript{29} were synthesized according to Scheme 2.10.

\[ \text{Scheme 2.10: Synthetic route for diazirine modifiers 32 and 37.} \]

2.1.5 Cross-Coupling: Synthesis of Diazirine-Functionalized Compounds under Suzuki Conditions

The standard approach towards the introduction of a diazirine moiety into a polymerizable substrate requires the tedious four-step synthesis from CF\textsubscript{3}-ketone as starting materials (Scheme 2.1). Instead, it is possible to utilize diazirine modifiers under Suzuki conditions for this purpose. Currently, “modifiers” 32 and 37 were synthesized and successfully tested for this purpose.
This concept is shown in Scheme 2.11.

**Scheme 2.11:** Diazirination of molecules by modifiers 32 and 37 under Suzuki condition followed by oxidation step. $X = \text{I or Br}$.

Firstly, phenylboronic acid was used as a model for the Suzuki-cross-coupling conditions (Scheme 2.12).

**Scheme 2.12:** Suzuki coupling reaction ($I - \text{yield } 72\%, \text{Br} - \text{yield } 44\%$).

Iodine is described to be the most reactive halogen ($I > \text{Br} >> \text{Cl}$) for palladium catalyzed cross-coupling reactions.\(^4\) The observed yields correspond to this statement.

Few more coupling were successfully accomplished under the same conditions (Scheme 2.13).
Scheme 2.13: *Suzuki coupling reaction.*

Moreover, the previously reported four-step synthesis of 3,3’-(9,9-Dihexyl-9H-fluorene-2,7-diyl)bis[3-(trifluoromethyl)-3H-diaziridine-3-yl-phenyl]⁹ (45) with an overall yield of 48% (scheme 1.1) was successfully redesigned into a one-step reaction with diazirine modifier, with a total yield of 36% (Scheme 2.14).

Scheme 2.14: *Suzuki coupling reaction.*
2.2 CROSS-LINKING AND PHOTOPATTERNING

2.2.1 Carbene and Diazirine Chemistry

Diazirine compounds undergo decomposition reaction (irreversible nitrogen loss) upon UV irradiation or pyrolysis forming highly reactive carbenes (Scheme 2.15) and a certain proportion of liner diazo isomer. Carbenes react rapidly with the surrounding chemical environment\textsuperscript{45} by inserting nonspecifically into chemical bonds.\textsuperscript{46,47}

\begin{center}
\includegraphics[width=\textwidth]{s2f15.png}
\end{center}

\textbf{Scheme 2.15:} \textit{Ring opening of diazirines, nitrogen loss and isomerization.}

Carbenes are neutral molecules that have divalent carbons with two non bonding, unpaired electrons,\textsuperscript{48} and react in various ways to complete their valence shells. An overview of typical reactions of carbenes is represented in Scheme 2.16. Carbenes are capable of reacting with a full range of functional groups including the insertion into saturated C-H bonds, O-H, N-H bonds, addition to unsaturated hydrocarbons, including aromatic rings.\textsuperscript{49,50}
2.2.2 Thin Film Fabrication

Photo- and thermo-polymerizable diazirine molecules are used to prepare low-cost spin-coated films suitable for the preparation of organic mono- and multi-layers for OLEDs applications. Soluble precursor molecules were deposited on a substrate where they are reacted to become an insoluble polymer after UV-light irradiation or thermal treatment, therefore, are suitable for a second spin-coating step. The general scheme of this method is introduced in Figure 2.2.

Scheme 2.16: Overview of carbene reactions.
Figure 2.2: Cross-linking approach to obtain insoluble organic semiconductor layer for OLED application.

Spin coating from dilute solutions is a widely used method to produce a thin film on a planar substrate.\textsuperscript{14} Thin films of diazirine functionalized α-NPD and fluorene derivatives were fabricated by spin coating from chloroform, cyclohexane, or xylene solutions onto different substrates. A mercury lamp (365 nm) or hot plate was used to cross-link the monomers. The thickness of the fabricating films can be controlled by varying rotation speed, concentration of the initial solutions, and by solvents choice.

For most experiments conducted with α-NPD derivative (16) chloroform was chosen as the solvent. Figure 2.3 plots thickness of 16 as a function of spin speed and initial monomer solution concentration in chloroform. Since chloroform is very volatile solvent the thickness of films is much larger compared to those spun from xylene or toluene at the same initial concentrations.
Figure 2.3: α-NPD derivative film thickness as a function of spin speed and initial monomer solution concentration.

The obtained thicknesses were determined with surface profiler and ellipsometer. Several profiles from these measurements are shown in Figure 2.4.

**Figure 2.4:** Step height analysis of fabricated films by surface profiler.
To observe the surface morphology and estimate the roughness atomic force microscopy (AFM) was employed. Figure 2.5 shows the AFM images of cross-linked α-NPD (16) film spun on top of PEDOT:PSS onto Silicon substrate. No defects such pinholes or cracks were observed. The $R_{\text{max}}$ value measured AFM is equal to 1.46 nm, which makes it suitable to use in OLEDs where homogeneous and smooth films are required for efficient device fabrication.

![AFM Image]

**Figure 2.5:** The AFM images of cross-linked α-NPD (16) film. α-NPD (16) was coated on PEDOT:PSS onto Silicon substrate.

### 2.2.3 Cross-Linking of Diazirine-Functionalized Organic Semiconductors

As mentioned above, diazirines undergo photo- or thermo-decomposition to form highly reactive carbenes almost instantly, which tend to form a polymer due to their high ability for bond insertions. Since diazirines absorb consistently in the 350-400 nm range the most common way to generate the reactive carbenes is by using near-UV mercury lamp. In the current work diazirine-functionalized semiconductor molecules were photolyzed with a mercury lamp at 365 nm wavelength and an approximate distance (sample-to-lamp) of 3 cm to ensure an almost-
constant photon flux. Moreover, the polymerization was carried out in oxygen containing and oxygen free atmosphere. The crosslinking process of α-NPD, Fluorene, and TPA derivatives upon UV-irradiation was followed by UV-vis spectroscopy on the solid sample (Figure 2.6).

*UV polymerization of α-NPD at oxygen containing atmosphere*

![Graph showing UV polymerization of α-NPD at oxygen containing atmosphere.](image)

*UV polymerization of α-NPD at argon atmosphere*

![Graph showing UV polymerization of α-NPD at argon atmosphere.](image)

**Figure 2.6:** UV-vis spectra of thin films of α-NPD (16), Fluorene, and TPA (27) derivatives after irradiation with UV light at fixed time intervals. (continue on the next page)
Figure 2.6: UV-vis spectra of thin films of α-NPD (16), Fluorene, and TPA (27) derivatives after irradiation with UV light at fixed time intervals.

α-NPD derivative (16) shows decrease of absorption at the absorption maxima (348 nm) and increase at 380-460 nm region with one isosbestic point at 377 nm and 373 nm for oxygen and oxygen free environment respectively. Isotherms of absorption change at 348 nm and 412 nm are shown in Figure 2.7. After 30 minutes of UV irradiation almost no change in UV-vis spectra were observed which demonstrates that at least 30 minutes is necessary to accomplish α-NPD derivative complete polymerization.
TPA derivative (27) shows a 2-band spectrum, whose absorption maxima are centered at 323 nm and 400 nm, respectively. The spectra undergo a general red-blue shift (323→308 nm, 400→383 nm), while the band at 323 nm decreases, the band centered at 400 nm increases its intensity. Almost no changes in its UV-vis spectra were observed after 45 minutes of irradiation.

To compare the polymerization velocity with the newly synthesized compounds, Uv-vis spectroscopy was employed to observe crosslinking of the previously reported diazirine-functionalized Fluorene derivative. After 180 seconds (3 min) of irradiation only minor changes in UV-vis spectra were detected. The difference in polymerization velocity between α-NPD, TPD, and Fluorene derivatives can be explained by their molecular structure and reactivity toward carbenes. α-NPD and TPD have only aromatic rings in their structure while Fluorene contains both aromatic and aliphatic moieties. Previously reported experiments of diazirine photolysis in aliphatic/aromatic matrix have indicated that aliphatic C-H bond insertions are faster than the addition to aromatic double bond or aromatic C-H bond insertions. This evidence suggests that TPA cross-linker will be most efficient with molecules containing aliphatic chains or other functional groups like O-H, N-H, etc.

