Building Organic Light Emitting Diodes with Superconducting Electrodes

Anna Kremen

Submitted in partial fulfillment of the requirements for the Master's Degree in the Physics Department, Bar-Ilan University

Ramat Gan, Israel 2013
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This work was carried out under the supervision of

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1. Abstract

The purpose of this work was to build an organic light emitting diode (OLED) with superconducting electrodes in order to investigate contribution that the correlated Cooper pairs from a superconductor can have on the radiative recombination in the organic semiconductor. The key assumption of this thesis is that Cooper-pairs of electrons can be injected into the organic active material of the OLED, and that their quantum correlation can be maintained within the OLED layers. Recent work by Suemune et. al. on inorganic LEDs with one superconducting electrode showed a Josephson Effect within the semiconductor active layer of the device and a corresponding enhancement of the electroluminescence and shorter radiative recombination lifetime below the critical temperature (T_c) of the superconductor. The use of organics for LED gives us flexible deposition strategies, since in the case of organic small molecules and polymers lattice matching is not constrained. Organic materials show several mechanisms that might enhance the superconductivity's influence, namely large optical transition dipoles that have the tendency to couple to surface plasmons and photons. Furthermore, OLED structures show strictly consistent spin-statistics in their electroluminescence (EL) properties which could be affected by Cooper-Pair injection.

In this work, we present the fabrication challenges we overcame in order to build a functional superconductor (Sc) / organic-semiconductor (Sm) interface. We present electrical and optical measurements of a unique OLED device with two superconducting electrodes at temperatures above and below the T_c of the superconductor. The top electrode of this device is both superconducting and semi-transparent, allowing for emission to be collected through the top contact. Finally, we present strong evidence of the Josephson Effect in a light emitting organic polymer
(MEH-PPV) situated between two superconductor contacts, thus, confirming the basic assumption of this thesis.
2. Organic Light Emitting Diodes (OLED)

2.1 Mechanism and structure of OLEDs

OLEDs are composed of at least one layer of organic semiconductor situated between two electrodes. The organic molecules are electrically conductive and optically active as a result of delocalization of π-electrons caused by bonding of sp² molecular-orbitals. When a voltage is applied across the OLED, electrons are injected into the lowest unoccupied molecular orbitals (LUMO) of the organic layer at the cathode and withdrawn from the highest occupied molecular orbitals (HOMO) at the anode as shown in Figure 1. In this process electrons and holes combine to form excitons, bound states of an electron and a hole. Excitons may form into singlet or triplet states [1]. The decay of a singlet excited state results in rapid emission of radiation in the visible region (the wavelength depending on the difference in energy between the HOMO and LUMO). The decay from triplet states (phosphorescence) is quantum-mechanically spin-forbidden and therefore occurs over a longer timescale, limiting the internal efficiency of most OLED devices [2].

Figure 1: OLED electroluminescence processes (carrier injection, transport, recombination, exciton formation/decay, and light emission) and their efficiencies. Numbers in parentheses represent refractive indices [3].
2.2 Differences between organic and inorganic LEDs

While the working principles of organic and inorganic LED’s are similar, one of the main differences can be the form of the created excitons. Excitons can be categorized by the binding energy of the Coulomb force between the electron and the hole. **Inorganic** semiconductors have a large dielectric constant, $\varepsilon_r \sim 10$, resulting in efficient Dielectric charge screening and therefore small electron-hole binding energies, usually tens of meV (30meV in GaN) [3]. Weakly bound excitons are called Wannier-Mott excitons. Due to the small binding energy in some inorganic materials excitons cannot be formed at room temperature. Once weakly bound Wannier-Mott excitons are formed, they have a large radius spanning over several lattice points and the ability to move freely throughout the lattice as illustrated in Figure 2a.

![Figure 2: Depiction a) Wannier-Mott and b) Frenkel excitons.](image)

**Organic** semiconductors are molecular materials with characteristically wide band gap, low carrier mobility and low melting point. Organic materials are characterized by charge localization to a single molecule and a low dielectric constant, $\varepsilon_r \sim 3$, resulting in strongly bound excitons called Frenkel excitons. Frenkel excitons are localized to individual molecules with binding energy of hundreds of meV (700meV at MEH-PPV) and therefore very small exciton radii, on the order of one lattice cell unit [4]. The type of exciton which is present can significantly affect the light
emitting probability. In inorganic materials, if there is a high defect density (e.g. 0.1% defects), then the weak binding energies and the excitons' ability to move freely throughout the lattice will reduce the light emitting efficiency since a large radius particle moving throughout the lattice has a significant probability of being scattered from lattice defects. On the other hand, in inorganic materials, the small exchange-interaction between the electron and the hole results in almost identical singlet and triplet wave functions, meaning all excitons are radiative. In organic materials due to the localization and small radii of the Frenkel excitons the scattering due to defects is negligible even up to defect densities of 1%. Nevertheless, most organics have the drawback that when electrically excited 75% of the excitons which are formed are non-radiative triplet states [5]. In order to overcome this problem newer research and technology have been used to create Phosphorescent OLED’s which allows close to 100% internal quantum efficiency [6]. As far as device fabrication, OLEDs have the great advantage over inorganic LEDs. Inorganic semiconductor devices use crystalline structure with strong covalent bonds between atoms. Therefore, growth of crystalline inorganic thin films requires a close lattice match to the substrate or the layer on to which it is grown. The thin layers of OLEDs are usually amorphous and therefore lattice matching is not a constraint. Organics can also form crystalline structure which is held by intermolecular Van der Waals interaction. Since this is a relatively weak interaction even organic crystals can be grown with substantial lattice mismatch. This allows compatibility with a large number of substrates, including flexible substrates and relatively cheap and simple fabrication techniques of multilayer device structures.


2.3 Conjugated Polymers

Polymer organic light emitting diodes were first reported in 1990 [7]. Polymer OLEDs are made from organic semiconducting conjugated polymers. The polymer is placed between two metal contacts of asymmetric work-function. One metal contact has a high work function and can only inject holes efficiently. The other contact has a low work function and can only inject electrons efficiently. The injected electrons and holes combine in the light emitting polymer forming excitons. Conjugated polymers are carbon based molecular compounds that are made of a repeating base unit, which can repeat many thousands of times. The conjugation of the polymer is between the double bonded carbon electronic wave functions, which creates collective delocalized \( \pi \)-orbital. The polymer chains may consist of a number of conjugated polymer segments separated by twists or kinks that disrupt the \( \pi \) bonds between different segments of the same physical polymer chain [8]. The mean length of these conjugated segments is described by the term “conjugation length”. The distribution of the conjugation lengths produces a distribution of electronic states in the polymer film. There is also disorder in the electronic structure of the polymer films due to variations in the local arrangement of the polymer chains. The energy structure of conjugated polymer segments is modified by the surrounding polymer chains because of local dipole interactions between neighboring polymer chains. The combined effect broadens the electronic density of the states by about 0.1-0.2 eV [9].

2.4 Carrier Injection

One of the fundamental processes occurring in OLEDs is charge injection from an extended band-like state in the metal contact into a localized molecular polaronic state in the polymer film. Conjugated polymers have negligible intrinsic carrier
concentrations ($< 10^5 \text{cm}^{-3}$) at room temperature and therefore can be treated as undoped semiconductors. The carrier injection from the metal contact into the semiconductor involves the injection of carriers across a potential barrier formed at a metal–semiconductor junction, known as the Schottky barrier. The Schottky barrier ($q\varphi_m$) is the energy difference between the Fermi level ($E_f$) of the metal contact and the LUMO level for electron injection, or similarly, the HOMO level for hole injection. Due to low charge mobility in the semiconductor, after the injection, many electrons will remain at the surface of the organic layer near the interface and will induce equivalent positive charges in the metal layer. As a result of these image charges, the potential of the metal-organic interface is lowered by:

$$\Delta \varphi = \frac{q^2 F}{4\pi \epsilon}$$

Where $F$ is electric field, $q$ is electron charge and $\epsilon$ is the dielectric constant. For a typical polymer dielectric constant $\epsilon = 3$ and electric field of $2 \times 10^5 \text{ V/cm}$, the image force causes the Schottky energy barrier to be lowered by 0.1 eV.

![Diagram of charge transport](image)

**Figure 3:** Illustration of charge transport due to thermionic emission (blue) and tunneling (red).

Two distinctly different mechanisms exist for injection of charge carriers across an interface barrier: thermionic emission of carriers across the Schottky barrier and quantum-mechanical tunneling through the barrier as described in Figure 3 [10].
2.4.1 Thermionic emission
Charge injection at low applied bias is primarily due to thermal emission of charge carriers over the interface potential barrier. The thermionic emission theory assumes that electrons moving towards the barrier will cross the barrier if they are provided with energy larger than the top of the barrier. In this case, the current density through the interface is given by Richardson’s equation:

\[ J = A T^2 e^{-\frac{q\phi_B}{kT}} \]

Were A is the Richardson constant: \[ A = \frac{4\pi q e m k^2}{h^3} \]

The current density is strongly dependent on the temperature (T) and the barrier potential, taking into account the effect of the image force barrier lowering (\( q\phi_B = q\phi_m - q\Delta\phi \)).

Due to disorder in the polymer film, the injected carriers occupy the molecular sites at the contact interface and also at the low-energy end of the distribution. To move further into the organic materials, the carriers must overcome random energy barriers. For this reason, at low applied field, injected carriers can fall back into the metal contact. This process is called interface recombination and it is the inverted process of thermionic emission.

2.4.2 Fowler-Nordheim tunneling
Some charge may overcome the Schottky barrier by thermionic emission at low electric field strengths, but the dominant process for charge injection into the polymer is Fowler-Nordheim (FN) electron tunneling also known as field emission.

