

Design and Fabrication of Light-Emitting Electrochemical Cells

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“Don’t Panic”

– Douglas Adams, *The Hitchhiker’s Guide to the Galaxy*

Sammanfattning

Glödlampan, en gång symbolen för mänsklig uppfinningsförmåga, är idag på väg att försvinna. Lysdioder och lågenergilampor har istället tagit över då dessa har betydligt längre livstid och högre effektivitet. Den tidigare så hyllade glödlampan anses numera vara en miljöbov, och förbud och restriktioner mot den blir allt vanligare. Trots detta så är de nya alternativen bara att betrakta som provisoriska steg på vägen mot en ideal ljuskälla, som idag tyvärr inte existerar. Lågenergilampor innehåller exempelvis kvicksilver, och utgör därmed ett direkt hot mot en användares hälsa. Både lysdioder och lågenergilampor består även av höga halter av andra tungmetaller, och är väldigt komplicerade att tillverka. Återvinning är därför ett måste, och en fullödig energibesparingsanalys måste ta hänsyn till den betydande energin som går åt vid tillverkningen. Till viss del kan detta lösas genom att göra komponenterna små och ljusstarka, men för att göra en sådan belysning angenäm används istället utrymmeskrävande och ofta energislukande lampskärmar. Lysdioder och lågenergilampor är helt enkelt bra, men långt ifrån perfekta.

All elektronisk utrustning är idag beroende av metaller och inorganiska halvledare, vilket gör återvinning viktig och tillverkning komplicerad. Detta är kanske på väg att ändras då även organiska material, t.ex. plast, har visat sig kunna ha elektroniska egenskaper. Idag är organisk elektronik ett hett forskningsområde där material med liknande egenskaper som plast, fast med funktionella elektroniska egenskaper, undersöks och appliceras.

Något som gör organiska material extra intressanta är att många kan lösas upp i vätskor, vilket möjliggör för skapandet av bläck. Detta leder i sin tur till möjligheter för användandet av storskaliga trycktekniker, t.ex. tidningspressar och bläckstråleskrivare, vilka leder till en stor kostnadsreduktion och förenklad tillverkning av lysande komponenter. Idag har plast redan ersatt många andra material i en mängd olika tillämpningar. Plastflaskor är vanligare än glasflaskor, och ylletröjor konkurrerar idag med kläder gjorda av fleece och andra syntetiska fibrer. Med ljusemitterande plast finns det helt klart en möjlighet att en liknande utveckling kan ske även för lampor.

Den här avhandlingen fokuserar på den fortsatta utvecklingen av den ljusemitterande elektrokemiska cellen (LEC), som 1995 uppfanns av Pei et al. LEC-tekniken använder sig av organiska halvledare för att konvertera elektrisk ström till ljus, men även en elektrolyt som möjliggör *elektrokemisk dopning*. Detta förbättrar den organiska halvledarens elektroniska egenskaper signifikant, vilket leder till mindre resistans och högre effektivitet hos den färdiga lysande komponenten.

Visionen för denna och besläktade tekniker har sedan länge varit förverkligandet av en lysande tapet. Den här avhandlingen har försökt närma sig denna vision genom att visa hur en LEC kan uppnå hög effektivitet och lång livslängd, och samtidigt tillverkas i luft med storskaliga produktionsmetoder. Orsaker till en tidigare begränsad livslängd har identifierats och minimerats med hjälp av nya komponentstrukturer och materialformuleringar. En inkapslingsmetod presenteras också, vilken skyddar komponenten från syre och vatten som annars lätt reagerar med det dopade organiska materialet. Detta resulterar i en signifikant förbättring av livslängden.

Genom att använda slot-die bstrykning och sprayning, båda kompatibla med rulle-till-rulle tillverkning, har möjligheter för storskalig produktion demonstrerats. Slutligen har en speciell metod för spraymålning av stora lysande ytor utvecklats.

Abstract

The incandescent light bulb, once the very symbol for human ingenuity, is now being replaced by the next generation of lighting technologies such as the compact fluorescent lamp (CFL) and the light emitting diode (LED). The higher efficiencies and longer operational lifetimes of these new sources of illumination have led to the demise of the classic traditional bulb. However, it should be pointed out that the light sources that are taking over are better, but not perfect. The complex high-voltage electronic circuits and health hazardous materials required for their operation make them far from a sustainable eco-friendly option. Their fabrication is also complex, making the final product expensive.

A new path forward might be through the use of *plastics* or other organic materials. Though not traditionally seen as electronically active, some organic materials do behave like inorganic semiconductors and substantial conductivity can be achieved by *doping*. Since plastics can be easily molded into complex shapes, or made into an ink using a solvent, it is expected that organic materials could revolutionize how we fabricate electronic devices in the future, and possibly replace inorganic crystals in the same way as plastics have replaced glass and wool for food storage and clothes.

This thesis has focused on the light-emitting electrochemical cell (LEC), which was invented by Pei et al. in 1995. It employs organic semiconductors that can convert electricity to light, but also an electrolyte that further enhances the electronic properties of the semiconductor by allowing it to be electrochemically doped. This allows light-emitting films to be driven by a low-voltage source at a high efficiency. Unfortunately, the electrolyte has been shown to facilitate rapid degradation of the device under operation, which has historically severely limited the operational lifetime. Realizing the predicted high efficiency has also proven difficult.