After UV irradiation polymers were tested for their solubilities. Polymer films onto glass substrates were dipped in different solutions. Photo-cross-linked α-NPD and TPD films demonstrated a weak solvent resistance, but they were insoluble in hexane and cyclohexane. Fluorene-based photo-cross-linked films had moderate solvent resistance and were insoluble in hexane, cyclohexane, acetone, DCM, Chloroform.

Pyrolysis of diazirines is another possible way to form cross-linked polymers. Thermopolymerized films showed excellent solvent resistance to every tested solvent (DCM,
chloroform, THF, acetone, toluene, xylene, DMSO). Even after soaking the thermo-cross-linked films overnight no changes in film thickness were observed.

Pyrolysis of diazirine-functionalized α-NPD derivative (16) was monitored by Uv-vis spectroscopy as well (Figure 2.7).

![Thermally polymerized α-NPD](image)

**Figure 2.7:** UV-vis spectra of thin film of α-NPD (16) derivative after heating it on a hot plate at 75°C for various time periods.

Similarly to UV-polymerization α-NPD derivative (16) shows decrease of the 348 nm centered and increase of the absorption in the 380-500 nm region with one isosbestic point at 372 nm. Isotherms of absorption change at 348 nm and 412 nm are shown in Figure 2.8. After 300 seconds of heating no significant changes in UV-vis spectra were detected.

IR and data obtained from cross-linked films of α-NPD derivative (16) show that carbene, formed by α-NPD diazirine decomposition, can react with atmospheric oxygen during the cross-linking process. IR spectra are shown in Figure 2.8.
Ketone

UV polymerization in atmosphere

UV polymerization in nitrogen chamber
From the recorded IR spectra one can conclude that photo-cross-linking (at 365nm) of 16 in atmosphere yields carboxylic compounds as a side products during the polymerization. The same process conducted in nitrogen atmosphere forms only traces of ketones. During the thermo-cross-linking (at 90°C) of 16 no ketone formation was observed at all, even in aerobic conditions. This evidence was also supported by obtained $^{19}$F NMR data of the same samples. $^{19}$F signal corresponding to trifluoromethyl ketone (CF$_3$-C(O)-) at -70.254 ppm was clearly observed in $^{19}$F NMR spectra of photo-polymerized α-NPD in atmosphere, and was hardly seen in the sample polymerized in nitrogen chamber.

The results described above can be explained by different spin states of forming carbenes. As was mentioned previously carbenes may exist in two possible electronic spin states: the paired singlet state and the unpaired triplet state. The triplet ground state is proposed for most trifluoromethylaryl carbenes. In the literature it is claimed that singlet state is favored initially, but it rapidly converts to the triplet state. A multiplicity allowed reaction may occur between

Figure 2.8: IR spectra of α-NPD ketone (4) and α-NPD films photo-polymerized in atmosphere and nitrogen chamber and thermo-polymerized in atmosphere.
triplet carbene and atmospheric oxygen (triplet). This reaction is reported to have high efficiency.\textsuperscript{54} It was also shown that triplet carbene generated by photo decomposition of diphenyl diazo compounds in the presence of oxygen yields mostly benzophenone oxide which reacts further to release one oxygen atom.\textsuperscript{55}

The literature and observed results suggest that photo decomposition of $\alpha$-NPD diazirine (16) yields triplet ground state carbenes, which are highly reactive with oxygen and tend to form ketones in presence of oxygen, upon UV irradiation. Contrary, thermal decomposition of $\alpha$-NPD diazirine (16) produces singlet ground state carbenes that are inert towards oxygen. An overview of photo- and thermo- cross-linking processes in the presence of oxygen is depicted in Scheme 2.17:

**Scheme 2.17:** Reaction of diazirine group with aromatics and presence of oxygen. Scheme partially adapted from reference 7.
2.2.4 Photo-Patterning

The fabrication of OLED display requires different layers to be structured to form pixels and subpixels. Several methods are available for such structuring purposes: inkjet printing\textsuperscript{56}, screen printing,\textsuperscript{57} and usage of shadow masks.\textsuperscript{58}

Diazirine containing organic semiconductor molecules were developed in order to obtain structured and insoluble layers by photo-cross-linking. Since the cross-linking of diazirines is induced by UV light, the organic films become not only insoluble, but can simultaneously be patterned as a negative photoresist using standard photolithography techniques.\textsuperscript{59} A schematic picture of this approach is shown in Figure 2.9.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{shadow_mask.png}
\caption{Patterning of photo-cross-linking molecules by using of shadow mask. Picture is reproduced from reference 19.}
\end{figure}

Photo-patterning is considered to be a very promising method among all commonly used techniques of fabricating structured OLEDs.

Deposition of layers and patterning by photo-cross-linking was performed as described in Figure 2.10.
Figure 2.10: *Layer deposition and patterning by photo-cross linking.*

1) The photo-crosslinkable monomeric material, dissolved in chloroform, is deposited onto a clean substrate by spin-coating.

2) A shadow mask is placed on top of the semi-dried monomer film.

3) UV light (365 nm) is shone through the shadow mask to crosslink the material and forms cross-linked polymeric network. The material covered by the shadow mask remains unreacted (monomeric form).

4) Upon removal of the shadow mask, the unreacted monomer is washed off by hexane. The cross-linked polymer is insoluble and remains deposited on the substrate.

The above-described deposition sequence may be repeated as many times as required by the device architecture. Because the cross-linked polymer is insoluble, the following cycles do not degrade the previously deposited layers. On the interface of two layers, the inter-layer polymerization reaction improves adhesion between to successive layers.

By using different masks one can achieve different patterns and shapes, which can be used for OLEDs pixel patterning. The photo-patterning technique was successfully employed within this work to obtained structures from µm to cm scale and higher. Patterned structures with a width of
60 µm and 30 µm gaps in between can be achieved by using a TEM grid as a shadow mask. Single layer patterned films are shown in Figure 2.11.

**Fluorene films:**

**α-NPD films:**

**Figure 2.11:** Fluorescence images of patterned single layer films of α-NPD and fluorene captured with a Kodak image station and confocal microscope.
As explained before, since cross-linking produces insoluble films, several layers can be spin-coated on top of each other and patterned with different shadow masks. Example of this principle are shown in Figure 2.12.

![Figure 2.12](image_url)

**Figure 2.12**: Fluorescence images of patterned fluorene film on top of patterned α-NPD film captured using a Kodak image station and confocal microscope. F = fluorene, NPD = α-NPD.

Fluorescence lifetime imaging microscope (FLIM) was employed to prove that the illustrated bilayer structures are fabricated from two different films (Figure 2.14). The FLIM image 1 was taken in region A and corresponds to the fluorene film (lifetime equal to 2.94 ns). Image 2, captured in region B, represents the fluorescence lifetime of α-NPD film (0.61 ns). The full
window FLIM image 3 shows pertinent to the two polymers (0.61 ns and 2.94 ns respectively), which demonstrates that two different compounds are present in the intersection in Figure 2.13.

![FLIM image of bilayer patterned structure formed by α-NPD and fluorene. τ_{fluorene}=2.94\text{ns}, \tau_{α-NPD}=0.61\text{ns.}]

**Figure 2.13:** FLIM image of bilayer patterned structure formed by α-NPD and fluorene. $\tau_{\text{fluorene}}=2.94\text{ns}$, $\tau_{\alpha-\text{NPD}}=0.61\text{ns}$. 

### 2.3 ELECTROCHEMICAL CHARACTERIZATION AND DETERMINATION OF HOMO AND LUMO OF NPD DERIVATIVES

Cyclic voltammetry (CV) is considered to be an effective method to investigate electrochemical properties of compounds and evaluate the energy of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.⁶⁰
The cyclic voltammograms were measured in solution and solid state (thin films) in a conventional three-electrode cell (Pt working electrode for solutions, glass/ITO working electrode for films) at room temperature. As a control experiment the electrochemical study of plain α-NPD was conducted. The obtained voltammograms in solution and solid state are shown in Figure 2.14 and Figure 2.15, respectively. In the solution state two reversible oxidations are observed while in the solid state α-NPD monomer shows two merged peaks and polymer films show only one visible wave (due to loose in definition). The extracted data (peak and half-way potentials) are summarized in a Table 2.1.

**Figure 2.14:** Cyclic voltammograms of α-NPD and α-NPD derivatives solutions showing oxidation in CH$_2$Cl$_2$/0.1 M TBAP (Pt working electrode, scan rate 100 mV S$^{-1}$).