In field emission, electrons tunnel through a potential barrier, rather than escaping over it as in thermionic emission. In other words, this process results in changing the height and geometry of the triangular potential barrier, and therefore increasing the electron injection. For a triangular barrier, the FN current density is given by:
\[ J = A F^2 e^{-F_0} \]

Where \( F \) is the electric field and \( A \) and \( F_0 \) are parameters related to the potential barrier through the image-force lowering effect \( \varphi_B \) and are given by:

\[
A = \frac{mq^3}{8\pi h m^* \varphi_B}; \quad F_0 = \frac{8\pi \sqrt{2m^* \varphi_B^3}}{3qh}
\]

In an OLED structure, while some holes can be injected by thermionic emission, the Schottky barrier is much higher for electron injection usually. Hence, an external voltage must be applied to lower the barrier and allow for sufficient carrier injection. The light emitting process in an OLED originates from FN tunneling carrier injection.

### 2.5 Carrier transport

In OLEDs, current density behavior is defined by both the injection properties at the metal-organic interfaces and the bulk transport properties of the organic materials themselves.

Transport of the injected charge inside the polymer depends on the free carrier mobility and the effective density of trapping states within the material.

Charge transport in disordered polymers is regarded as a hopping process between localized sites, which consist of conjugated polymer chain segments [11]. The actual transit rate from one site to another depends on the energy difference and on the distance between the two sites as described by Miller-Abrahams expression [12]:

\[
R(E) = A_0 \exp\left(\frac{-\Delta E}{k_B T}\right) \quad \Delta E > 0
\]

\[
R(E) = A_0 \quad \Delta E \leq 0
\]

Here \( A_0 \) is the maximum hopping rate determined by the intermolecular electronic orbitals and \( \Delta E \) is the energy separation between sites. When \( \Delta E \geq 0 \), the hopping
process from an initial state of lower energy to a final state of higher energy is made difficult by the exponential temperature dependence. Still, the carriers may hop to a site with a higher energy by absorbing a phonon of appropriate energy or by gaining the necessary energy from an applied electric field according to the Poole-Frenkel effect. The Poole-Frenkel effect describes the electric-field assisted detrapping phenomenon. When an electric field is applied, the trap-potential is lowered allowing the carrier to escape the trap and resume the hopping process. Direct time-of-flight (TOF) measurements of the mobility in organic semiconductors show that it is actually field-dependent and can be modeled by [13,14]:

$$\mu(E,T) = \mu_0 \exp\left(-\frac{E_0}{K_B T_{eff}}\right) \exp\left(-\frac{\beta \sqrt{F}}{K_B T_{eff}}\right)$$

The current-voltage relation of an organic semiconductor is ohmic at low fields but becomes space charge limited (SCL) at high fields. The voltage upon which the conduction becomes SCL is referred to as the activation voltage of the diode. In a trap-free semiconductor with an ohmic contact it was shown that when the concentration of carriers injected from the ohmic contact exceeds the thermally generated carrier concentration the current density \( J \) is given by Child's law [15,16]:

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3}$$

Semiconducting polymers are typically characterized by a set of shallow traps with spatially uniform distribution. Trap states, originating from imperfections or impurities in the polymer structure, creating energy levels inside the forbidden energy band gap [17].

In this case, the effective mobility \( \mu_{eff} \), given by:

$$\mu_{eff} = \frac{\theta}{1 + \theta^\mu}$$
Where $\theta$ is the ratio of free to trapped carriers. At low injection rates, $\theta \ll 1$, and transport is dominated by trapping. As higher voltage is applied, the traps are filled by injected charge carriers. The filled traps then become electrically charged centers, which contribute to the formation of the space charge. At even higher injection rates, the free carrier concentration greatly exceeds the trapped concentration. In this case, $\theta \gg 1$, $\mu_{eff} \approx \mu$ and the current behaves according to trap-free SCLC.

### 2.6 Charge Recombination

Electrons and holes that are injected into the polymer from the separated contacts join in a bound state to form excitons which can then recombine. The excitons may form in to singlet or triplet states with the ratio of three triplets for every singlet. Only the singlet excitons have a quantum mechanically allowed optical transition, and therefore, only the singlet states result in efficient radiative emission. Polymers are low mobility semiconductors and therefore follow Langevin type bimolecular recombination model. In Langevin recombination, when oppositely charged carriers are within the Coulomb attraction radius, $r_c = \frac{e^2}{4\pi\varepsilon_0 k_BT}$, the charge carriers are attracted to each other by Coulomb field. Since the hopping distance in low mobility materials is usually much smaller than $r_c$, the carriers have high probability to find each other and recombine. The recombination coefficient is proportional to the charge carrier mobility of electron and hole, i.e., to the two carriers finding each other and given by [18]:

$$\gamma = \frac{q}{\varepsilon} (\mu_n + \mu_p)$$

The Langevin recombination rate is: $$\frac{dn}{dt} \propto \gamma np$$

Where $\mu_n$ and $\mu_p$ are the electron and hole mobility.
### 2.7 Efficiency

The efficiency of the OLED is determined by two essential characteristics: electrical efficiency and quantum efficiency. Electrical efficiency is defined by the activation voltage upon which light will be emitted from the OLED. Quantum efficiency is defined by injected carriers’ recombination and corresponds to the relative brightness of the OLED.

To reduce the operating voltage, the polymer layer should be as thin as possible, at the minimum thickness that allows complete recombination. Additionally, the right contact materials must be chosen to match the HOMO and LUMO levels of the polymer, to result in low Schottky barriers (as presented in Figure 4).

![Figure 4: Position of Fermi levels for various electrode materials relative to the HOMO and LUMO levels of a polymer](image)

To achieve high efficiency all the current should lead to recombination. This requires the electron and hole currents to be equal. Although Conjugated polymers can transport both electron and holes, severe electron trapping renders an imbalance between electron and hole currents even if both anode and cathode are perfect [20,21]. Imbalance in the electron and hole mobility results in a shift of the recombination zone toward the cathode, which lowers the device efficiency due to exciton quenching by the metal electrode [22]. These problems can be solved by
creating a multi-layer device so that recombination is confined at the hetero-junction between two organic materials [23,24]. Additional layers are usually used to improve hole or electron injection. For example, in MEH-PPV based OLED, Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) can be used as a “buffer” layer next to the anode to improve hole injection while polybenzobisazoles (PBZ), placed next to the cathode, can be used as an electron transport layer which improves the electrons mobility resulting in a highly efficient OLED compared to a single layer MEH-PPV device [25]. Another way to improve charge balance is by creating a hybrid organic-inorganic LED where the inorganic layer is used a blocking layer next to one of the electrodes. A blocking layer provides an energy barrier that the injected carrier must overcome, thus lowering the carrier mobility. For example, in MEH-PPV based OLED placing a vanadium Oxide V$_2$O$_5$ layer next to the anode will lower the holes mobility (which is higher than electron mobility) resulting in charge balance [26].

OLED optical efficiency is defined by internal and external quantum efficiency (IQE and EQE). IQE is defined by: $IQE = \frac{\text{number of created photons}}{\text{number of electrons}}$

EQE is the measured QE that is defined by:

$$EQE = \beta \cdot \frac{\text{number of collected photons}}{\text{number of electrons}}$$

Where $\beta$ is a tooling factor that describes the collection efficiency from the OLED.
3. Superconductivity

3.1 Introduction to superconductivity

Superconductivity was observed for the first time in 1911 by Kamerlingh Onnes while measuring the resistance of mercury as a function of temperature. He discovered that below 4.2K the resistance of mercury dropped to zero [27]. Since this discovery the same phenomenon was observed in many metals and compounds which experience zero resistivity below a critical temperature ($T_c$).

3.2 BCS theory

The present understanding of superconductivity is based on the microscopic theory proposed by J. Bardeen, L. Cooper, and J. R. Schrieffer in 1957, known as the BCS theory [28]. According to this theory, at low temperature, the movement of the electrons inside the lattice is dominated by a second order interaction with the lattice phonons. This interaction causes a weak attraction between the electrons, forming pairs of electrons with opposite momentum and spin, called Cooper pairs. Although this interaction is considered weak, at low temperatures, the inelastic scattering does not excite the electrons enough to break it, and therefore a current shows no dissipation and the resistivity drops to zero. Cooper pairs carry a charge of -$2e$ and the total spin of zero and therefore can be considered as bosons and the system is analogues to Bose-Einstein condensation at low temperature. Therefore, Cooper pairs are coherent, all found in the same quantum mechanical state. As a result, an energy gap $\Delta$ is formed around the Fermi surface in the density of states which determines the amount of energy needed to break the Cooper pairs. In the weak-coupling limit the zero temperature gap is:
\[ \Delta_0 = \frac{E_0}{2} e^{-1/V_0 D_n(0)} \]

Where \( V_0 \) is the strength of electron-phonon coupling, \( E_0 = \hbar \omega_D \) is the typical phonon energy and \( D_n(0) \) is the density of states near the Fermi energy.

The critical temperature is related to the energy gap in the BCS theory by [29]:

\[ 2\Delta_0 \approx 3.53K_B T_c \]

### 3.3 Proximity effect

The Proximity effect in superconductors describes the phenomenon occurring when a superconductor (Sc) is placed in proximity to a normal metal (N) or a different superconductor. At an N-Sc interface, some Cooper pairs will leak to the non-superconductor while some quasi-particles leak into the superconductor. Due to the reduction of the Cooper-pair density close to the interface, the superconductivity is "weakened" in the superconductor over a length \( L_S \), while it is induced to some extent in the N layer, over the length \( L_N \). The propagation of the correlated pairs in N in the dirty limit is governed by diffusion. When one considers the whole electron distribution at thermal equilibrium, then the thermal length, \( L_N = \sqrt{\hbar D / 2\pi k_B T} \) is the relevant length scale for the proximity effect. Here \( D \) is the diffusion constant for electrons in the N layer, \( \hbar \) is Plank’s constant, \( K_B \) is the Boltzmann constant and \( T \) is the temperature. This phenomenon can facilitate the existence of super-currents across a thin N layer as is further described below.

