1. **Title of the Project**

Fully Solution-Processed Multilayer Organic Light-Emitting Diodes

2. **Applicant**

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Molecular Electronics – Physics of Organic Semiconductors

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4. **Abstract**

Organic light-emitting diodes (OLEDs) have attracted a lot of interest due to their capability in the fabrication of flexible full-color displays and lighting applications. Although highly efficient OLEDs are produced via high-vacuum evaporation techniques, in order to access a roll-to-roll processing of organic materials on flexible substrates, a solution processing technique, in which layers are coated or printed from solution, is highly preferred. In order to pursue an efficient OLED comparable with their inorganic heterojunction counterparts, a multilayer stack of active materials is needed, including charge injection/transporting/blocking functionalities. In the area of solution-processed OLEDs, realizing multilayer OLED remains problematic; the beneath layer may dissolve due to the solvent of the subsequent layer or an interface mixing problem could occur. Also, in order to fully exploit the ease of fabrication of polymer LEDs, all layers are required to be solution processable. The objective of this project is to investigate a solution-processable electron injection layer that can replace conventional layers deposited by thermal evaporation under high vacuum. In addition, it is of particular interest to improve and optimize the device performance by employing smart strategies to develop multilayer OLEDs processed from solution.

5. **Duration of the Project**

4 years, starting from September 2012

6. Personnel

6.1 Senior-Scientists

Name	Task in Project	Time
Prof. dr. ir. Paul W.M. Blom	Supervision and Management	10 %
Ir. G.A.H. Wetzelaer	Analysis	10 %

6.2 Junior-Scientists and Technicians

Name	Task in Project	Time
PhD Student	Experiments and Analysis	90 %
Jan Harkema	Technical Support	10 %

7 Cost Estimates

7.1 Personnel Positions
One 'onderzoeker in opleiding' position for four years.

7.2 Running Budget
15 K€/year for conferences, summer schools and maintenance.

7.3 Equipment
This project will be supported by the Zernike Institute for Advanced Materials, Groningen University. The equipment needed for this project is already present in the laboratories of the research groups involved or within the Zernike Institute for Advanced Materials and no other support of this kind will be required for this project.

7.4 Budget Summary (in k€)
The expenses are summarized in the following table:

		2012	2013	2014	2015	2016	Total
Position	PhD Student	1	1	1	1	1	
	Postdocs	-	-	-	-	-	
	Technicians	-	-	-	-	-	
	Guests	-	-	-	-	-	
Costs	Personnel	25	50	50	50	25	200
	Running Budget	15	15	15	15	10	70
	Equipment	-	-	-	-	-	-
Total		40	65	65	65	35	270

8   Research Programme

8.1 Introduction

Organic light-emitting diodes (OLEDs) have attracted a lot of interests among scientists due to their great potential in fabricating low-cost, flat-panel and even flexible displays. In this category of light-emitting diodes, organic semiconductors are employed as an active or emissive layer due to their unique electronic properties which combine the electrical properties of conventional inorganic semiconductors and the versatility of organic chemistry. A simple design of OLED consists of a single layer of semiconductor material sandwiched between two electrodes; the anode and cathode, respectively [figure 1(a)]. Main processes that govern the operation of an OLED are charge injection, charge transport and recombination. By considering figure 1 (b), the bottom contact (anode) injects holes into the HOMO level of the organic semiconductor and the top contact (cathode) injects electrons into the LUMO level. The charge carriers move toward each other and due to the coulomb interaction they attract each other which results in the formation of excitons. The formation of excitons is followed by emission of light which is due to a so-called recombination process. Depending on the band gap of the semiconductor, the light output may be created in a region of the visible spectrum.
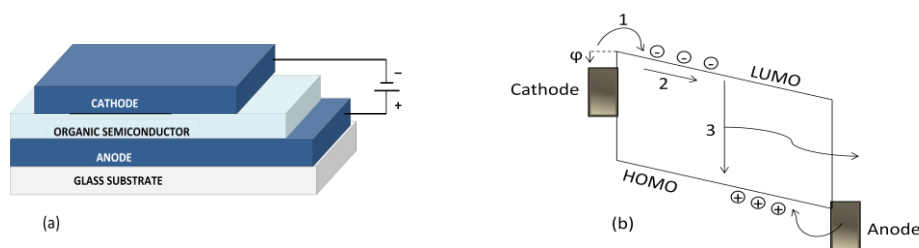
Figure 1. a) Design of a single-layer organic light-emitting diode, b) basic operating processes of OLEDs; 1- charge injection, 2- charge transport and 3- recombination.