*Regular NPD (solution in DCM)*
*Diazirinated NPD monomer (solution in DCM)*

*UV polymerized NPD (solution in DCM)*
*Thermally polymerized NPD (solution in DCM)*
Figure 2.15: Cyclic voltammograms of α-NPD and α-NPD derivatives in a solid state showing oxidation in CH$_3$CN/0.1 M TBAP (glass/ITO working electrode, scan rate 500 mV S$^{-1}$).

Table 2.1: Peak, half-wave potentials, and peak separations extracted from cyclic voltammograms in Figure 2.31 and Figure 2.32. Potentials in [V].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^1_{pa}$</th>
<th>$E^2_{pa}$</th>
<th>$E^2_{pc}$</th>
<th>$E^1_{pc}$</th>
<th>$E^1_{1/2}$</th>
<th>$E^2_{1/2}$</th>
<th>$\Delta E^{1,2}_{p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD (solution)</td>
<td>0.69</td>
<td>0.94</td>
<td>0.87</td>
<td>0.61</td>
<td>0.65</td>
<td>0.905</td>
<td>0.255</td>
</tr>
<tr>
<td>NPD monomer (solution)</td>
<td>0.81</td>
<td>1.04</td>
<td>0.93</td>
<td>0.72</td>
<td>0.765</td>
<td>0.985</td>
<td>0.22</td>
</tr>
<tr>
<td>NPD UV polymer (solution)</td>
<td>0.82</td>
<td>1.03</td>
<td>0.93</td>
<td>0.72</td>
<td>0.77</td>
<td>0.98</td>
<td>0.21</td>
</tr>
<tr>
<td>NPD T polymer (solution)</td>
<td>0.8</td>
<td>1.1</td>
<td>0.95</td>
<td>0.72</td>
<td>0.76</td>
<td>1.025</td>
<td>0.265</td>
</tr>
<tr>
<td>NPD monomer (film)</td>
<td>0.76</td>
<td>0.88</td>
<td>0.79</td>
<td>0.64</td>
<td>0.7</td>
<td>0.835</td>
<td>0.135</td>
</tr>
<tr>
<td>NPD UV polymer (film)</td>
<td>0.85</td>
<td>0.78</td>
<td>0.815</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPD T polymer (film)</td>
<td>0.93</td>
<td>0.77</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The first oxidation half-wave potentials of α-NPD derivatives (monomer, UV polymerized polymer, and thermally polymerized polymer) are fairly similar and centered at approximately 0.765 V vs Ag/Ag⁺. The second oxidation appears at about 0.99 V. These processes correspond to the formation of corresponding mono- (α-NPD⁺) and dications (α-NPD²⁺) respectively. Moreover, electrochromic properties of cross-linked α-NPD films were detected during the cyclic voltammetry experiments. Anodic oxidation of polymer films lead to reversible color change from yellowish (in neutral state) to deep blue (in oxidized state) (Figure 2.16). This observation is in agreement with the fact that substituted phenylenediamines have blue-violet color in their oxidized state. For example, N,N,N',N'-tetramethyl-p-phenylenediamine received the trivial name as “Wurster’s blue” because of characteristic blue-violet color of its radical cation form.⁶¹

![Figure 2.16: Electrochromic behavior of the thermally cross-linked α-NPD film on the ITO-coated glass plate in CH₃CN/0.1 TBAP.](image)
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the combination of the oxidation potentials and optical band gaps of corresponding materials as reported previously. According to this method, the value for ferrocene (Fc) was used as -4.8 eV. The HOMO was estimated using the following equation \( E_{\text{HOMO}} = -e \left[ E_{\text{ox}} + 4.8 \right] \) eV, the LUMO was determined by \( E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{optical gap}} \), where \( E_{\text{ox}} \) is the oxidation potentials obtained against Fe\(^{3+}/Fc\). The optical band gap was estimated from the UV-Vis absorption onset. The obtained data are summarized in Table 2.2.

**Table 2.2:** HOMO and LUMO values of \( \alpha \)-NPD and \( \alpha \)-NPD derivatives measured in a solution and in a solid state.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO, eV</th>
<th>LUMO, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD (solution)</td>
<td>-5.18</td>
<td>-2.16</td>
</tr>
<tr>
<td>NPD monomer (solution)</td>
<td>-5.24</td>
<td>-2.18</td>
</tr>
<tr>
<td>NPD UV poly (solution)</td>
<td>-5.23</td>
<td>-2.18</td>
</tr>
<tr>
<td>NPD T poly (solution)</td>
<td>-5.22</td>
<td>-2.14</td>
</tr>
<tr>
<td>NPD monomer (film)</td>
<td>-5.27</td>
<td>-2.22</td>
</tr>
<tr>
<td>NPD UV poly (film)</td>
<td>-5.38</td>
<td>-2.37</td>
</tr>
<tr>
<td>NPD T poly (film)</td>
<td>-5.44</td>
<td>-2.41</td>
</tr>
</tbody>
</table>

In literature the reported HOMO and LUMO levels of \( \alpha \)-NPD varies from -5.0 – -5.5 eV for HOMO and -2.1 – -2.4 eV for LUMO. Within this work the HOMO and LUMO levels of \( \alpha \)-NPD derivative (16) in monomer and polymer states in a solution were relatively close to each other and to the value of plain \( \alpha \)-NPD, while the HOMO and LUMO of the thin films were slightly below. Since these molecular orbital energies are affected by intermolecular interactions, depending on the distance and relative orientation of the molecules, the observed differences in
energies for the solutions and the films are not surprising. The obtained values show that
diazirine groups introduced on a $\alpha$-NPD core do not change its HOMO and LUMO levels
significantly and polymers fabricated by photo- or thermo-cross-linking can be successfully
employed as a hole transport layer in OLEDs.

### 2.4 HOLE CONDUCTIVITY OF CROSS-LINKED $\alpha$-NPD FILMS

To investigate the electrical properties of the films, so-called “hole-only” devices by using
thermally and photo-cross-linked $\alpha$-NPD were fabricated. The device configuration is shown in
Figure 2.17.

![Device Configuration](image)

**Figure 2.17**: Schematic illustration of hole-only devices of the general structure $\text{ITO/PEDOT:PSS/}\alpha$-NPD-polymer/Al.

Figure 2.18 (left) shows the current-voltage diagrams of hole-only devices consisting from cross-
linked $\alpha$-NPD.
**Thermally cross-linked α-NPD film**

**Photo-cross-linked α-NPD film**

**Figure 2.18:** Current-voltage and \([\text{Current density}]^2 - \left(\frac{V^2}{L^3}\right)^2\) diagrams of hole-only devices shown in Figure 2.17.

Since the current vs voltage shows a quadratic dependence at high electric fields, it suggests that the charge transport in hole-only device is coherent with a space charge limited (SCL) model. This model indicates that an Ohmic contact between the organic layer and electrodes is established and allows use of the trap-free SCL current density to estimate the average hole-mobility.⁶⁶

SCLC can be described by
\[ J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \]  

where \( \epsilon \) is dielectric constant (for organic is taken as 3), \( \epsilon_0 \) is vacuum permittivity \((8.85417887 \times 10^{-12} \text{ F} \cdot \text{m}^{-1})\), \( \mu \) is carrier mobility, \( V \) is voltage applied, and \( L \) is film thickness.\(^{67}\)

To determine the mobility, experimental data are plotted as \( J^2 \) vs \( \frac{[V^2/L^3]^2}{L^3} \) (Figure 2.18 right). The best linear fitting is calculating above the inflection point (SCLC portion of the curve) and the slope of the fitted function is used to calculate charge mobility using the equation 2.2.

\[
\mu = \frac{9 \cdot \sqrt{\text{Slope}}}{8 \epsilon \epsilon_0 \frac{J^2}{[V^2/L^3]^2}} \]  