#### 3.3.1 Josephson junction

The Josephson Effect refers to where two superconductors are separated by a thin layer of an insulating (I) material (forming a Josephson junction) [30]. This structure, known as Sc-I-Sc junction, is equivalent to two superconductors coupled by a weak
link resulting in overlap of the two superconductors' wave functions across the junction.

The DC Josephson effect is the flow of DC current across the junction without any electric or magnetic field applied. This current originates from the difference in phase between the two superconductors and is given by:

\[ I = I_c \sin \Delta \phi \]

\[ I_c(T) = \frac{1}{4} \pi G_n \left[ \frac{2\Delta(T)}{e} \right] \tanh \left[ \frac{\Delta(T)}{2k_B T} \right] \]

Here, \( \phi \) is the phase difference between the two superconductors across the barrier, \( I_c \) is the Josephson critical current, \( \Delta(T) \) is the temperature dependent gap, and \( G_n \) is the normal tunneling conductance.

This equation is simplified at the extreme cases where \( T \approx 0 \) and \( T \approx T_c \) becoming:

\[ I_c(0) = \frac{1}{4} \pi G_n \left[ \frac{2\Delta(0)}{e} \right] \]

\[ I_c(T_c) = \frac{1}{4} \pi G_n \left[ \frac{\Delta^2(T_c)}{ek_B T_c} \right] \]

3.3.2 Andreev reflection

The Andreev Reflection (AR) provides a conversion channel of the dissipative electrical current in the normal metal (N) into a super-current in the superconductor [31]. Due to existence of an energy gap at the Fermi energy in the density of states of the superconductor, only electrons with energy above the superconducting gap can penetrate the N-Sc interface by occupying quasi-particle states in the superconductor. An electron with energy below the superconducting gap,

\[ \xi_K = \sqrt{\frac{k^2}{2m} - E_F} < \Delta, \]

cannot propagate from a normal metal into the superconductor. It is possible, however, for the electron to get reflected via an AR
process. In contrast to a normal reflection process, the reflected particle has the opposite charge and spin as the incident particle and is reflected along the same trajectory as the incident electron, shown in Figure 5.

Figure 5: Normal reflection (Left) versus Andreev reflection (Right) by a superconductor (Sc) of an electron with energy below the superconducting gap where the missing charge of 2e is absorbed as a Cooper pair by the superconducting condensate.

The missing charge of 2e is absorbed into the superconducting ground state as a Cooper pair. The electron has a wave vector $K_e = K_{F+q}$ ($K_F$ is the Fermi wave vector), thus, the AR hole has a wave-vector $K_h = K_{F-q}$, leading to a wave vector mismatch of $\delta_k = 2q$ (Figure 6). This mismatch makes the phase difference between the incident electrons and the reflected holes grow monotonically.

Figure 6: a) Schematic representation of the Andreev reflection process which extends in space from $x_0$ to $x_1$. Depending on the actual value $\Delta(x)$ in the interface region an electron (e) approaching the superconductor occupies different states in the energy parabola $E(k)$ of the quasi-particle states and finally changes its character from a quasi-electron into a quasi-hole at a position $x''$. This hole is Andreev reflected and simultaneously two electrons are transferred as Cooper pairs into the BCS ground state [35]. b) (left) The mismatch in the momentum between the incoming electron and the retro reflected hole. b) (right) Length scales appearing in the proximity effect relative to one another.
Therefore, the electron and the reflected hole are considered phase correlated until the phase shift between the two particles is of order $\pi$ and correlation is lost [32].

The consequences of Andreev reflection on the current vs. voltage characteristics of a Sc-N junction and its dependence on the barrier strength were studied in detail by Blonder, Tinkham and Klapwijk, called today the BTK theory [33]. When a bias voltage is applied, the total current flowing from the normal metal to the superconductor is:

$$I(V) \propto N(0) \int_{-\infty}^{\infty} [f(E - eV) - f(E)][1 + |A(E)|^2 - |B(E)|^2]dE$$

Parameters $A(E)$ and $B(E)$ are the probabilities of charge transfer into the superconductor for Andreev reflection and normal reflection respectively. Those parameters depend on the barrier strength $Z$. In the limit of zero-barrier height, the conductance within the superconducting gap nearly doubles because most of the incident electrons are Andreev-reflected and the transmitted electron pairs across the interface carries double the amount of charge of the incident electrons. On the contrary, in the high-barrier limit ($Z \geq 3$) the amount of normal reflected electrons increases over the whole energy range except at $E = \pm \Delta$.

### 3.4 Sc-N-Sc junction

The Sc-N-Sc structure, where two superconductors are separated by a normal metal, results in a weak link between the normal metal and the superconductor. Unlike tunnel junctions, both normal and superconducting current can exists within the N layer. From the Josephson currents prospective, in the case of a weak link the normal ohmic behavior of the junction has to be taken care of by additional ohmic resistance $R_N$ in parallel with the junction. The expression for the critical current is given by [34]:
\[ V_c = I_c R_N = \frac{\pi \Delta_1 \Delta_2 d}{\kappa e k_B^2 \xi_n} e^{-d/\xi_n} \]

Where \( \Delta_1 \) and \( \Delta_2 \) are the gaps for Sc on each side of the N material. The current is limited by the width of the N layer and \( \xi_n \) the coherence length which is defined by:

\[ \xi_n = \frac{2h\nu}{\pi \Delta} \]

From Andreev reflection prospective, a particle that moves in the normal region to the right will be Andreev reflected from the N-Sc interface into a hole. The hole will then move to the left and is Andreev reflected into the particle, and so on. Under the assumption that \( d \) is shorter than \( \xi_n \) and \( E \leq \Delta \), the Andreev reflected particles are localized in the N region having a discrete energy spectrum due to superposition of electron and Andreev reflected hole states.

\[ E_{\pm} = \pm \Delta_0 \sqrt{\cos^2 \left( \frac{\phi}{2} \right) + 4Z^2} \]

The phase difference \( \phi \) is related directly to a particular Josephson current, which flows without any resistance \( (U = 0) \). Depending on the strength of the Josephson current, the eigenvalues vary in energy.

Within the model of multiple Andreev reflection in a Sc-N-Sc junction there are interesting effects even in the case where there is no coherence between the two superconducting wave-functions. If the critical Josephson current has been exceeded but the external bias is smaller than the equivalent gap energy of the two superconductors, current transport through the structure can be described by an idealized scheme as in Figure 7. With the electric field \(-U/d\) in the direction indicated, electrons within the normally conducting barrier are then accelerated to the right, whereas Andreev reflected holes are accelerated to the left. The external voltage results in a tilted carrier trajectory in the energy–position diagram. Between the Andreev reflection events at the interface the particles climb or descend the so-called
Andreev ladder. As long as the energy of the particles at the Sc-N interface is within the superconducting gap, ideal Andreev reflection occurs. If the external voltage is increased, more and more Andreev reflections are necessary to gain or lose enough energy before the particle can enter the superconductor as a quasi-particle. In other words, the total current through the junction will increase at particular discrete external voltage values $U_n$, where:

$$\frac{2\Delta_0}{en} = U_n, \quad n = 1, 2, 3$$

![Figure 7: trajectories of Andreev and normal reflected particles (e, h) in a SC-N-SC junction plotted on an energy-position diagram E(x), where the action of the electric field U/d is described by tilted trajectories \[35]\]

In conclusion, even in the case that a measurement does not show super-current across an SNS junction, coherent particles may still reside in the N layer, and they will be evidenced as peaks in the differential conductance.

### 3.5 Sc-Sm-Sc junction

The full analysis for a superconductor/semiconductor/superconductor (Sc-Sm-Sc) junction must take account of the existence of Schottky barriers at the interfaces with the superconductors. A degenerate semiconductor is approximately a weak metal so the junction can be treated as superconductor / insulator / normal metal/
insulator/superconductor (Sc-I-N-Sc) junction [36,37]. The current for the transmitted electrons through the barrier at applied voltage $V_0$ is given by [38]:

$$I_T = \left(\frac{e\hbar}{Am^*}\right) \int \Gamma(E)\left[F(E) - F(E + eV_0)\right]dE$$

Where A is the area of the interface, F(E) is the Fermi-Dirac distribution function, $m^*$ is the effective electron mass. $\Gamma(E)$ is the tunneling probability of an electron through the Schottky barrier:

$$\Gamma(E) = \exp\left\{(\frac{-2eV_{b}}{e^2hN_d\Omega})^2\left[(2\Delta + V_{b} - E)^{3/2} - \left(2\Delta + V_{b} - E - \frac{e^2DN_d\Omega}{\epsilon}\right)\right]\right\}$$

where $E$ is the total energy of the incident electron on the interface, $\Delta$ is the energy gap of the superconductor, $V_{b}$ is the Schottky barrier height, $D$ is the distance between the two superconducting electrodes, $N_d$ is the semiconductor doping density and $\epsilon$ is the permittivity of the semiconductor. $\Omega$ is the depletion layers width and is given by:

$$\Omega = \frac{\sqrt{2\epsilon(V_{b}-V_0)}}{en_d\Omega}.$$ 

In other words, the signature of this stat will be a significant drop in resistance as a function of decreasing temperature below $T_c$. Above $T_c$, where $\Delta \rightarrow 0$, the resistance will shift back to its original value.