Most organic semiconductors have unbalanced charge transport; frequently, hole transport is superior to electron transport. As a result, exciton formation takes place close to the cathode, leading to exciton quenching at the metallic contact. Therefore, a significant portion of the excitons is lost and hence do not generate light. Consequently, the conversion of charges into photons is inefficient. Therefore, engineering or architecting the design of the device is a main step in OLEDs investigations. One of the routes to improve the performance of single-layer OLEDs or polymer light-emitting diodes (PLEDs) is to employ multilayer structures. In this respect, there are a lot of attempts to render OLEDs competitive with inorganic ones [1-6].

8.2 Multilayer OLEDs

In order to overcome the disadvantage of single-layer OLEDs, which is unbalanced charge transport, other materials are employed to play the role of enhancing charge injection or charge transport. These materials are known as hole transporting/injecting or electron transporting/injecting materials. Incorporating these layers into the device gives rise to a multilayer OLED. Based on the class of these materials or the applied technical method for depositing them, two different types of multilayer OLED fabrication routes are realized. One type corresponds to the small molecule OLEDs, in which the device is fabricated via evaporation of low molecular weight molecules under high vacuum. The other one is related to the solution-based polymer LED, concerning all types of organic semiconductors including small molecules, oligomers, polymers and nanoparticles that can be deposited by solution-based methods such as spin coating. The disadvantage of the former method is that thermal evaporation requires relatively expensive vacuum technology, while the latter is a promising route in low-cost fabrication of large-area devices. Many efforts have been done to synthesize new materials that exhibit sufficient charge transport as well as being solution processable [1-6], although there are still big challenges to overcome the limitations of this method. The most important problem in preparation of solution-processed multilayer OLEDs can be summarized as follows: the bottom layer, in most of the cases, can be affected by the solvent of the subsequent layer. Therefore, many attempts have been devoted to propose a general solution for this problematic process. One approach is using intermediate liquid buffer layer to separate layers with different functions [7-9]. The material that is used as a buffer layer must be a viscous nondissolving liquid which, favorably, has a low boiling point. Example of such materials are glycerol and 1,2-propylene glycol [7]. They have high protection capability due to the high viscosity, which arises from hydrogen bonding. In this method, the buffer layer is spin coated on top of the first polymer layer, followed by spin coating the second polymer layer, which cannot be mixed with the buffer layer because of the large difference in viscosities. The buffer layer may evaporate during spin coating the second active layer and the residual of that can be removed by backing in vacuum. This process can be repeated for coating other layers and thus multilayer of solution processed polymers even from the same solvent could be achieved, although the buffer layers may not completely removed and the remaining residue might reduce the device performance.

Using water/alcohol soluble polymers or salts is another approach to fabricate multilayer OLEDs. Since most of the materials used as active layer or emissive layer are hardly soluble in highly polar solvents, water/alcohol soluble materials are suggested for charge transporting layers. Due to their unique solubility, the used polar solvent does not cause erosion of the underlying emissive layer materials upon deposition. Along these lines, a series of triphenylamine-based conjugated polyelectrolytes were reported as effective hole transporting materials [10-12].

Sulfonate groups are characteristic of these materials, which leads to good solubility in polar solvents, while being resistant to commonly used nonpolar solvents such as toluene, chlorobenzene and others. Alternatively, for the first time Cao and coworkers introduced amino-/ammonium-functionalized polyfluorene as electron transporting material and pointed to the water/alcohol soluble property of this material [10, 13-16]. Other efforts in this area can be found in Refs [17-20].