The estimated hole mobility of thermally cross-linked \( \alpha \)-NPD was found as 2.41x10\(^{-5} \) cm\(^2\)/Vs and photo-cross-linked film as 8.54x10\(^{-6} \) cm\(^2\)/Vs. The reported value of plain \( \alpha \)-NPD, measured by time-of-flight (TOF) technique, is 4.07x10\(^{-4} \) cm\(^2\)/Vs.\(^{68}\) Since TOF measurements require quite thick films of several microns and the real thickness of organic layer in OLED device is 50-100 nm, the mobility data obtained by TOF may not be directly applicable in the performance simulation because the mobility shows thickness dependence.\(^{69}\) It was shown in literature\(^{69}\) that SCLC measurements conducted for ITO/C\(_{60}\)(2.5 nm)/\( \alpha \)-NPD/Al hole-only device had a mobility decrease from 7.64x10\(^{-4} \) cm\(^2\)/Vs to 1.63x10\(^{-5} \) cm\(^2\)/Vs when the thickness of organic layer was reduced from 1000 nm to 50 nm, respectively. In the current work the thickness of organic layers was in the range of 100-150 nm, consequently the obtained mobility values are in a good agreement with previously reported results.
2.5 CONCLUSION

A new approach towards solution processable organic semiconductor materials for organic electronics has been attempted. The synthesis of target compounds 16, 20, 27, 32, and 37 was successfully accomplished. These materials contain attached diazirine groups which are used to cross-link spin-coated layers by UV irradiation or heating. α-NPD derivative (16) presents the first functionalization of organic hole-transport materials with a diazirine moiety and TPA-based compound (27) is the first diazirine-bearing cross-linker for use in organic electronics. UV-vis spectroscopy was employed to obtain insights in the kinetics of the cross-linking process. Solubility tests have demonstrated the solvent resistance of the cross-linked organic materials. Because of the multilayer architecture of OLEDs this is a beneficial property towards fully solution processable devices. In this work it was also demonstrated that diazirine-functionalized organic semiconductor materials could be patterned by standard photolithographic techniques. By using UV-photomasks of a whole variety and shapes, the patterned image could be transferred onto the organic layer in the device with a feature size down to 50µ. Photolitographic techniques and high patterning resolution may be advantageous for future OLEDs applications. Cyclic voltammetry measurements allowed us to determine the energies of HOMO and LUMO levels and have shown that introduction of diazirine moiety do not change significantly electronic properties of the molecules. HOMO and LUMO energies are coherent with the cross-linked α-NPD as a hole-transport layer in OLEDs. Hole-mobility was measured by SCLC method and was demonstrated in a good agreement with plain α-NPD values.
CHAPTER 3: EXPERIMENTAL SECTION

3.1 GENERAL

Materials: Commercially available solvents and reagents were used as received from the chemical suppliers. All manipulations of air and water sensitive materials were performed in an atmosphere of dried inert gas using oven-dried glassware. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from K-Na alloy under Nitrogen. DCM was distilled from calcium hydride (CaH₂). All other solvents were used as received from the suppliers. Organic phases were dried either over anhydrous Na₂SO₄ or anhydrous MgSO₄ during the reaction work-up. All reactions were monitored using Whatman K6F silica gel 60 Å analytical thin layer chromatography (TLC) plates by UV detection (254 nm and 365 nm). Column chromatography was performed with silica gel 60 Å, 32-63 mm received from EMD Science.

Instrumentation: NMR spectra were obtained from 300 MHz, 500 MHz Bruker Instrument and from 400 MHz Varian Unity 400. Chemical shifts as δ values were referenced to the residual proton resonance of the deuterated solvent (for ¹H NMR) and to the signal of the deuterated solvent (for ¹³C NMR). The signal multiplicity was described as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). GC/MS-spectra were recorded using a gas chromatograph with a 30 m column, 0.25 mm diameter, 0.25 μm thickness combined with a Shimadzu GC-MS QP5050A mass spectrometer. Bruker Daltonics Omniflex spectrometer was used to get MALDI spectra. Absorption spectra were recorded using a diode array HP 8453 UV-Vis spectrophotometer. IR spectra were measured by IR200 spectrometer from Thermo.
Thin films were fabricated by using a WS-400B-6NPP/LITE/8K spin coater from Laurrell. Photolysis was performed with a Spectroline ENF 280C UV lamp at 365 nm, at a voltage of $U = 115$ V, working with $f = 60$ Hz, 0.2 AMPS and equipped with an 8 W tube. Thickness of thin films was determined by Alpha-Step IQ surface profiler (KLA Tencor) and was in agreement with values measured by PHE101 discrete wavelength ellipsometer (Armstrong Advanced Inc.). The Dimension Edge Atomic Force Microscope System from Bruker was used to get AFM images of fabricated films and to estimate their roughness. The AFM images were processed by NanoScope software and $R_{max}$ values were obtained after the plane fit procedure. Fluorescence images were captured by the KODAK Image Station 4000 mm PRO system and Olympus FluoView 1000 confocal microscope equipped with a lifetime imaging (FLIM).

Cyclic voltammetry measurements were carried out at room temperature by employing Electrochemical Workstation. The experiments were performed in solution (nitrogen-purged millimolar DCM solution of 16, containing 0.1M of the recrystallized supporting electrolyte tetrabutylammonium perchlorate TBAP) and solid states (nitrogen-purged 0.1 M solution of TBAP in Acetonitrile). The conventional three-electrode configuration consisted of platinum working electrode (solutions) or glass/ITO working electrode (films), a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Each measurement was calibrated using a ferrocene/ferrocenium redox system. Cyclic voltammograms were measured at scan rates of 100 mV s$^{-1}$ (solutions) and 500 mV s$^{-1}$ (films).

Cross-linking and patterning: Thin films were fabricated from diluted solutions (5 mg/1 ml, 10 mg/1 ml, or 20 mg/1 ml) of materials (in chloroform, cyclohexane, or xylene) by spin coating on
clean glass substrates at different rpms. Cross-linking was achieved by a mercury lamp at 365 nm wavelength and an approximate distance (sample-to-lamp) of 3 cm or by heating the sample on a hot plate at 75°C, 90°C, or 110°C.

Photolithography was achieved by UV irradiation through photomasks with different patterns. The sample-to-lamp distance was 3 cm. After development in hexane (or pentane), the un-cross-linked molecules in the unexposed areas could be dissolved and removed. The complete procedure and scheme are shown in Figure 2.10.

_Hole-only device fabrication:_ The ITO-covered glass substrate, which served as an anode, was cleaned with detergent, water, acetone and isopropanol and then dried with nitrogen flow. The cleaned substrate was treated with UV-ozone to remove all the organic materials and to increase the ITO work function. PEDOT:PSS was spin-coated over 1 × 1 in. ITO substrates at 3000 rpm for 15 s and 4000 rpm for 15 s, and annealed at 140°C for 10 min. Compound 16 was dissolved in chloroform (20 mg/1 ml) and spin-coated onto the PEDOT:PSS layer. Cross-linking of 16 was performed by UV light at one sample and by heating at another sample. Aluminum cathode were then deposited by thermal evaporation (~1.5 Å/s) in a high-vacuum chamber (~10^{-6} torr) through a shadow mask with pixel area of 0.04 cm². All the characterization of the devices was performed inside a nitrogen-filled glovebox.
3.2 SYNTHESIS

3.2.1 Synthesis of Diazirine-Functionalized α-NPD

\( N,N'-\text{bis(1-naphtyl)-1,1'-biphenyl-4,4'-diamine} \)

\[
\begin{align*}
\text{Pd}_2(\text{dba}_3) & \quad (0.22 \text{ g, 0.24 mmol}) \quad \text{and} \quad \text{DPPF} & \quad (0.26 \text{ g, 0.48 mmol}) \quad \text{were} \\
\text{dissolved in degassed toluene (100 ml) stirred for 10 minutes in} \\
\text{argon atmosphere.} \quad \text{1-Naphtylamine (2.64 g, 18.4 mmol),} \\
\text{4,4'-dibromodiphenyl (2.5 g, 8.01 mmol), and} \quad \text{t-BuONa (2.45 g, 25.6 mmol) were added and the} \\
\text{resulting solution was stirred at 90°C for 16 hours. The precipitate was filtered and washed with} \\
\text{toluene followed by THF in a separate flask. After evaporation of THF the residue was purified} \\
\text{by column chromatography on silica gel (DCM/ethyl acetate, v/v, 15/1) to give a solid 1 (3.1 g,} \\
\text{90%).} \\
\text{1H NMR (500 MHz, DMSO-d_6) } \delta (\text{ppm}): & \quad 8.29 \text{ (s, 2H),} \\
& \quad 8.22-8.20 \text{ (m, 2H),} \\
& \quad 7.90-7.88 \text{ (m, 2H),} \\
& \quad 7.54-7.48 \text{ (m, 10H),} \\
& \quad 7.43-7.41 \text{ (m, 2H),} \\
& \quad 7.37-7.36 \text{ (m, 2H),} \\
& \quad 7.14-7.11 \text{ (m, 4H). MALDI-TOF: } m/z = 436.31
\end{align*}
\]