### 3.6 Superconductor based LED

Although there are many interesting possible outcomes of light emission from semiconductor quantum wells in the presence of superconducting proximity effect, there is not much literature on the subject. This is probably due to the complexity in realizing such a system. The initial idea of a superconducting light emitting diode was first proposed by Eiichi Hanamura in 2002 [39]. In his work he discussed the theory of super-radiant emitted light from a layer structure of p-type superconductor–insulator–n-type superconductor. According to this theory, electron Cooper pairs from
the n-type superconductor and hole Cooper pairs from the p-type superconductor tunnel into the insulating layer and recombine in it. In his work two processes are described. In the first process, one of the electrons recombines with one of the holes by emitting a photon. Therefore the frequency of the emitted photon can take any value below the difference in chemical potentials of the n- and p-Cooper pair and the emission angle is arbitrary. In the second process, electron Cooper pair recombines with a hole Cooper pair, all photons have exactly the energy of the chemical potential difference and the momentum of the two emitted photons sum up to zero. Hence, the emitted photon-pair is strongly entangled with respect to a single photon basis. In 2009, Asano et. al. theoretically investigated the emission spectrum of a forward biased p-n junction which has a superconductor coupled to the n-doped side as shown in Figure 8 [40].

![Figure 8: A theoretical model of energy diagram of forward biased p-n junctions (left) and a realistic junction in experiments [40]](image)

On the basis of the second order perturbation theory the number of emitted photons is calculated as:

$$\langle N_{ph} \rangle = \langle N_{ph}(1) \rangle + \langle N_{ph}(2) \rangle$$

Where $\langle N_{ph}(1) \rangle$ is the number of emitted photons at $T > T_c$ and $\langle N_{ph}(2) \rangle$ is the number of emitted photons at $T \leq T_c$. $\langle N_{ph}(1) \rangle$ Depends on temperature through the
Fermi distribution function, however, this dependence is very weak and almost constant below and near above $T_c$.

By calculating the short time average of the photon number, i.e. the photon emission rate, Asano concluded that in the limit of vanishing relaxation rate $\langle N_{ph}(2) \rangle$ is proportional to the density of states in the superconductor divided by the superconducting gap. Therefore, since the density of states of a superconductor diverges above and below the gap and because the superconducting gap is usually very small, the luminescence is greatly enhanced in comparison to a normal light emitting diode. Finally the total number of emitted photons in a highly elastic impurity scattering medium when $T \leq T_c$ is presented as:

$$\langle N_{ph}(2) \rangle \propto \sum_{q,\sigma} \frac{|\Delta|^2 \tau^2 \exp \left(-\frac{2L_w}{\xi}\right)}{T \left[(\omega_q - \omega_0)^2 + \Gamma^2\right]}$$

Where $\Delta$ is the superconducting gap, $L_w$ is the length of the junction, $\xi$ is the coherence length, The emission spectra have a peak at $\omega_0$ and the peak width $\Gamma$ is given by $\Gamma = t_w^2 N_0$ where $t_w$ is the transfer integral between the quantum well and the semiconductor. According to this equation, unlike $\langle N_{ph}(1) \rangle$, $\langle N_{ph}(2) \rangle$ show a strong dependence in the temperature and is enhanced with the growing superconductors gap and decreasing coherence length.

![Figure 9: a) Schematic structure of the superconductor-based LED [41] b) and a Josephson junction measurement of this device [42].](image-url)
A Superconductor-based Light Emitting Diode device (Sc-LED) was first reported by Hayashi and Suemune et. al. in 2008 [41]. The superconductor-based LED was prepared on a p-type (100) InP substrate as illustrated in Figure 9a. The superconducting Nb electrode was deposited on a highly doped InGaAs contact layer. To measure the EL an 110nm slit was fabricated in the Nb cathode and an Au anode was deposited to the back surface of the InP substrate. In this experiment a dramatic enhancement of the EL intensity was observed at temperatures lower than the superconducting critical temperature as shown in Figure 10. Although, it is not specified by the author, the data shows the EL is about 15 times greater for 2K than it is for 11K. In further experiments (done by Suemune in 2010) Josephson current was measured in the device demonstrating successful Cooper-pair injection shown in Figure 9b. From this measurement it is not clear if the super-current is confined to the highly doped n-layer, or whether Cooper-pairs are present in the recombination area.

![Temperature dependence of EL spectra (left) and EL integrated intensity (right) from a superconductor based OLED [41].](image)

Measurement of the excitons recombination time reviled a noticeable decrease in the radiative recombination time below $T_c$ (reported to be of 8.4K) and that the increase in internal quantum efficiency below $T_c$ is strongly correlated with the steep reduction of the radiative recombination lifetime as shown in Figure 11.
Figure 11: Temperature dependence of (left) internal quantum efficiency and (right) radiative recombination lifetime. Solid line in (b) represents the theoretical calculation [43].

In recent years there were only a few reports of proximity induced effects by organic molecules [44,45]. In spite of the growing development of OLED application and research, to date, there have been no reports of superconductor proximity induced effects on organic light emitting molecules and polymers.
4. Experimental Methods

4.1 Deposition techniques

4.1.1 Physical Vapor Deposition (PVD)

Figure 12: A picture on the sputtering chamber during sputter deposition (a) and an illustration of the sputtering process (b).

All inorganic materials (metals, semiconductors and superconductors) were deposited using a high vacuum magnetron sputtering system (manufactured by AJA Int.). The system allows deposition of thin layers by accelerating Argon ions toward a target made of a desired material. Electrically neutral Argon atoms are introduced into a vacuum chamber at a pressure of 1 to 30 mTorr. A DC or RF voltage is placed between the target and a near-by anode which results in an argon ion plasma. The ions are accelerated towards the target. The target material is bombarded by the arriving ions and is sputtered from the target as small aggregates. The flux of the material accumulates on a substrate, which is positioned above the target as shown Figure 12.

In a magnetron sputtering system, an additional strong magnetic field is applied near the target area. This field causes traveling electrons to spiral along magnetic flux lines near the target. As a result, the plasma is confined to an area near the target. This generates a stable plasma with high density of ions, thus, improving the efficiency of the sputtering process. It is possible to flow additional gases into the chamber, such as oxygen and/or nitrogen for creating oxides and nitrides such as vanadium Oxide.
(V$_2$O$_5$) and niobium nitride (NbN). The deposited layer’s properties depend on the deposition conditions, including argon pressure, plasma power, and substrate temperature; all which can be calibrated and controlled during the deposition.

4.1.2 Spin coating
Deposition of organic materials was done by spin-coating as illustrated in Figure 13. Spin coating is performed by placing a solution containing the material dissolved in a suitable solvent on to a substrate which is rotated at high speed in order to spread the fluid by centrifugal force. The rotation continues while the fluid spins off the edges of the substrate and the solvent evaporates, resulting in a thin film. The thickness of the film and other properties depends on the solvent, concentration of the solution, the angular speed of spinning, and acceleration of the spinner.

![Figure 13: Illustration of spin coating process.](image)

4.2 Measurement systems

4.2.1 Physical Property Measurement System (PPMS)
Characterization of the superconducting materials was done in a Physical Property Measurement System (PPMS, Quantum Design Inc.). The PPMS is an exchange gas cryostat that is cooled with liquid helium. The PPMS operates in the temperature range of 400K-1.9K and in a vacuum of 10 Torr. The sample is glued with double sided tape onto a sample holder with 12 golden pads for electrical measurements. Electrodes on the sample are connected via wire-bonding to the pads and the assembly is inserted into the cryostat via a top loading port. The sample holder connects to a matching connector at the bottom of the cryostat which in turn is connected to an
external feed-through and high precision electronics. The system is very stable at any given temperature within its range with a resolution of temperature 0.005K. This allows for very accurate measurement of the superconductors dependence on temperature.

### 4.2.2 Optical cryostat (OC)

In order to perform optical measurements at low temperatures we use an optical cryostat (by Advanced Research Systems, Inc.). The optical cryostat has a quartz window in the top cover and the relatively close position of the sample to the window allows collecting light from the sample (shown in Figure 14a).

**Figure 14:** a) A top view of the OC with the top cover. b) The shield which is placed under the top cover. c) Under the shield there is a cold finger, electrical wires and a side shield. d) The sample holder and the sample on top of it can be viewed through the window and the hole in the shield.

In this system, the sample is placed upon a flat copper sample holder which is screwed into the cold finger (Figure 14d). The cold finger which is also made of copper is then cooled by liquid helium running through a thermally connected copper capillary. Temperature control of the sample within the cryostat is performed by controlling the flow rate of the helium into the cryostat and the temperature of the
helium. The helium temperature is varied by a heating wire and temperature controller. The temperature sensor is placed in the upper part of the cold finger near the interface with the sample holder. Although the system is kept in high vacuum of $10^{-6}$ Torr, in the absence of exchange gas, the actual temperature of the sample depends on the balance between cooling and heating powers, and the heat load from external sources of radiation. The heat sink between the sample, sample holder, and the cold finger is cooling the sample; and the radiation coming through the radiation shields is heating the sample. The thermal insulation is critical, and a shield is placed at the samples level and around the cold finger to shield the cold finger from absorbing black body radiation from the body of the OC (shown in Figure 14b).

### 4.2.3 Atomic force microscope (AFM)

We confirmed the thickness of the deposited layers using Atomic Force Microscope (AFM). The AFM consists of a cantilever with a sharp tip which has 15-40nm radius at its end. The basic idea of the AFM is that the local attractive or repulsive force between the tip and the sample causes a bending or deflection, of the cantilever. The cantilever deflection is usually detected by a small change in the position of a laser beam that is reflected from the back of the cantilever onto a detector. Using a feedback loop, the laser position is kept constant by changing the relative height of the sample. Topography Mapping is done by monitoring this height change while scanning the sample. Vertical scanning resolution of the AFM tip can reach 0.1nm.

### 4.2.4 Transmission electron microscope (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto
an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM image contrast is due to absorption of electrons in the material and due to the thickness and composition of the material. Alternative modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, and electronic structure.

**4.2.5 LabRAM HR Evolution systems**
The LabRAM system is a scanning micro-spectrometer system that consists of a confocal microscope coupled to a high resolution spectrometer. The sample is probed with a laser through the microscope lens. The light collected from the sample is filtered from the initial laser wavelength and analyzed in the systems spectrometer. Although the system is initially designed for RAMAN measurements it is also adequate for other spectroscopic measurements such as micro-photoluminescence.