Another suitable method to prevent erosion or mixing of the interfaces in solution-processed OLEDs is to employ cross-linkable materials. These materials consist of special agent groups, which, after being exposed to ultraviolet (UV) irradiation, create an insoluble network. Using this approach, there are many reports on the synthesis of conjugated polymers that include reactive agents, to create optimal conditions for cross-linking [1-5].

Although numerous studies have been done to improve multilayer solution-processed OLEDs, a fully solution-based OLED has still not been achieved. In addition to the hole transport layer (HTL), emissive layer (EML) and electron transport layer (ETL), an organic light-emitting diode includes electrodes. To realize a fully solution-based OLED, the electrodes should also be fabricated from solution-processable materials whose performances are comparable with the efficient traditional ones. An important point is that besides low electrical resistance of these materials, a suitable work function is required, to have efficient charge injection. While Ohmic charge injection is accessible through thermally evaporated charge injection layers, providing such layers from solution is not straightforward. The aim of this project is to develop multilayer solution processed OLEDs by investigating the solution-processable electron injection layer, which is a novel electron injection material called caesium stearate. The general perspective of this work is first to access an efficient electron injection from a solution-based cathode layer, then improve the efficiency of such a single-layer OLED by developing that into multilayer via different approaches discussed above.
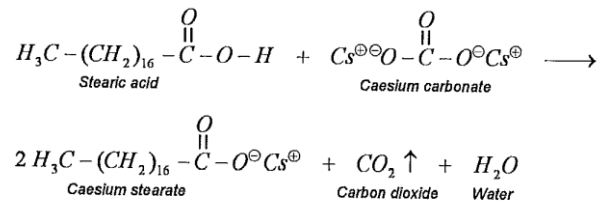
8.3 Scientific Details of the Project

The first step in the operation of an OLED is to have good charge injection. Since inefficient charge injection will strongly limit the device performance, especially in case of semiconductors with low mobility, it is important that the Fermi levels of the electrodes align with the HOMO and LUMO of the organic materials that are used as ETL and HTL in multilayer OLEDs, or EML in single layer OLEDs. Creation of interface barriers between electrodes and organic layers hinder the injection process, resulting in unbalanced charge injection, and as a consequence an excess of one type of charge carrier would decrease the conversion efficiency. In case of a very small energy barrier, the contact can provide any required injection rate and the limitation relates to the intrinsic properties of the polymer. In that case charge transport can be referred to as bulk

limited. In this project, a new caesium salt will be investigated as electron injection material and is introduced below.

8.3.1 Solution Processable Electron-Injection Material

In order to develop a solution-processed electron injection layer that can be spin coated, we propose to use a new salt of caesium that is synthesized from stearic acid and caesium carbonate (Figure 2). A white caesium stearate powder with a high yield can be formed using such a straightforward synthesis. The advantage of caesium stearate (CsSt) with respect to caesium carbonate is that a better solubility as well as better adhesion on top of the polymer surface on which it is spin coated can be obtained, which is due to the long hydrocarbon chain on the caesium stearate.

$$H_3C-(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-O-H \quad + \quad Cs^{\oplus\ominus}O-\overset{\overset{O}{\|}}{C}-O^{\ominus}Cs^{\oplus} \quad \longrightarrow$$

Stearic acid $\qquad\qquad$ Caesium carbonate

$$2\ H_3C-(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-O^{\ominus}Cs^{\oplus} \quad + \quad CO_2\uparrow \quad + \quad H_2O$$

Caesium stearate $\qquad\qquad$ Carbon dioxide $\quad$ Water

Figure 2. The Synthesis of the caesium stearate (CsSt).