\( N,N'-\text{bis(1-naphtyl)-N,N'-di(4-bromophenyl)-1,1'-biphenyl-4,4'-diamine} \)

\[
\begin{align*}
\text{Amine 1} & \quad (0.7 \text{ g, 1.6 mmmol),} \\
\text{1-bromo-4-iodobenzene} & \quad (1.79 \text{ g, 6.4 mmol),} \\
\text{K}_2\text{CO}_3 & \quad (1.98 \text{ g, 14.4 mmol),} \\
\text{Cu} & \quad (0.252 \text{ g, 4 mmol),} \\
\text{18-crown-6 ether} & \quad (0.1 \text{ g, 0.4 mmol) were mixed in 1,2-} \\
\text{dichlorobenzene (15 ml). The reaction mixture was stirred for} \\
\end{align*}
\]
days at 230°C. The precipitate was filtered and the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, v/v, 10/1) to give a compound 2 (0.75 g, 61%) as a solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.93-7.90 (m, 4H), 7.81 (d, \(J = 8.5\) Hz, 2H), 7.52-7.46 (m, 6H), 7.41-7.39 (m, 6H), 7.35 (d, \(J = 7\) Hz, 2H), 7.31-7.29 (m, 2H), 7.10-7.06 (m, 4H), 6.93-6.92 (m, 2H), 6.81-6.79 (m, 2H). \(^1\)C NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 146.81, 146.62, 142.76, 137.94, 135.30, 134.49, 134.34, 132.04, 130.98, 128.52, 127.32, 126.9, 126.65, 126.39, 126.32, 124.01, 122.53, 122.34. MALDI-TOF: \(m/z = 746.21\)

\(N,N^\prime\)-bis(1-naphtyl)-\(N,N^\prime\)-di(4-(trifluoroacetophenone))-1,1'-biphenyl-4,4'-diamine

\[ \text{To a stirring suspension of bromide 2 (0.5 g, 0.67 mmol) in dry THF (10 ml) under argon atmosphere at -78°C, } \]
\(\text{n-butillithium (0.98 ml, 1.55 mmol, 1.6 M in hexanes) was added slowly and the solution was stirred for 40 minutes at -78°C. Then ethyltrifluoroacetate (0.22 ml, 1.67 mmol) was added and the solution was stirred for 40 more minutes. The reaction was quenched with water (10 ml), extracted with diethylether (100 ml) and dried over MgSO}_4. \]
\(\text{Filtration, removal of the solvent, and purification by column chromatography in hexanes/DCM (v/v, 1.5/1) yielded the compound 4 (0.27 g, 52%) as a yellow solid. } \)
\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.98 (d, \(J = 8.5\) Hz, 2H), 7.92 (d, \(J = 8\) Hz, 2H), 7.90-7.88 (m, 6H), 7.59-7.52 (m, 8H), 7.49-7.45 (m, 4H), 7.36-7.33 (m, 4H), 6.93-6.90 (m, 4H). \(^1\)C NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 178.23 (q, \(J = 33.4\)Hz), 154.19, 144.80, 141.04, 136.92, 135.29, 132.25, 130.68, 128.79, 128.30, 128.02, 127.61, 127.32, 126.70, 126.42, 125.23, 123.35,
121.078, 117.20, 117.13 (q, J = 289.7 Hz). $^{19}$F NMR (400 MHz, CDCl$_3$) δ (ppm): -70.25. MALDI-TOF: $m/z = 780.45$.

$N,N'$-bis(1-naphthyl)-$N,N'$-di(4-(trifluoroacetophenone oxime))-1,1'-biphenyl-4,4'-diamine

The solution of ketone 4 (0.45 g, 0.57 mmol) and hydroxylamine hydrochloride (0.225 g, 2.85 mmol) in ethanol (2 mL) and pyridine (4 ml) was stirred at 70°C for 5 h. The solvents were evaporated and the residue was partitioned between diethyl ether (100 ml) and citric acid (30 ml, 10% in water). The organic layer was washed with water (30 ml) and dried over MgSO$_4$. After evaporation of the solvents, the crude oxime was purified by column chromatography in DCM to furnish 0.42 g (89%) of the title compound as a yellowish solid. $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.53 (s, 2H), 7.94 (d, J = 8.5 Hz, 4H), 7.86 (d, J = 8Hz, 2H), 7.55-7.41 (m, 16H), 7.24-7.23 (m, 4H), 7.03-7.02 (m, 2H). $^{13}$C NMR (500 MHz, CDCl$_3$) δ (ppm): 150.06, 146.88 (q, J = 31.6 Hz), 145.88, 142.18, 135.36, 135.32, 131.13, 130.05, 128.56, 127.66, 127.54, 127.43, 126.87, 126.42, 123.86, 123.68, 120.87 (q, J = 274.3 Hz), 118.86, 117.20. $^{19}$F NMR (400 MHz, CDCl$_3$) δ (ppm): -65.13. MALDI-TOF: $m/z = 810.47$
N,N'-bis(1-naphthyl)-N,N'-di(4-(trifluoroacetophenone-O-(p-Tolysulfonfonyl)oxime)-1,1'-biphenyl-4,4'-diamine

To a solution of oxime 7 (0.3 g, 0.37 mmol), TEA (0.14 ml, 1 mmol), and DMAP (0.009 g, 0.07 mmol) in DCM (2.5 ml) p-toluenesulfon chloride (0.21 g, 1.11 mmol) dissolved in DCM (1 ml) was added dropwise at 0°C. The reaction mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the crude material was partitioned between diethyl ether and water and the organic layer was dried over MgSO₄ and concentrated. Purification by column chromatography in hexanes/ethyl acetate (v/v, 4/1) yielded 0.3 g (74%) of compound 14 as a yellowish solid in the form of mixture of E/Z-isomers. (The purification can be skipped and crude material can be used in the next step).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.96-7.87 (m, 10H), 7.57-7.42 (m, 12H), 7.39-7.35 (m, 8H), 7.29-7.26 (m, 4H), 6.95-6.92 (m, 4H), 2.48 (s, 6H).

N,N'-bis(1-naphthyl)-N,N'-di(4-((3-trifluoromethyl)-3-phenyl)diaziridine)-1,1'-biphenyl-4,4'-diamine

14 (0.3 g, 0.27 mmol) was placed in an autoclave and dissolved in DCM (20.0 ml). After cooling to -78°C, liquid ammonia was introduced to the reaction flask via cannula. The resulting mixture was stirred for 18 h while it was warmed up to room temperature. DCM and excess ammonia was carefully evaporated and the residue was partitioned between water and diethyl ether. The organic layer was separated and dried over
MgSO₄. Purification by column chromatography was done in DCM/ethyl acetate (v/v, 15/1) to give 0.15 g (69%) of diaziridine 15. ¹H NMR (500MHz, CDCl₃) δ (ppm): 7.94-7.90 (m, 4H), 7.84 (d, J = 8.5 Hz, 2H), 7.54-7.49 (m, 4H), 7.44-7.38 (m, 12H), 7.17-7.15 (m, 4H), 7.02-7.01 (m, 4H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 149.78, 146.37, 142.59, 135.32, 134.88, 131.11, 128.95, 128.54, 127.49, 127.42, 127.17, 126.74, 126.40, 126.35, 123.93, 123.63 (q, J = 276.9 Hz) 123.53, 123.07, 120.156, 57.66 (q, J = 36 Hz). ¹⁹F NMR (400 MHz, CDCl₃) δ (ppm): -75.12. MALDI-TOF: m/z = 808.49

N,N'-bis(1-naphthy)-N,N'-di((3-trifluoromethyl)-3-phenyl)-3H-diazirine)-1,1'-biphenyl-4,4'-diamine

Diaziridine 15 (0.2 g, 0.0.248 mmol) was dissolved in MeOH (10.0 mL) and TEA (0.44 mL) and a solution of iodine (0.129 g, 0.508 mmol) in MeOH (5 mL) was introduced dropwise at room temperature in the dark. The mixture was stirred for 30 min and MeOH and TEA were removed under reduced pressure. Aqueous work-up using diethyl ether and purification by column chromatography in hexanes/acetone (v/v, 6/1) yielded 0.158 g (70 %) of diazirine 16 as a yellowish solid. ¹H NMR (500MHz, CDCl₃) δ (ppm): 7.93 (d, J = 8Hz, 2H), 7.88 (dd, J₁ = 8.5 Hz, J₂ = 1 Hz, 2H), 7.84 (d, J = 8 Hz, 2H), 7.53-7.49 (m, 4H), 7.44-7.39 (m, 6H), 7.36 (dd, J₁ = 7.5 Hz , J₂ = 1Hz, 2H), 7.16-7.13 (m, 4H), 7.01-6.97 (m, 8H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 149.44, 146.21, 142.39, 135.32, 135.05, 131.03, 128.56, 127.46, 127.44, 127.43, 127.26, 126.78, 126.38, 123.83, 123.20, 122.25 (q, J = 273.5 Hz), 120.82, 120.08, 28.32
(q, J = 39.8 Hz). $^{19}$F NMR (400 MHz, CDCl$_3$) δ (ppm): -64.68. MALDI-TOF: m/z = 749.49 (M$^+$-2N$_2$).