**4.3 Optical cryostat modification**

**4.3.1 Electrical measurements in the OC**
Since the system is designed for optical measurements, the sample holder had to be modified to allow electrical measurements as well. The system has a 10 wire feed-through on the cryostats body. We connected eight of these wires to small pieces of gold coated un-doped silicon chips which were glued with VGE-7031 high thermal conductivity insulating varnish onto the sample holder (as shown in Figure 14c,d) . Electrodes on the sample were connected to the gold coated silicon contacts via wire bonding.

**4.3.2 Characterization of substrates surface temperature.**
As was mentioned before the temperature sensor in the OC is located in at the interface between the cold finger and the sample holder, thus, the precise temperature...
of the sample’s surface is unknown. Since our sample is made from a superconductor it was easy for us to determine the actual temperature of the sample by comparing the resistance curve measured in the OC to the resistance curve measured in the PPMS.

**Figure 15** shows the resistance as a function of temperature of a 100nm layer of NbN on top of Si. The sample was glued onto the sample holder using VGE-7031 high thermal conductivity insulating varnish. The black curve represents a measurement taken in the PPMS that serves as a baseline for the transition temperature. The green curve represents the measurement of the same sample inside the optical cryostat where the temperature is for the cold finger near the interface. This measurement was done with a top cover that did not have a window in order reduce direct radiation and further isolate the sample from the external environment. By comparing the resistance curves we see that there is a difference of about 8K between the temperature of the cold finger and the actual temperature of the sample.

![Figure 15: temperature vs. resistance of 100nm NbN as was measured in the PPMS (black) and in the OC without the window (green). The same sample was used in both measurements.](image)

At this point, we verified that the bottom of the sample is heat-sinked well with the cold finger leading to the assumption that the problem was caused by absorption of
black body radiation by the sample’s surface. The existing radiation shield covers the cold finger and the copper capillary but leaves the sample exposed to black body radiation from the OC’s body (Figure 14 b). To confirm this and correct the situation we needed to modify the shield to completely cover the sample without disturbing the electrodes, since the regular shield is placed at the level of the sample and leaves the sample exposed a bit. To accommodate a taller shield, we needed to modify the height of the cryostat top cover. The cryostat was designed originally to have a short distance between the sample and the top window, so in order to modify the heat shield, the height of the top shield had to be extended by 13mm, as shown in Figure 16a. Once the top cover was raised, we could modify the heat shield by covering the sample area with elevated aluminum foil that was then glued with varnish to the original shield as shown in Figure 16b.

The blue curve in Figure 17 is of the electrical resistance through the sample while placed under the aluminum foil shield without a hole in it. Although in the OC, the
measurement resolution is much lower than achieved in the PPMS, we can clearly see that the blue curve follows the black curve behavior and that the critical temperature is roughly reached at the same point. Since optical measurements cannot be performed in this shield configuration, we needed to open a small hole in the foil shield. The red and purple curves represent a resistance vs. temperature measurement with 2mm and 4mm holes respectively. The 2mm hole in the shield has very little effect on the resistance measurement with a difference in $T_c$ of about 0.4K. A 4mm hole has a larger effect and the difference in $T_c$ is about 1K. Although this solution in fact limits the amount of light that can be collected through the window, it allows for the samples surface to be at the same temperature as the cold finger, and therefore, to cool down the sample several Kelvins below $T_c$.

**Figure 17**: Temperature vs. resistance of 100nm NbN as was measured in the PPMS (black) and in the OC with a foil shield without a hole (blue), with a 2mm hole (red) and with a 4mm hole (purple). The same sample was used in all the measurements.
5. Results

5.1 MEH-PPV characteristics at low temperatures

In this work we used a fluorescent semiconducting conjugated polymer, poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) (Sigma-Aldrich) as the light emitting excitonic layer in the OLED device. MEH-PPV is a particularly attractive material for OLED fabrication since it is soluble in the conjugated form in common organic solvents and has a low operating voltage for light emission. MEH-PPV was spin-cast from solution of chloroform (Sigma-Aldrich) with a concentration of 4mg/ml in chloroform (Sigma-Aldrich) at a rate of 1000rpm. After spin-coating the sample was dried overnight in high vacuum of $10^{-7}$ Torr before the cathode deposition of the cathode layer. The thickness of the MEH-PPV layer obtained under these conditions, confirmed by AFM, was 40nm ± 3nm.

At room temperature, the HOMO level of MEH-PPV is 5.3eV and the LUMO is 3eV [46]. Both the PL and EL emission spectra have a main peak at 2eV and a secondary peak at 1.9eV. Conjugated polymers in general are composed of segments with different conjugation lengths and hence can be regarded as a semiconductor material, with a distribution of semiconductor energy gaps and different excitation energies resulting in a broad emission spectrum, with a spread of roughly 0.2eV in MEH-PPV [47].

The goal of this work is to successfully build an OLED with superconducting contacts. In order to witness the influence of superconductivity on the electroluminescence, the OLED must operate at 4K and below. Therefore the dependence of MEH-PPV properties on temperature had to be taken into account. The optical properties of conjugated polymers are related to the conjugation segment
length which is shortened by chemical defects and thermally induced torsion and liberation modes. Hence, changing the temperature of the polymer not only effect the electronic transitions, but also changes the morphology of the polymer. As the temperature is decreased the structural order of the polymer chains is increased due to the freezing of torsions along the polymer backbone and lower density of localized phenylene ring twists [9,48].

**Figure 18** presents the PL spectrum of a 40nm MEH-PPV layer. The measurement was performed in the optical cryostat and measured using a LabRAM HR spectrometer with 532 nm laser excitation. The red shift in the spectrum with decreasing temperature indicates that the polymer chains become more planar, increasing the extent of electron delocalization, thus reducing the energy of the $\pi - \pi^*$ transition. With decreasing temperature there is also an increase in efficiency in the two main peaks which is related to the narrowing distribution of semiconductor energy gaps.

![Figure 18: a) PL spectrum of MEH-PPV layer at different temperatures. b) Inset illustration of the MEH-PPV polymer chemical structure.](image)
At room temperature MEH-PPV is considered to be a hole transporting material since electron transport is severally reduced by traps. The electron and hole mobility is given by:

\[ \mu = \mu_0 \exp(\gamma \sqrt{E}) \]

Where \( \gamma \) is the temperature depended electric-field coefficient due to the interaction between charge carriers and randomly distributed permanent dipoles in semiconducting polymers [49].

At room temperature the holes mobility is found to be:

\[ \mu_0 = 5.6 \times 10^{-11} \, m^2 / V \, s \] and \( \gamma = 5 \times 10^{-4} \, (m/V)^{1/2} \]

While the electrons mobility is found to be:

\[ \mu_0 = 1 \times 10^{-12} \, m^2 / V \, s \] and \( \gamma = 8 \times 10^{-4} \, (m/V)^{1/2} \]

Upon decreasing the temperature the mobility of both electrons and holes decrease, since in the absence of thermal excitations, the charge transport depends mainly on the application of an electric field.

**Figure 19:** Currents from space-charge-limited conduction for the electrons and holes in MEH-PPV-based devices at 200 K and 300 K. Both electrons and holes are space charge limited at working voltages. The lines are fits to space-charge-limited behavior [50].
Figure 19 shows the current density dependency of the electric field for electrons and holes, as reported by Bozano et. al. [50]. In this measurement they observe space-charge-limited current for both types of carriers above moderate voltages (>4V). At 300K, the electron-dominated current is lower than the hole-dominated current. Although both carriers’ mobilities decrease at low temperature, the charge balance actually improves. At 200K, the electron current becomes comparable and even exceeds the hole current. The charge balance achieved at low temperatures results in increasing quantum efficiency of the OLED. This effect is also noticeable in the OLED investigated in this work, and is discussed further in section 5.4.2.
5.2 Bottom emitting OLED fabrication

A general structure of an OLED is illustrated in Figure 20.

![General OLED structure](image)

**Figure 20**: General OLED structure. The cathode and anode lines are orthogonal to each other resulting in several OLED junctions.

Bottom emitting devices were prepared on 1.1mm thick glass sputter-coated with 100nm Indium Tin Oxide (ITO) (Lumtec). The ITO was patterned into 1mm lines by wet-etching with hydrochloric acid (HCL) and nitrous acid (HNO2) diluted in water with the concentration of 40%:10%:50% respectively. The glass was then cleaned with Micro-90 semiconductor grade detergent, De-ionized water, acetone, and boiling iso-propanol, and oxygen plasma. In a bottom emitting device, 100nm of aluminium (Al) was used for a regular cathode and 60nm niobium (Nb) was used for a superconductive cathode. Both materials were deposited using high vacuum magnetron sputtering. Al was sputtered from Al 99.99% target (Kurt J. Lesker) in an Argon environment. The deposition was done at room temperature at deposition rates starting from 0.04 A/s at pressure of 12mTorr, rising gradually by lowering the pressure up to 0.9 A/s at a pressure of 3mTorr. Nb was deposited by sputtering at room temperature from a 99.95% Nb target (Kurt J. Lesker), in an Argon environment at pressure of 2.4mTorr with deposition rate of 1.8 A/s. The sputtering of all metallic contacts was done through a stainless still shadow mask with 1mm lines.

The key for successful fabrication of a superconductor based OLED is the ability to integrate superconductors and organic materials into working device structures. This
is not trivial, since growing superconducting thin films requires very strenuous process conditions, such as high deposition rates and deposition temperatures. So the first challenges are twofold: 1. preparing well behaved Sc on top and underneath an organic semiconductor layer and 2. retaining the properties of the excitonic active organic layer after deposition of the top Sc electrode.