Our preliminary results after a broad series of electrical measurements with different polymers and structures based on CsSt spin coated from ethanol solution revealed comparably efficient OLEDs with respect to reference structures containing Ba as cathode interlayer. We expect that using a dual-function material, which can pose electron transporting and hole blocking properties at the same time, would result in significant improvement in the electron injection from CsSt. This material could be polyfluorene with polyethylene glycol (PF-PEG) side chains [21]; an amphiphilic material which is soluble polar solvents like methanol and ethanol. The idea is that a thin layer of PF-PEG doped with CsSt [figure 3] can properly control the electron flux such that a balance in charge injection would be achieved, which is of particular important issue regarding to blue emitting polymers in which electron charge carriers are the dominating carriers. In addition, due to a much higher HOMO level of PF-PEG with respect to HOMO level of emitting polymers, this layer can act as a hole blocking material as well; therefore much reduction in quenching effects close to cathode will be obtained. So, hopefully, PF-PEG can influence the efficiency of device significantly. Due to air-sensitivity of the charge injection layer, it is required to be covered by a stable unreactive metal.
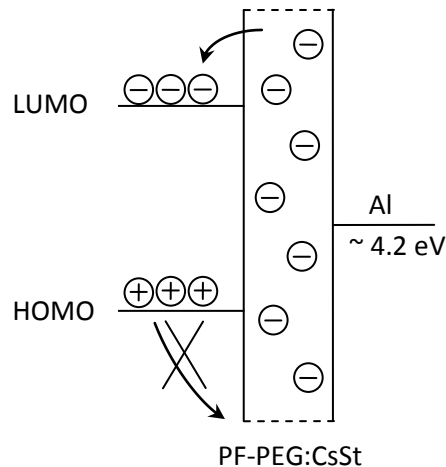
Figure 3. The schematic diagram of interface of PF-PEG:CsSt layer and emitting polymer layer.

8.3.2 HTL Materials

In most of the OLEDs, a conjugated polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT-PSS) is used as a hole injection layer between anode and emissive layer. Although PEDOT-PSS is recognized as a good HTL in PLEDs, the main reason of usage is that it acts as a flattening layer and prevents current leakage caused by local shorts. However, since it is heavily doped, PEDOT-PSS does not function as an electron blocking layer. So, using an additional HTL which is electron blocking at the same time could effectively increase the performance of device. Incorporating an additional HTL in the multilayer stack requires deposition of the sequential layers using orthogonal solvents or a cross-linking method. Some examples of such materials are introduced below.