3.2.2 Synthesis of Diazirine-Functionalized Diphenyl ether

$1,1'$-(4,4'$^-$-(trifluoroacetophenone))ether

To a stirring suspension of bromide 6 (1 g, 2.98 mmol) in dry THF (25 ml) under argon atmosphere at -78°C n-butillithium (4.65 ml, 7.45 mmol, 1.6 M in hexanes) was added slowly and the solution is stirred for 50 minutes at -78°C. Ethyl trifluoroacetate (1.06 ml, 8.94 mmol) was added dropwise and the solution was stirred for 40 minutes. After being warmed to room temperature the reaction is quenched with water (50 ml), extracted with diethylether (250 ml) and dried over MgSO$_4$. Filtration, removal of the solvent, and purification by column chromatography in hexanes/DCM (v/v, 2/1) yielded a compound 7 (0.53 g, 49%). $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.18-8.15 (m, 4H), 7.23-7.20 (m, 4H).

$1,1'$-(4,4'$^-$-(trifluoroacetophenone oxime))ether

The solution of ketone 7 (0.8 g, 2.2 mmol) and hydroxylamine hydrochloride (0.55 g, 8.8 mmol) in EtOH (4 mL) and pyridine (8 ml) was stirred at 70 °C for 5 h. After evaporation of the solvents under reduced pressure, the residue was partitioned between diethyl ether (100 ml) and citric acid (50 ml, 10% in water). The organic layer was washed with water (50 ml), dried over MgSO$_4$ and filtered. After evaporation of the solvents, the crude oxime
was purified by column chromatography in DCM to furnish 0.66 g (78%) of the title compound as a white solid. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.77 (s, 2H), 7.62-7.60 (m, 4H), 7.18-7.15 (m, 4H).

**1,1’-(4,4’-(trifluoroacetophenone O-(p-Tolylsulfonyl)oxime)ether**

![Diagram](image)

To a solution of oxime \( 17 \) (0.87 g, 2.22 mmol), TEA (0.84 ml, 6 mmol), and DMAP (0.056 g, 0.44 mmol) in DCM (20 ml) p-toluenesulfonyl chloride (1.05 g, 6.7 mmol) dissolved in DCM (10 ml) was added dropwise under stirring at 0°C. After completion of the addition, the reaction mixture was stirred at room temperature for 12 h and the solvent evaporated. The crude material was partitioned between diethyl ether and water and the organic layer was dried over MgSO\(_4\), filtered and concentrated. Purification by column chromatography in hexanes/ethyl acetate (v/v, 4/1) yielded 1.21 g (78%) of compound \( 18 \) as a yellow solid in the form of mixture of E/Z-isomers. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.94-7.91 (m, 4H), 7.49 (d, \( J = 8.7 \) Hz, 4H), 7.42 (d, \( J = 8.1 \) Hz, 4H), 7.17-7.14 (m, 4H), 2.51 (s, Me, isomer 1), 2.49 (s, Me, isomer 2).

**1,1’-(4,4’-((3-trifluoromethyl)-3-phenyl)diaziridine)ether**

![Diagram](image)

Tosylate \( 18 \) (0.6 g, 0.85 mmol) was placed in an autoclave and dissolved in DCM (20.0 ml). After cooling to -78°C, liquid ammonia was introduced to the reaction flask via cannula. The resulting mixture was stirred for 18 h
while it was warmed up to room temperature. DCM and excess ammonia were carefully evaporated and the residue was partitioned between water and diethyl ether. The organic layer was separated and dried over MgSO₄. Purification by column chromatography in DCM/ethyl acetate (v/v, 10/1) yielded 0.3 g (91%) of diaziridine 19 as a white solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.63 (d, J = 8.7 Hz, 4H), 7.09-7.06 (m, 4H), 2.82 (d, J = 8.4 Hz, 2H), 2.23 (d, J = 8.4 Hz, 2H).

1,1′-(4,4′-(3-trifluoromethyl)-3-phenyl)-3H-diazirine)ether

Diaziridine 19 (0.15 g, 0.38 mmol) was dissolved in MeOH (15.0 mL) and TEA (0.63 mL) and a solution of iodine (0.202 g, 0.798 mmol) in MeOH (7.5 mL) was added dropwise at room temperature in the dark. The mixture was stirred for 30 min. The solvent was removed under reduced pressure followed by aqueous work-up and extraction with diethyl ether. Purification by column chromatography in hexanes/acetone (v/v, 6/1) yielded 0.125 g (85%) of diazirine 20 as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.22 (d, J = 9 Hz, 4H), 7.05-7.00 (m, 4H).

3.2.3 Synthesis of Diazirine-Functionalized Triphenylamine

Tris(4-bromophenyl)amine

Triphenylamine 21 (3.5 g, 14.3 mmol) was dissolved in 30 ml of chloroform and cooled down to 0°C prior to the dropwise addition of bromine (6.9 g, 43 mmol) in the dark. The resulting solution was stirred
for 1 hour. The product was precipitated by addition of 50 ml ethanol-water (1:1) mixture. After the filtering of white solid, it was recrystallized from from 25 ml of chloroform, filtered off, and dried in vacuum. 22 was obtained as white crystals with yield of 88%. $^1$H NMR (300 MHz, CDCl3): $\delta = 6.92$ (d, $J = 8.8$ Hz, 6H), 7.35 (d, $J = 8.8$ Hz, 6H); $^{13}$C (300 MHz, CDCl3): $\delta = 146.07, 132.54, 125.63, 116.08$

**Tris-(4-(trifluoroacetophenone))amine**

To a stirring solution of bromide 22 (1 g, 2.98 mmol) in dry THF (25 ml) under argon atmosphere at -78°C $n$-butillithium (4.65 ml, 7.45 mmol, 1.6 M in hexanes) was added slowly and the solution is stirred for 30 minutes at -78°C. Ethyl trifluoroacetate (1.06 ml, 8.94 mmol) was added dropwise and the resulting solution was stirred for 30 minutes. After being warmed to room temperature the reaction was quenched with water (40 ml), extracted with diethylether (100 ml) and dried over MgSO$_4$. Filtration, removal of the solvent, and purification by column chromatography in hexanes/DCM (v/v, 2/1) yielded a compound 7 (0.65 g, 41%). $^1$H NMR (500 MHz, CDCl3) $\delta$ (ppm): 8.10 (d, $J = 8$ Hz, 6H), 7.31-7.28 (m, 6H). $^{13}$C (500 MHz, CDCl3) $\delta$ (ppm): 178.79 (q, $J = 36$ Hz), 151.32 132.28, 126.20, 124.50, 116.44 (q, $J = 227.75$ Hz).
**Tris-(4-(trifluoroacetophenone oxime))amine**

The solution of ketone 23 (0.5 g, 0.94 mmol) and hydroxylamine hydrochloride (0.26 g, 3.75 mmol) in ethanol (4 mL) and pyridine (8 ml) was stirred at 70°C for 5 h. The solvents were evaporated and the residue was partitioned between diethyl ether (50 ml) and citric acid (20 ml, 10% in water). The organic layer was washed with water (15 ml) and dried over MgSO₄. After evaporation of the solvents, the crude oxime was purified by column chromatography in DCM and then in DCM/acetone mixture (v/v, 9/1) to furnish 0.41 g (76%) of the title compound as mixture of E/Z-isomers. ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): 13.01 (s, 2H, isomer 1), 12.78 (s, 1H, isomer 2), 7.53-7.47 (m, 6H), 7.19-7.14 (m, 6H).