Depositing the organic layer on the Sc is relatively easy and was done by spin coating the polymer from solution directly on top of the Sc followed by drying the film to remove residual solvent. The deposition of a Sc on top of the polymer, however, is more difficult. Usually the top electrode is deposited by thermal evaporation with extremely low deposition rate, thus ensuring that the arriving material does not damage or penetrate the organic layer, which can produce pinholes that create electrical shorts between the non-organic electrodes. On the other hand, Sc Nb deposition must be done at very high rates to reduce impurities in the Sc layer that destroy superconductivity. Therefore the deposition of Nb directly on the polymer was not successful. To overcome this problem, we sputtered first a 10nm protective layer of Al on top of the polymer before the deposition of Nb. We found that Al can be deposited without causing damage to the organic layer if it is sputtered at a very low rate of 0.04 A/s. From superconductivity point of view, such a thin aluminum layer in contact with Nb will display superconducting behavior, due to the proximity effect and therefore should not prohibit the injection of Cooper pairs into the organic layer. The characterization of the Sc materials was done using the PPMS. Figure 21 displays the resistance vs. temperature measurement of a Nb electrode below (a) and on top (b) of the organic material. The measurement presented in Figure 21 b is of a full Sc-OLED device which is illustrated in Figure 22c. Both Nb electrodes were deposited simultaneously through similar aluminum contact masks. The transition temperature in the case shown is higher for the top Nb electrode (7.8 K) compared to
bottom Nb (7.4K). We note in passing that in most cases the bottom Nb electrode had a higher $T_c$. The width of the transition (90% to 10% of normal resistance) is narrower for the bottom electrode, with 0.06K relative to 0.11K.

This confirms not only that the niobium remains superconducting but also that the deposition on and proximity to the polymer does not reduce the $T_c$ of the full Nb layer. This measurement, of course, does not provide information about the Nb properties near the interface.

The next step was to make sure that the deposition did not harm the excitonic properties of the polymer. For this purpose we fabricated 3 types of devices, as illustrated in Figure 22. The band energy for these materials and a side view of the schematic OLED are shown in Figure 23.

![Figure 21: Resistance vs. Temperature measurement of Nb electrode. a) bottom Nb electrode. b) Nb electrode on top of MEH-PPV.](image)

![Figure 22: Bottom emitting OLED devices. a) Single layer device with a normal metal electrode. b) Double layer device with V$_2$O$_5$ and a normal metal electrode. c) Double layer device with V$_2$O$_5$, a thin protective Al layer and a Nb superconductive electrode.](image)
To maximize light output it would be ideal to create roughly equal amounts of both charge carriers. At room temperature, the holes mobility in MEH-PPV is higher than the electron mobility which lowers the device efficiency due to exciton quenching by the metal electrode. For this reason a single layer device (as presented in Figure 22a) did not emit a measurable amount of light. To balance the charge carriers, we introduce a 50nm hole blocking layer of V$_2$O$_5$ next to the anode. V$_2$O$_5$ was sputter deposited from a vanadium (V) target (99.5% Kurt J. Lesker) at room temperature. The sputtering was done in an Argon and oxygen environment, 88% and 12% respectively, at a total pressure of 3 mTorr with deposition rate of 0.2 A/s. This layer's purpose is to “slow down” the injected holes creating roughly equal mobility of electrons and holes, so charge carrier recombination takes place away from the polymer metal interface.

![Figure 23: Band energy of the OLED materials (left) and a side view of a OLED device (right).](image)

We compared the operation of the devices illustrated in Figure 22b and c. Both devices were identical except for the top electrode. We measured the devices’ current vs. voltage characteristics via 2-prob measurements and we recorded electroluminescence (EL) using an OPHIR photo-diode sensor which was placed underneath the OLED at a fixed distance. Figure 24, plots current vs. voltage and the optical power vs. voltage for a device with Al (a) and Nb (b) electrodes. Our results show that both OLEDs have a similar behavior at room temperature. The activation
voltage is roughly the same, indicating that the Nb deposition did not change the junction characteristics. The difference in EQE is probably due to difference in the effective OLED area or due to small differences in the measurement system, e.g. positioning of the photo-sensor.

Nevertheless, the optical power of both OLEDs is only a factor two lower, reassuring that the integration of a Sc electrode with an OLED was effective.

![Figure 24: Device Performance. Current vs. voltage and optical power vs. voltage of a device with Al electrode (a) and with a Nb electrode for the top contact (b).]

### 5.3 Top emitting OLED fabrication

In order to perform optical measurements below the superconductors’ critical temperature the substrate has to be thermally connected to the cooling block and then light must be collected from the top of the OLED. Therefore we needed to fabricate a top superconducting electrode which will be thin enough to ensure sufficient light transmission.

This requirement was challenging for several reasons. Below some thickness the Sc transition temperature is dependent on the layer thickness of the Sc. A lower $T_c$ may be detrimental for us since it is crucial for us to be as far below $T_c$ as possible. This is because the coherence-length of Cooper pairs strongly depends on temperature and our objective is to inject Cooper pairs deep into the polymer layer. Additionally, since
Nb must be deposited at a high rate it is sputtered on top of a 10nm Al protection layer which is reflective by itself. In conclusion, we were in need of a Sc with $T_c$ - as high as possible that will maintain a sufficient $T_c$ in a thin layer and could be deposited at lower rates which would allow minimizing the thickness of the Al protective layer. For this purpose we made the top electrode from NbN which has a bulk $T_c$ of 16K and above 9K even in very thin layers of a few nanometers. We have successfully grown superconducting NbN thin films using DC reactive sputtering at room temperature. The sputtering was done in a mixed Argon and Nitrogen environment, 73% and 27% respectively, at a pressure of 2 mTorr. Figure 25 a and b presents the resistivity as a function of temperature of 15nm thick NbN films deposited at rates of 0.9 A/s, 0.7 A/s, 0.4 A/s. The NbN had a thin 5nm Al layer underneath in order to examine its properties in a structure similar to that which will be deposited for the OLED. The measurement was done in the PPMS under an applied current of 10µA. The deposition rate has an effect on the resistivity and superconducting properties, as is evident from the results. The $T_c$ is lowered with decreasing deposition rate and the transition width is broadened.

Figure 25: a) Resistance vs. temperature of NbN deposited in several rates, measured near the transition temperature b) and near room temperature at applied current of 10µA. c) Light transmission of this layer.
At the highest deposition rate the $T_c$ is 10.28K and the transition width is 0.68K while at the lowest rate we get a $T_c$ of 9.9K with 0.92 K transition widths. The sheet resistance of the sample is also affected by the deposition rate. Deposition at a lower rate results in increased sheet resistance, even at room temperature as shown in Figure 25b.

Although low rate sputtering of a thin layer of NbN reduces the superconductivity, eventually, if compared to the Nb electrode, we reached a higher $T_c$ in a thinner layer which allows light transmission. Additionally, by sputtering NbN at rates of 0.4 A/s we were able reduce the protective Al layer thickness to only 5nm. The transmission spectrum as a function of the relevant wavelengths (measured with a Carry spectrophotometer) of such a layer is shown in Figure 25 c.

Thin layers tend to be more affected by the morphology and the roughness of the layer upon which they are deposited. For this reason we needed to verify once again that the deposition of a 15 nm NbN layer on top of the polymer layer does not dramatically reduce the superconductivity.

Figure 26: a) Resistance vs. temperature. The red curve is of a sheet resistance of 5nm Al and 15nm NbN deposited on Si. The blue curve is of an OLED top electrode made of 5nm Al and 15nm NbN deposited on MEH-PPV. b) Critical current measurement in different temperatures for an OLED top NbN electrode.
**Figure 26a**, show the resistance vs. temperature of the top NbN electrode (blue curve) of an OLED as illustrated in **Figure 27** and of the same layer deposited simultaneously on silicon (red curve). The Al and NbN layers were sputtered at rates of 0.04 A/s and 0.4 A/s, respectively. As is evident from the results, deposition on top of MEH-PPV only slightly reduces the $T_c$ from 9.9K to 9.88K and broadens the superconducting transition width from 0.92K to 1.07K. This very small change ensures us that we are able to successfully fabricate a top electrode for the OLED which is both superconductive and semi-transparent.

**Figure 26 b**, shows the critical current of the Sc electrode (1mm wide an 15nm thick) for several temperatures below $T_c$. According to this measurement, the critical current is above 2mA even at temperatures close to $T_c$, which corresponds to current density of $13 \times 10^{10}$ mA/m$^2$. At 4K the critical current and is above 6mA. Hence, as long as the current needed for the OLED activation is lower than these values the superconductivity of the electrode should be preserved.

From here on, our research focuses on top emitting OLEDs with structures as illustrated in **Figure 27**. To minimize light being wave-guided through the glass and to provide better heat-sinking, the OLEDs were prepared on a 300 um thick Si substrate which had 1um of oxide thermal oxide on top. The anode in this design was made from 60nm Nb layer, sputtered through a stainless steel mask. $V_2O_5$, MEH-PPV and Al-NbN layers were deposited as described earlier.

**Figure 27**: Band energy levels of the OLED materials (left) and top emitting OLED structure (right).
### 5.4 $V_2O_5$ efficiency calibration

Since the top electrode transmits only about 27% of the light, the efficiency of the OLED should be as high as possible. The efficiency is strongly affected by the balance of charge in the polymer. For this reason, we had to optimize the thicknesses of the MEH-PPV layer and the $V_2O_5$ blocking layer. $V_2O_5$ is a semiconductor and therefore it strongly affects the resistivity of the device, especially at low temperatures. While contributing to the EL efficiency, a thick layer of $V_2O_5$ severely increases the activation voltage of the diode. Figure 28 shows the current vs. voltage and optical power vs. voltage for the devices as illustrated in Figure 27 with different $V_2O_5$ thicknesses. A device made without the $V_2O_5$ layer (black curve) is clearly the most efficient electrically, with an activation voltage of less than 1V, yet it does not emit light. Once a $V_2O_5$ layer is introduced the electrical efficiency is limited, raising the activation voltage to about 7 V. Higher thickness for the $V_2O_5$ layer also increases the device’s total resistance, as can be seen by comparing devices with 30nm (red curve) and 10nm (blue curve) thick $V_2O_5$ layers.