8.3.2.1 Water/ Alcohol Soluble HTL Materials

With the aid of orthogonal solvents one can produce bilayer structures in such a way that polymer layers with a varying degree of polarity can be deposited on top of each other without erosion at the interfaces. As most of the luminescent polymers used in OLEDs such as poly(phenylene vinylene) (PPV) and polyfluorene derivatives are dissolved in nonpolar solvents, HTL materials are chosen from water/alcohol soluble polymers salts. As an example, a series of triphenylamine-based conjugated polyelectrolytes are shown in figure 4 [10-12]. The common feature of them is the presence of sulfonate groups, which cause a high solubility in polar solvents. Having a relatively high LUMO level is their other unique property, which render them suitable electron blocking materials at the same time.
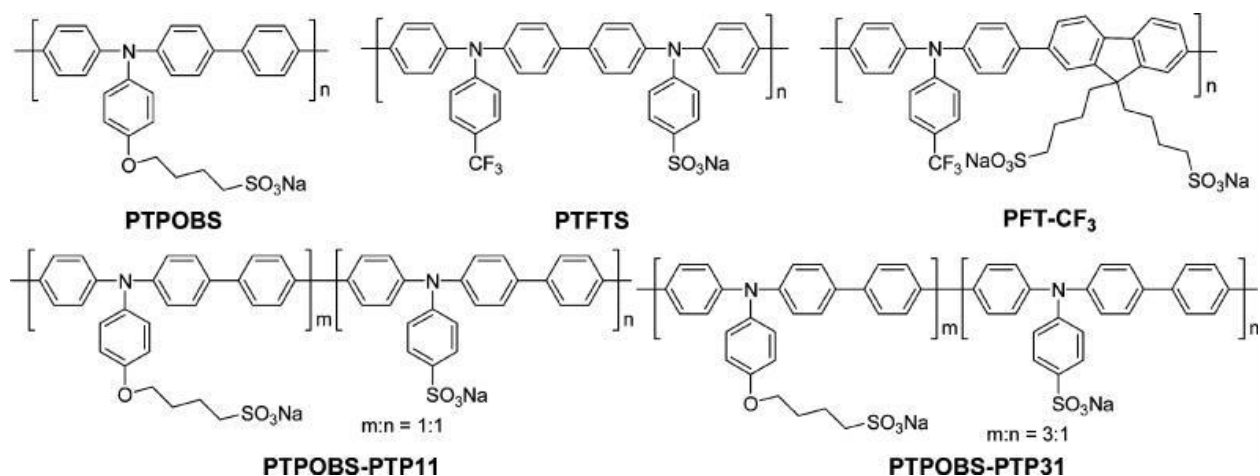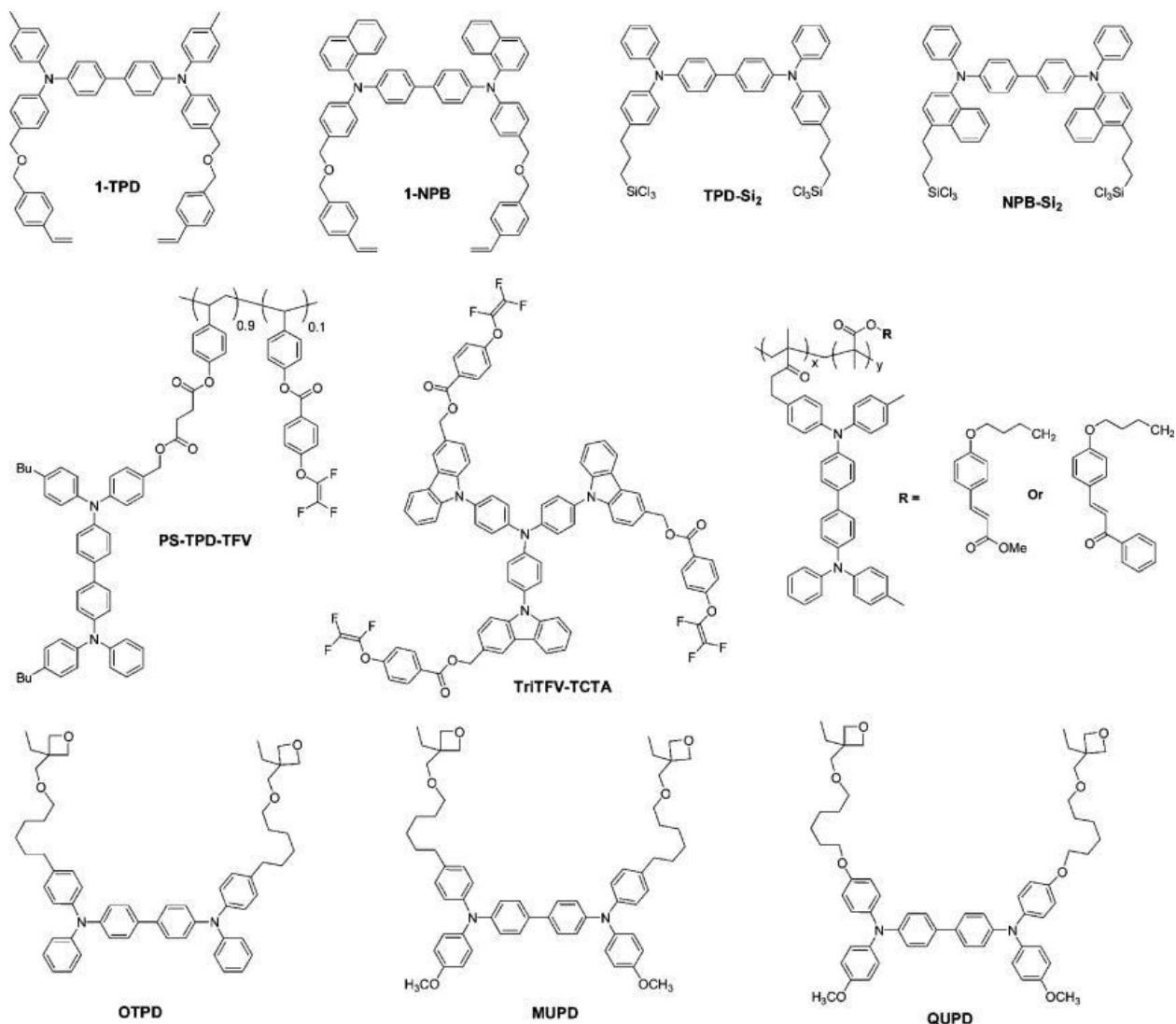
Figure 4. Chemical structures of some Water/ Alcohol soluble HTL materials [10].