**Tris-(4-(trifluoroacetophenone O-(p-Tolylsulfonyl)oxime))amine**

To a solution of oxime 24 (0.32 g, 0.54 mmol), TEA (0.52 ml, 3.78 mmol), and DMAP (0.004 g, 0.32 mmol) in DCM (10 ml) p-toluenesulfonyl chloride (0.36 g, 1.89 mmol) dissolved in DCM (3 ml) was added dropwise at 0°C. The reaction mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the crude material was partitioned between diethyl ether and water and the organic layer was dried over MgSO₄, and concentrated. Purification by column chromatography in hexanes/DCM (v/v, 1/1) yielded 0.39 g (69%) of compound 25 as a solid. (The purification can be skipped and crude
material can be used in the next step). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.95-7.93 (m, 6H), 7.45 (d, J = 8.5Hz, 6H), 7.43 (d, J = 8 Hz , 6H), 7.24-7.22 (m, 6H), 2.51 (s, 9H).

**Tris-(4-(((3-trifluoromethyl)-3-phenyl)diaziridine))amine**

25 (0.4 g, 0.38 mmol) was placed in an autoclave and dissolved in DCM (20.0 ml). After cooling to -78°C, liquid ammonia was introduced to the reaction flask via cannula. The resulting mixture was stirred for 18 h while it was warmed up to room temperature. DCM and excess ammonia was carefully evaporated and the residue was partitioned between water and diethyl ether. The organic layer was separated and dried over MgSO$_4$. Purification by column chromatography was done in DCM/ethyl acetate (v/v, 10/1) to give 0.14 g (65%) of diaziridine 26. $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.51 (d, J = 8.5 Hz, 6H), 7.07-7.04 (m, 6H), 4.11 (d, J = 8 Hz, 3H), 3.97 (d, J = 8 Hz , 3H); $^{13}$C (500 MHz, CDCl$_3$) δ (ppm): 147.97, 130.58, 127.44, 124.67 (q, J = 276.8 Hz), 123.90, 57.48 (q, J = 34.6 Hz).

**Tris-(4-(((3-trifluoromethyl)-3-phenyl)-3H-diazirine))amine**

Diaziridine 26 (0.03 g, 0.052 mmol) was dissolved in MeOH (7 ml) and TEA (0.11 ml) and a solution of iodine (0.04 g, 0.17 mmol) in MeOH (3 ml) was introduced dropwise at room temperature in the dark. The mixture was stirred for 30 min and MeOH and TEA were removed under reduced pressure. Aqueous work-up using diethyl ether
and purification by column chromatography in pentane yielded 0.027 g (90%) of diazirine 16 as a solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 7.11-7.09 (m, 6H), 7.07-7.05 (m, 6H). $^{13}$C (500 MHz, CDCl$_3$) $\delta$ (ppm): 147.65, 127.88, 124.32, 124.23, 122.09 (q, $J = 272.6$ Hz), 28.25 (q, $J = 40.6$ Hz).

### 3.2.4 Synthesis of Diaziridinene-Modifiers

The synthesis of 32 and 37 was reproduced from references 30 and 44.

**1-(4-iodophenyl)-2,2,2-Trifluoroethanone**

![Formula of 29](image)

To a stirring suspension of 1,4-diiodobenzene (4.00 g, 12.12 mmol) in diethyl ether (50 mL) at -78°C n-butyllithium (8.3 mL, 13.4 mmol, 1.6 M in hexanes) was added slowly over 30 minutes and stirred for 30 minutes at -78°C. Ethyl trifluoroacetate (1.98 g, 13.9 mmol) was added drop wise and the solution is stirred for 1 h at room temperature. The reaction was quenched with 50 mL of water, extracted with 150 mL diethyl ether and dried over MgSO$_4$. Filtration, removal of the solvent and purification by column chromatography in hexanes/DCM = 1/1 yield 2.55 g (69%) of 29 as a pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 7.98-7.85 (m, 2H), 7.80-7.68 (m, 2H). GC-MS: m/z = 300 (M$^+$) 231 (M$^+$-CF$_3$), 203 (M$^+$-CF$_3$C(O)), 104 (M$^+$-CF$_3$I)
**1-(4-iodophenyl)-2,2-Trifluoroethanone Oxime**

The solution of ketone 29 (1.07 g, 3.57 mmol) and hydroxylamine hydrochloride (0.25 g, 3.6 mmol) in ethanol (3 mL) and pyridine (6 ml) was stirred at 70°C for 5 h. The solvents were evaporated and the residue was partitioned between diethyl ether (50 ml) and citric acid (30 ml, 10% in water). The organic layer was washed with water (30 ml) and dried over Na₂SO₄. After evaporation of the solvents, the crude oxime was purified by column chromatography in DCM to furnish 0.85 g (76%) of the title compound as a colorless solid in the form of a mixture of E/Z-isomers. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.30 (s, 1H, isomer 1), 8.03 (s, 1H, isomer 2), 7.87-7.77 (m, 2H), 7.29-7.24 (m, 2H). GC-MS: m/z = 315 (M⁺), 203 (M⁺-CF₃CNOH).

**1-(4-iodophenyl)-2,2-Trifluoroethanone O-(p-Tolylsulfonyl)Oxime**

To a solution of oxime 30 (0.3 g, 0.95 mmol), TEA (0.16 ml, 1.18 mmol), and DMAP (0.009 g, 0.09 mmol) in DCM (5 ml) p-toluenesulfonyl chloride (0.2 g, 0.95 mmol) dissolved in DCM (1.5 ml) was added dropwise at 0°C. The reaction mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the crude material was partitioned between diethyl ether and water and the organic layer was dried over MgSO₄, and concentrated to give 0.34g (77%) of 31 as a colorless solid in the form of mixture of E/Z-isomers. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.91-7.78 (m, 2H), 7.42-7.38 (m, 2H), 7.2-7.13 (m, 2H), 2.50 (s, 1.5H, isomer 1), 2.48 (s, 1.5H, isomer 2). GC-MS: m/z = 469 (M⁺), 299 (M⁺-OTs).
**1-(4-iodophenyl)-3-(trifluomethyl)diaziridine**

31 (0.3 g, 0.63 mmol) was placed in an autoclave and dissolved in DCM (5.0 ml). After cooling to -78°C, liquid ammonia was introduced to the reaction flask via cannula. The resulting mixture was stirred for 18 h while it was warmed up to room temperature. DCM and excess ammonia was carefully evaporated and the residue was partitioned between water and diethyl ether. The organic layer was separated and dried over MgSO₄. Purification by column chromatography was done in chloroform to give 0.123 g (63%) of diaziridine 32. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.82-7.80 (m, 2H), 7.79-7.77 (m, 2H), 2.80 (d, J = 8.5 Hz, 1H), 2.20 (d, J = 8.5 Hz, 1H). GC-MS: m/z = 314 (M⁺), 230 (M⁺-CF₃NH), 203 (M⁺-CF₃CNH₂).

**1-(4-bromophenyl)-2,2,2-Trifluoroethanone**

To a stirring suspension of 1,4-dibromobenzene (3.00 g, 12.76 mmol) in dry THF (50 ml) at -78°C n-butyllithium (8.75 mL, 14 mmol, 1.6 M in hexanes) was added slowly over 30 minutes and stirred for 30 minutes at -78°C. Ethyl trifluoroacetate (2.35 g, 16.5 mmol) was added dropwise and the solution is stirred for 1 h at room temperature. The reaction was quenched with 50 mL of water, extracted with 150 mL diethyl ether and dried over MgSO₄. Filtration, removal of the solvent and purification by column chromatography in hexanes/DCM = 1/1 yield 2.16 g (67%) of 34 as colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.99-7.87 (m, 2H), 7.76-7.64 (m, 2H).
**1-(4-bromophenyl)-2,2-Trifluoroethanone Oxime**

![Chemical Structure](image1.jpg)

The solution of ketone 34 (1 g, 3.96 mmol) and hydroxylamine hydrochloride (0.29 g, 4.2 mmol) in ethanol (3 ml) and pyridine (6 ml) was heated to 70°C for 5 h. The solvents were evaporated and the residue was partitioned between diethyl ether (50 ml) and citric acid (30 ml, 10% in water). The organic layer was washed with water (30 ml) and dried over Na₂SO₄. After evaporation of the solvents, the crude oxime was purified by column chromatography in Hexane/EtOAc (v/v, 10/1) to furnish 0.85 g (81%) of the title compound as a colorless solid in the form of a mixture of E/Z-isomers. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.92 (s, OH, isomer 1), 8.88 (s, OH, isomer 2), 7.65-7.53 (m, 2H), 7.42-7.32 (m, 2H), 8.30 (s, 1H, isomer 1), 8.03 (s, 1H, isomer 2), 7.87-7.77 (m, 2H), 7.29-7.24 (m, 2H).