![Figure 28](image.png)

**Figure 28**: PLED measurement of current vs. voltage (Left) and optical power vs. voltage (right) of three devices with different $V_2O_5$ thickness. The measured devices were of the structure described in Figure 27. The black, blue and red curve fit a device without $V_2O_5$, with a 10nm $V_2O_5$ layer and a device with 30nm $V_2O_5$ layer respectively.
Figure 29 shows the optical power vs. current. This graph presents the OLED’s external quantum efficiency (EQE) since this curve gives us estimation for the photon created for a given electron current passing through the device.

This analysis reveals quite a different dependence on V₂O₅ thickness, since the 30nm layer is actually proven to be more optically efficient than the 15nm layer.

We conclude from this that although the V₂O₅ layer harms the conductivity of the device, it plays an important role in balancing the carriers and improving the EL. In other words, the presence of V₂O₅ increases the turn-on voltage for the device but improves the exciton recombination efficiency. Methods and plans to improve both the turn-on voltage and EQE are described in the Future Work section (chapter 7).

![Figure 29: OLED measurement of optical power vs. current of three devices with different V₂O₅ thickness. The measured devices were of the structures described in Figure 27. The blue and red curves fit a device with a 5nm V₂O₅ layer and a device with 15nm V₂O₅ layer, respectively.](image)

### 5.5 OLED optical and electrical measurements at low temperature

#### 5.4.1 Description of the measurement configuration

The OLED configuration that was used in this experiment is as follows: 60nm of Nb were sputtered on an oxide covered Si substrate through a stainless steel mask with 1mm wide lines, followed by sputtering on the entire substrate a 30nm layer of V₂O₅ and deposition of about 40nm of MEH-PPV by spin coating. The top electrode was
5nm of Al and 15nm of NbN that were sputtered through the mask with 1mm lines orthogonal to the Nb lines, forming an OLED junction. Figure 30a depicts a cross-section of the junction. A thin slice of the junction was cut using Focused Ion Beam (FIB) and measured in a high-resolution TEM. As evident, the MEH-PPV layer under the NbN electrode is only about 27nm thick. The thickness of the polymer layer on the same device without the electrode was confirmed by AFM measurements to be 42nm in thickness. This can be explained by the polymer being squashed by the metallic layer or sputtered off during the cathode deposition. Most importantly, this image confirms that the organic layer is intact and that there are no pinholes resulting from the cathode deposition. Figure 30b) illustrates a top view of the device indicating the measurement configuration. Usually this kind of device is activated with applying a voltage, yet, in this measurement configuration we applied current and measured the voltage, in order to be sensitive to the critical current of the Sc.

Figure 30: a) An image of the junction cross-section as taken with high-resolution TEM. b) Illustration of the upper view of the device describing the measurement configuration.

The OLED was activated and measured via a 4-point measurement by applying current and measuring the voltage on the junction with a Keithley 2400 source-meter. A Keithley 2000 voltmeter was simultaneously used to measure the voltage on the Sc electrode while running current. The Sc voltage measured as a function of applied
current on the junction enabled inspection of the superconducting properties of the electrode along with the activation of the OLED. A photodiode was used to collect the emitted light.

**5.4.2 Superconductivity of the top electrode**

*Figure 31* presents the voltage measured on the top electrode as a function of applied current and measured voltage on the junction at 4.8K. The destruction of superconductivity is evident from this measurement. So long as the applied current is below 100 µA, which corresponds to applying about 4V, there is no dissipation in the electrode and therefore the measured voltage is zero. Above 100 µA the superconductivity is destroyed and a voltage drop is measured across the electrode. The power at this critical point is about 400 µW. We assume that the superconductivity destruction is caused by local heating of the device, since, as shown in *Figure 26* b, the critical current of the electrode is larger than 2 mA even at temperatures close to $T_c$.

![Figure 31: a) Voltage measured on the Sc electrode (black curve) and CF sensor measured temperature (red curve) as a function of the voltage measured on the junction b) and as a function of the applied current on the junction.](image)

This assumption was confirmed by examining the temperature sensor readings. The red curve in *Figure 31* presents the temperature measured on the cold finger as a function of applied current and measured voltage on the junction. It is clear that the
measurements coincide. Although the total difference is only of 0.007K, one must keep in mind that the sensor is placed at the interface between the cold finger and the sample holder that is 1mm thick. Presumably this small change measured by the sensor actually indicates that the device’s local Joule heating is enough to increase the temperature above the Tc of the Sc.

### 5.4.2 Electroluminescence at low temperature

The current device presents low electrical efficiency and high activation voltage due to the V₂O₅ layer. This aspect is enhanced at low temperature. Therefore the activation voltage of the OLED is much above the critical voltage for heating the to the point of losing superconductivity. Figure 32 shows the current vs. voltage and the optical power vs. voltage for different temperatures.

![Figure 32: current vs. voltage (left) and the optical power vs. voltage (right) at different temperatures.](image)

Since, the resistivity is much higher at low temperatures, a sufficient current for recombination and EL is reached only at higher voltages. Yet, once a sufficient current is flowing through the device, recombination and EL occur even at low temperatures. The local heating of the device is evident from these results as well, since there is no change in the I-V curves between 5K and 20K. From this we can deduce that during device activation at 5K the actual temperature of the device is
close to 20K. It was mentioned earlier that the quantum efficiency of the OLED actually increases upon cooling due to improvement in charge balance. This behavior is also evident in this OLED device. Figure 33 shows the optical power as a function of applied current at different temperatures. It is evident from this measurement that this OLED device is not only optically active at low temperatures, but actually exhibits higher quantum efficiency than at room temperature.

![Figure 33: Measured optical power as a function of applied current three different temperatures.](image)

### 5.6 Single layer device measurements at low temperature

The hole-blocking layer, V$_2$O$_5$, improves the EL efficiency but strongly limits the electrical efficiency and is the main cause for local heating of the device since most of the voltage drops on this layer. For this reason we decided to measure the electrical properties of a single layer device as illustrated in Figure 34 b). This device is made from a bottom contact of Nb (50nm) an organic layer of MEH-PPV (40nm), and since this device does not emit light the top contact does not have to be transparent and was made from a 5nm layer of Al and a 30nm layer of NbN. The device was measured in the PPMS using a Keithley 6221 Current Source and a Keithley 2182 Nano-voltmeter. The device was measured in pulsed mode in order to minimize the effect of local heating. In this method, called Delta-Mode, we apply current for short
pulses <2 ms and measure the voltage during this interval. An illustration of the measurement configuration is shown in Figure 34 a). While current is driven through the junction the voltage is measured both on the junction and on the top NbN electrode, probing the state of the superconductor during the junction activation.

![Figure 34](image)

**Figure 34:** a) A single layer device cross-section b) Illustration of the measurement configuration on the OLED device

Figure 35 shows the current vs. voltage curves of the device measured at different temperatures. The first noticeable difference in these results is the low activation voltage of this device compared to a device with V₂O₅. Even at temperatures below 20K where current transport is at its worst, the diode activation current is about 1mA corresponding to activation voltage of 0.4V.

![Figure 35](image)

**Figure 35:** Current vs. voltage of the OLED junction measured at different temperature via 4-prob measurement.
When looking at the diode behavior close to the NbN transition temperature and high currents, we can observe the effect of destroying NbN superconductivity on the junction. **Figure 36** shows the I-V curves measured near the transition temperature of NbN. Although we expect the resistance to grow as a function of temperature, there is a clear jump in resistance measured between 15K and 10K. The cause of this jump in resistance is found at the curve taken at 11K. This temperature is very close to the NbN $T_c$ ($T_c = 11.4$ K) where the superconductivity is relatively weak and therefore the critical current is relatively low. At 11K and below, at currents of 8mA the NbN is superconducting. Once we pass the critical current for this temperature the superconductivity breaks, resulting in current dissipation in the NbN followed by local heating which increases the temperature of the junction.

![Figure 36: Current vs. voltage of the OLED junction measured via 4-prob measurement at temperatures close to the NbN transition temperature.](image)

This effect drives the diode to a dynamic state were the local temperature of the device suddenly becomes higher and therefore the resistivity of the MEH-PPV becomes smaller. Yet, the most interesting results of this measurement are discovered by zooming in on the small currents. **Figure 37** presents the I-V curves for currents
between 40µA and -40µA. Generally, in these small currents the diode is in its ohmic regime, and far from the activation voltage were the behavior is SCLC.

**Figure 37**: Current vs. Voltage at small current between 40µA and -40µA in several temperatures.

We find a noticeable effect of temperature around and below $T_c$. For all temperatures above $T_c$ the behavior is ohmic, as expected for this voltage range. But, at temperature below $T_c$ we see much different features. From the data we can clearly witness two different areas of linear behavior. First, when a current is applied, the diode exhibits a linear behavior with a constant resistance. Then, at a certain current level the curves break and follow a different linear line with a greater constant resistance. Although the behavior of the first regime does not fit the typical Josephson junction behavior, since the resistance is not zero, there is strong evidence to support that this behavior is indeed caused by supercurrent transport in the polymer diode. First, this effect corresponds to the superconductivity onset measured on both superconductors. The $T_c$ of the Nb layer is 8.2K and in fact, the effect is seen at its best below 9K. Above 9K, the effect is much smaller but still exists until 12K where the superconductivity of NbN breaks down. Additionally, the critical current, at which
the resistance changes, is clearly affected by the temperature. The critical current is higher at lower temperature, as expected in the case of supercurrent.

It is important to point out that the critical current referred to here is not the Nb or the NbN critical current which is much higher. During the measurement the Nb and NbN electrodes remain superconductive before and after the change in resistance.