8.3.2.2 Cross-Linkable HTL Materials

A well-studied way to synthesize cross-linkable materials is to add efficient side groups to traditional HTL molecules such as *N,N'*-diphenyl-*N,N'*-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), *N,N'*-di-[(1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl)-4,4'-diamine (NPB), 4,4',4''-tris(*N*-carbazolyl)-triphenylamine (TCTA), etc.. These functionalized side groups may be trifluorovinyl ether [22], styrene [23], siloxane [24], oxetane [25] and acrylate [26]. Containing such agent groups enable them to be cross linkable through thermal or UV irradiation treatments and convert them from soluble films into insoluble networks. Some chemical structures of such developed materials are presented in figure 5. Molecules containing trifluorovinyl ether or styrene side chains can be cross linked thermally without using initiators. Derivatives that are based on an oxetane group should be treated with ultraviolet (UV) radiation in the presence of a photoacid initiator.

Another benefit of using cross-linkable HTLs is that, one can form a multilayer of them in such a way that they exhibit a cascade of HOMO levels to facilitate hole injection on one hand, and avoiding quenching effects on the other hand.

Figure 5. Chemical structures of some cross linkable HTL materials [10].

8.4 Project Outline

The goal of this project is to achieve a fully solution-processed OLED, which remains a big challenge in the field of solution-processable OLEDs. To realize that, the first objective is to achieve efficient electron injection by solution depositing a thin film of polyfluorene with PEG side chains which is doped with CsSt, as a cathode interlayer, via spin coating method. The optimum layer with high performance would be generated by adjusting the solution concentration, spin coating condition and testing suitable solvents for making the solution. Once the first objective is reached, the device will be developed into multilayer structures [figure 6]. The use of highly polar polymers or cross-linkable materials are the two strategies

that will be investigated in order to gain efficient HTLs to increase the optical and electrical properties. Finally, characteristics of the device current, as well as the photocurrent, will be modeled to obtain a good understanding of the behavior of the layers, which can help a lot for further improvements in efficiency.
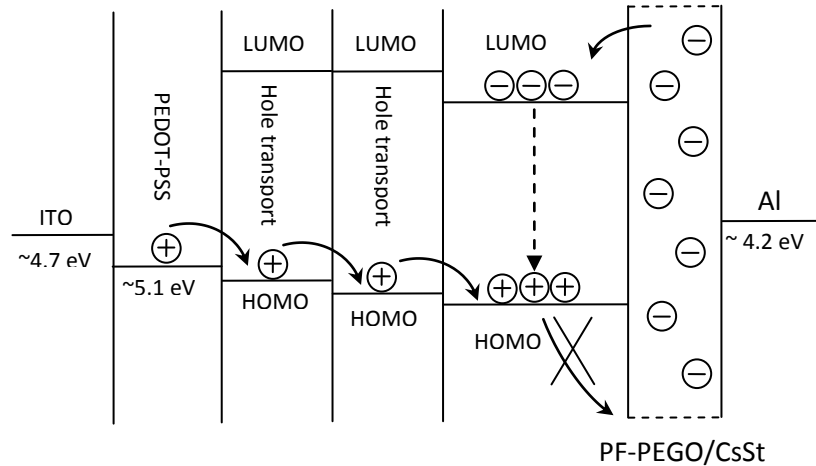
Figure 6. Schematic band diagram of a multilayer OLED.

8.5 Project Timetable

The plan of work is summarized in the following table:

Time	Activity
1st year	✓ Creating a solution-processed cathode layer.
2nd year	✓ Study the electron injection characteristics by modeling and further optimization of that.
3rd year	✓ Fabrication of multilayer OLEDs by developing HTLs.
4th year	✓ Optimizing multilayer OLED using modeling study and writing the thesis.

References

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