**1-(4-bromophenyl)-2,2-Trifluoroethanone O-(p-Tolylsulfonyl)Oxime**

![Chemical Structure](image2.jpg)

To a solution of oxime 35 (1 g, 3.75 mmol), TEA (0.8 ml, 5.6 mmol), and DMAP (0.007 g, 0.56 mmol) in DCM (5 ml) p-toluenesulfonyl chloride (0.9 g, 4.9 mmol) dissolved in DCM (1.5 ml) was added in portions at 0°C. The reaction mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the crude material was partitioned between diethyl ether and water and the organic layer was dried over MgSO₄, and concentrated to give 1.35g (85%) of 36 as a yellowish solid in the form of mixture of E/Z-isomers. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.86 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 2.45 (s, 3H).
1-(4-bromophenyl)-3-(trifluoromethyl)diaziridine

36 (0.3 g, 0.71 mmol) was placed in an autoclave and dissolved in DCM (5.0 ml). After cooling to -78°C, liquid ammonia was introduced to the reaction flask via cannula. The resulting mixture was stirred for 18 h while it was warmed up to room temperature. DCM and excess ammonia was carefully evaporated and the residue was partitioned between water and diethyl ether. The organic layer was separated and dried over MgSO₄. Purification by column chromatography was done in chloroform to give 0.136 g (72%) of diaziridine 37. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.55 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 2.80 (d, J = 8.4 Hz, 1H), 2.19 (d, J = 8.4 Hz, 1H).

3.2.5 Synthesis of Diaziridine-Functionalized Compounds under Suzuki Conditions

1,1'-biphenyl-4(3-(trifluoromethyl)-3-phenyl)diaziridine

32 (0.1 g, 0.318 mmol), phenylboronic acid (0.043 g, 0.35 mmol), palladium acetate (0.011 g, 0.016 mmol), and trio-o-tolylphosphine (0.015 g, 0.048 mmol) were mixed in 10ml of distilled THF and degassed for 30 minutes. K₂CO₃ was dissolved in distilled water and degassed. After solutions were combined, the reaction mixture was stirred at 60°C for 20 hours in nitrogen atmosphere. Then it was partitioned between water and diethyl ether. Organic layer was washed with 2M NH₄OH solution, water, and dried over MgSO₄. After evaporation of the solvent, the resulting solid was purified by column chromatography in DCM to give 0.06 g (72%) of 39 as a solid. ¹H NMR (500 MHz,
CDCl$_3$ $\delta$ (ppm): 7.72 (d, $J = 8$ Hz, 2H), 7.67-7.66 (m, 2H), 7.62-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.42-7.39 (m, 1H), 2.86 (s, 1H), 2.29 (s, 1H). $^{13}$C (500 MHz, CDCl$_3$) $\delta$ (ppm): 143.14, 140.09, 130.54, 128.93, 128.54, 127.91, 127.49, 127.21, 123.57 (q, $J = 276.5$ Hz), 57.88 (q, $J = 35.7$ Hz).

$^{4}$-(1-naphtyl)-(3-trifluoromethyl)-3-phenyl)diaziridine

32 (0.1 g, 0.318 mmol), 1-naphtylboronic acid (0.06 g, 0.35 mmol), palladium acetate (0.011 g, 0.016 mmol), and trio-o-tolylphosphine (0.015 g, 0.048 mmol) were mixed in 10 ml of distilled THF and degassed for 30 minutes. $\text{K}_2\text{CO}_3$ was dissolved in distilled water and degassed. After solutions were combined, the reaction mixture was stirred at 60°C for 20 hours in nitrogen atmosphere. Then it was partitioned between water and diethyl ether. Organic layer was washed with 2M NH$_4$OH solution, water, and dried over MgSO$_4$. After evaporation of the solvent, the resulting solid was purified by column chromatography in DCM to give 0.061 g (58%) of 41 as a solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 8.07 (s, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.96-7.90 (m, 2H), 7.81-7.79 (m, 2H), 7.77-7.74 (m, 3H), 7.57-7.52 (m, 2H), 2.88 (d, $J = 8.5$ Hz), 2.32 (d, $J = 8.5$ Hz). $^{13}$C (500 MHz, CDCl$_3$) $\delta$ (ppm): 143.05, 137.36, 133.58, 132.86, 130.612, 128.69, 128.64, 128.28, 127.75, 127.70, 126.52, 126.34, 126.14, 125.28, 123.59 (q, $J = 276.2$ Hz), 57.92 (q, $J = 35.2$ Hz).
3,3′-(9,9-Dihexyl-9H-fluorene-2,7-diyl)bis[3-(trifluoromethyl)-3H-diaziridine-3-yl-phenyl]

32 (0.1 g, 0.318 mmol), 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.09 g, 0.17 mmol), palladium acetate (0.011 g, 0.016 mmol), and trio-o-tolylphosphine (0.015 g, 0.048 mmol) were mixed in 10 ml of distilled THF and degassed for 30 minutes. K₂CO₃ was dissolved in distilled water and degassed. After solutions were combined, the reaction mixture was stirred at 60°C for 20 hours in nitrogen atmosphere. Then it was partitioned between water and diethyl ether. Organic layer was washed with 2M NH₄OH solution, water, and dried over MgSO₄. After evaporation of the solvent, the resulting solid was purified by column chromatography in DCM to give 0.043 g (36%) of 41 as a solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.82-7.78 (m, 2H), 7.75-7.71 (m, 8H), 7.63-7.58 (m, 4H), 2.86 (d, J = 8.9 Hz, 2H), 2.29 (d, J = 8.8 Hz, 2H), 2.08-2.02 (m, 4H), 1.16-1.02 (m, 12H), 0.78-0.66 (m, 10H). ¹³C (500 MHz, CDCl₃) δ (ppm): 151.8, 143.5, 140.4, 139.0, 130.4, 128.5, 127.5, 126.2, 123.6 (q, J = 278.1 Hz), 121.5, 120.3, 57.9 (q, J = 36.3 Hz), 55.4, 40.4, 31.3, 29.6, 23.8, 22.5, 14.0.
**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>α-NPD</td>
<td>N,N’-bis(1-naphtyl)-N,N’-diphenyl-1,1’-biphenyl-4,4’-diamine</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(dimethylamino)pyridine</td>
</tr>
<tr>
<td>EI</td>
<td>electron ionization (MS)</td>
</tr>
<tr>
<td>EL</td>
<td>electroluminescence</td>
</tr>
<tr>
<td>EML</td>
<td>emissive layer</td>
</tr>
<tr>
<td>ETL</td>
<td>electron-transport layer</td>
</tr>
<tr>
<td>FLIM</td>
<td>fluorescence lifetime imaging microscope</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>hole-transport layer</td>
</tr>
<tr>
<td>IR</td>
<td>infra red</td>
</tr>
<tr>
<td>ITO</td>
<td>indium-tin oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption/ionization</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
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</table>
NMR  nuclear magnetic resonance spectroscopy
OLED  organic light-emitting diode
PEDOT:PSS  poly(ethylenedioxythiophene) doped with poly(styrene-4-sulfonate)
PVD  physical vapor deposition
PVK  poly(9-vinylcarbazole)
SCLC  space charge limited current
TBAP  tetrabutylammonium perchlorate
TEA  triethylamine
THF  tetrahydrofuran
TLC  thin layer chromatography
TOF  time-of-flight
Ts-  4-toluenesulfonyl-
TFMPA  3-(trifluoromethyl)-3-phenyldiazirine
TPA  triphenylamine
UV  ultraviolet
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