A strong indication for a proximity induced effect is found when measuring the resistance at the low current regime as a function of temperature. The resistance at this range is temperature dependent unlike the resistance after the critical current which is the same for all temperatures below 12K. From this we can estimate the relative portion of the junction that becomes superconducting as a function of temperature by assuming that the junction is constructed of a resistive portion with the same resistivity of the junction and a Sc portion with zero resistivity. In this case the portion of Sc is given by: \[ P = 1 - \frac{R_{sc}}{R_{ic}} \]. Where, \( R_{sc} \) is the resistance at the low current regime and \( R_{ic} \) is the resistance above the critical current.

**Figure 38** a shows the portion of superconductivity as a function of temperature (black squares, the dashed red line is a guide to the eye). This graph shows remarkable similarity to the superconductive gap dependence of temperature. In fact, these results show this behavior twice. At the 2K-8K temperature range both Nb and NbN are superconductive. Above this temperature, the Nb is no longer superconductive and the difference in resistance becomes much smaller. Yet, the junction still seems to be affected by the supercurrent injected from the NbN resulting again in temperature dependence similar to the gap dependence in temperature. This ends once the critical temperature of the NbN is reached and the conductance becomes the same as it is at currents above 30\( \mu \)A.
This phenomenon might be explained by quasi-particles injected into the polymer as well as Cooper pairs. As presented in section 3.5, the existence of some dissipation in the system does not necessarily contradict the existence of coherent states as well. An evidence for these coherent states may be found as peaks in the differential resistance caused by Multiple Andreev Reflection (MAR) [51]. MAR peaks were reported in high resolution measurement even at 2K for smaller junction areas where the layer thickness is homogeneous [49]. We tried to identify mid-gap states in the differential conductance, as expected in the case of MAR in the extended Josephson Effect, but such states were not observed. We believe that this is due to the large area, 1mm$^2$ of the device and inhomogeneous thickness. The junction thickness varies by more than 4 nm (about 10%) which is enough to wash out these mid gap peaks.

We are working at developing devices with smaller areas and believe they will enable us to observe the MAR for temperature range available in our PPMS. Josephson supper-currents may be observed when Cooper pairs coherently tunnel across the
entire junction, in our case the 2 Schottky barriers. We did not reach this case for the measurement shown.

Therefore we conclude, that at the temperature of 2K the leading term is still of quasi-particles tunneling as opposed to Cooper pair tunneling and that a super-current will be observed only at lower temperatures where the tunneling leading term for both tunnel barriers (according to Sc-I-N-I-Sc model) will be of Cooper-pairs. A similar behavior was reported in a study made on proximity induced superconductivity in other semiconducting materials such as individual single wall nanotubes [52] and DNA [45]. In these studies, the critical temperature for the proximity was found to be ~0.5K. When the sample is above this temperature and below $T_c$, the resistivity decreases with decreasing temperature but does not drop to zero, consistent with the trends we observed in our results. Assuming that our samples will have a similar evolution of resistance vs. temperature changes to those reported in reference [49] we can estimate the $T_c$ for our junctions at ~1.5 K. Thus, we need to perform the measurements in a different cryostat, or develop samples with lower tunneling barriers, for which $T_c$ is expected to increase.
6. Conclusions

6.1 OLED optical measurements at low temperature

We have successfully integrated superconductors and organic materials in an OLED structure while retaining the superconductive properties of the Nb and NbN electrodes and the excitonic properties of the active organic layer, MEH-PPV.

Furthermore, we successfully created a thin top superconductive layer made from NbN. This thin layer not only presents a high $T_c$ of 9.8K for a 15nm layer but also enables us to further decrease the thickness of the protective Al layer and most importantly allows for 27% light transmission. The final OLED device was built using a V$_2$O$_5$ hole blocking layer to increase the light emitting efficiency. Although, this layer was essential for light emission, it severely lowered the electrical efficiency of the device, causing a five times higher voltage drop of the diode. This aspect is magnified at low temperatures raising the activation voltage to 15V. High resistance at low temperatures results in local heating of the device which ruins the superconductivity already at 4V, much before OLED activation is reached.

Optically, in spite of the high resistivity, the OLED turns on when sufficient current is injected. It is evident from our results that the quantum efficiency of the OLED improves at low temperatures as was shown in previous research.

In the OLEDs prepared we could not examine proximity induced effects on light emission because of problems with the V$_2$O$_5$ hole blocking layer. In particular, the superconductivity was destroyed due to Joule heating in currents below the current needed for OLED activation. This problem can be solved by replacing the V$_2$O$_5$ with a second thin organic semiconductor layer, i.e. by creating a bilayer device with two organic layers that have a lower activation voltage, and higher quantum efficiency.
6.2 Single layer device measurements at low temperature

We built a single layer device consisting of MEH-PPV situated between two superconducting electrodes of Nb and NbN in order to examine the electrical transport properties of such a device. This device showed typical semiconductor behavior at low temperature with activation voltage of 0.2 V and 0.4 V at 300K and 2K respectively.

At high currents, we observed that the NbN superconducting transition influences the polymer’s electrical behavior due to polymer sensitivity to local heating caused by current dissipation in the NbN above its $T_c$.

Measurements of the single layer device at small currents between -40µA and 40µA reveals strong evidence of proximity induced effects in the polymer. In this regime, we find a change in resistance which is both temperature and current dependent although the resistance is not zero. Given these results, it is safe to assume, that we did not reach a sufficiently low temperature in order to witness the Josephson super-current in the junction. The measurements were performed at temperatures higher than 2K on a junction area of 1mm$^2$. Presumably temperatures below 1.5K would be needed to observe a Josephson super-current, because, even in the case of ordered inorganic high resistance semiconductors, the Josephson super-current is witnessed at lower temperature.

Additionally, any possible peaks in the differential resistance caused by MAR would be averaged under the inhomogeneous thickness of the junction area and therefore would not be detectable in the current device geometry.

Our measurements suggest that Josephson supper-current will be observed in organic light emitting materials at temperature lower than 2K and that injection of coherent particles into the organic materials actually occurs.
7. Future work

In order to continue the study of proximity induced effects on the light emitting properties of excitons, our first objective is to replace the V$_2$O$_5$ layer in the OLED by creating a bilayer device with two organic layers. In such a device, the MEH-PPV will be used as the hole-transport layer. On top of the MEH-PPV, we will deposit a second organic semiconductor (using thermal evaporation) which is an electron transport layer, such as 3,5-Diphenyl-4-(1-naphthyl)-1H-1,2,4-triazole (TAZ). Therefore, instead of reducing the hole mobility with the V$_2$O$_5$ layer, we will increase the electron mobility, acquiring once again charge balance. A full organic device will lower the OLED resistance and strongly improve the quantum efficiency of the device. Additionally it will increase the probability for proximity induced effects from the bottom layer of Nb. Creating an OLED with high quantum efficiency will also reduce the local Joule heating of the device. Furthermore, the ability to collect more light from the device will allow for sensitive spectral and quantum correlation measurements.

In this work, we showed evidence of a Josephson Effect in MEH-PPV. Further measurements are also required to verify and characterize the Josephson Effect in organic semiconductors. To do so, we will perform the measurements at temperatures below 2K and compare the electrical properties of a single layer device with different top contacts, such as using Nb on top of Al or a thick Al contact (instead of Al-NbN). Comparing these devices with the NbN top (that we have already measured) device will allow us to contact device will allow us to determine the contribution of the top Sc in our devices. An Al top contact device will allow us to set a base line for the other measurements.
Additionally, we plan to repeat these measurements with higher electrical resolution and on a smaller area junction in order to detect peaks in the differential resistance caused by MAR. This measurement will provide conclusive proof of successful injection of coherent electron-hole pairs into the polymer.
References


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מטרת עבודת המחקר הזו היא לבנות דיו פולטת - אור מחומרים אורגניים עם אלקטרודות העשויות מממתנה על מוליכה על מנת לחקור את השפעת זוגות קופר קוהרנטיים של על-מוליקר על ריקומבינציה פולטת - אור בתווך האורגניים המופעל בדידות פלטת - אור וליישר את הקוהרנטית שלם בין צמד הפריטים. מחקר שבוצע בשנים האחרונות של Suemune et. al. על דיו פולטת אור הראה שהיחידה האורגנית שלה הפעילה בדיו פולטת - אור ויהמור באורגניות. מחקר שבוצע prost Savings in the electronic properties of the organic layer, provided that the junction between the two materials is properly designed. שלמים בשיטה זו, אנו מציגים את האתגרים שב_ADDRESS עלינו כדי לבנות ממשק פעיל של על-مولיך / על-مولיך. אנו מציגים מדידות חשמליות ואופטיות של דיו פולטת - אור ייחודית בעלת שתי אלקטרודות על-مولיכות בטמפרטורות מעל ומתחת לטמפרטורה הקריטית של על-مولיך. האלקטרודה העליונה בהתקן זה היא על-מוליך ושקופה למחצה וUIB allows the collection of the light emitted upwards. לבסוף, אנו מציגים עדות חזקה לקיומו של אפקט ג'וספסון בתוך שכבה פולימר פולטת אור (MEH-PPV) שנמצאת בין שני על-مولיכים ועל כן מאוששות למעשה את ההנחה הבסיסית של מחקר זו.
עבורה והباشرת במהרהם של

דר' יעקב טישלר,
המחלקה לכימיה

דר' עמוס שרוני,
המחלקה לפיזיקה

אמריקסיט בר-אילן.
בנין של דיודה אורגנית פולטת אור ואור ביצת
אלקטרודות על-مولיכות.

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全民健身 של דירוג אורגניזציה פולמת-אור בצלת
אלקטרודים על-מוליכות.

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עבורה זו מונה עות חוכל מחזורית לשם קבלת תואר מוסמך
במתחלה לפידיה של אוניברסיטת בר-אילן

רמחן גנ

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