The purpose of this thesis is to bridge the gap between the LEC and the CFL. This is done by demonstrating efficient devices and improved operational lifetimes. Possible degradation mechanisms are identified and minimized using novel device architectures and optimized active layer compositions. An encapsulation method is presented, and shown to increase the LEC stability significantly by protecting it from ambient oxygen and water. The thesis further focuses on up-scaled fabrication under ambient air conditions, proving that light-emitting devices are compatible with solution-based and cost-efficient printing. This is achieved by a roll-to-roll compatible slot-die coating and a novel spray-depositing technique that alleviates problems stemming from dust particles and phase separation. A practical ambient air fabrication and a subsequent operation of light-emitting electrochemical cells with high efficiency are thus shown possible.

Used abbreviations

AFM	Atomic Force Microscope
CFL	Compact Fluorescent Lamp
CV	Cyclic Voltammetry
EDL	Electric Double Layer
ETL	Electron Transport Layer
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
ITO	Indium tin oxide
KCF ₃ SO ₃	Potassium trifluoromethanesulfonate
LCD	Liquid Crystal Display
LEC	Light-emitting Electrochemical Cell
LED	Light Emitting Diode
LiCF ₃ SO ₃	Lithium trifluoromethanesulfonate
LUMO	Lowest Unoccupied Molecular Orbital
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
OLED	Organic Light-Emitting Diode
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PEO	Poly(ethylene oxide)
PET	Poly(ethylene terephthalate)
SB	Superblue
SY	Superyellow
THF	Tetrahydrofuran
TMPE	Trimethylolpropane ethoxylate

List of publications

The thesis is based on the following publications:

(Reprints made with the permission from the publishers)

- I. A. Sandström, P. Matyba, and L. Edman.
Yellow-green light-emitting electrochemical cells with long lifetime and high efficiency
Applied Physics Letters, 96(5) 053303 (2010)
- II. A. Sandström, P. Matyba, O. Inganäs, and L. Edman.
Separating ion and electron transport: the bi-layer light-emitting electrochemical cell
Journal of the American Chemical Society, 132(19) 6646-6647 (2010)
- III. A. Sandström, H. F. Dam, F. Krebs, and L. Edman.
Ambient fabrication of flexible and large-area organic light-emitting devices using slot-die coating
Nature Communications, 3, 1002 (2012)
- IV. A. Asadpoordarvish, A. Sandström, S. Tang, J. Granström, and L. Edman
Encapsulating light-emitting electrochemical cells for improved performance
Applied Physics Letters, 100(19) 193508 (2012)
- V. S. Tang, A. Sandström, J. Fang, and L. Edman
A Solution-Processed Trilayer Electrochemical Device: Localizing the Light Emission for Optimized Performance
Journal of the American Chemical Society, 134(34) 14050-14055 (2012)

Published work not part of thesis

- VI. A. Munar, A. Sandström, S. Tang, and L. Edman.
Shedding light on the operation of polymer light-emitting electrochemical cells using impedance spectroscopy
Advanced Functional Materials, 22(7) 1511-1517 (2012)

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Introduction

The discovery and taming of fire might be one of the most profound achievements in human history. The same statement can be made about the invention of the incandescent lightbulb, as it gave us a brighter and safer alternative to the open flame. However, the era of the incandescent lightbulb is coming to an end, as it is now being replaced with even better alternatives such as the light-emitting diode (LED) and the compact fluorescent lamp (CFL).[1] The longer lifetimes and higher efficiencies make these new technologies superior to the old lightbulb. However, LEDs and CFLs are not perfect. They are expensive to fabricate, require complex electronics to work, and they can actually be classified as hazardous due to their high metal content.[2, 3]

All of the examples above are based on the same idea, where light is created with a high intensity at a localized point in space, such as a candle on a table or a lightbulb in a fixture mounted on the wall. Practically, this is not ideal as space is consumed by the fixtures and the light source itself. Also, a small and intense source of light will inevitably result in shadows and an uncomfortable glare. A solution to this is an often elegant, but still space consuming, lampshade that diffuses the emission over a larger area. However, the efficiency value given for a light source is based on the lamp only, and does not take into account the often significant loss of light due to the diffusers that are typically used.

The ideal lamp should provide light over a large glare-free area but still consume a neglectable amount of space. Energy consumption should be minimized, both during initial fabrication, the final recycling, and especially during operation. This thesis will discuss a light-emitting technology that might bring this vision of the ideal source of illumination closer to reality.

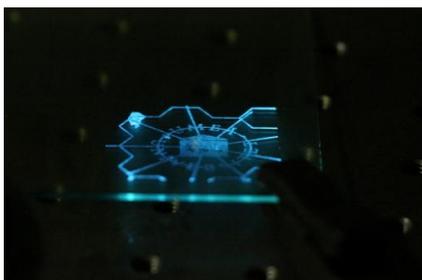
Organic electronics

Historically, electronics has been seen as a science of metals and inorganic semiconductors, and no one can deny the success of their combination. Organic materials have had the less glorious part of simply acting as insulating protective containers to the electronics that actually do all the work. Perhaps, this is about to change. The 2000 Nobel Prize in chemistry was awarded to Shirakawa, MacDiarmid, and Heeger for their work on organic semiconductors. They had 23 years earlier collectively demonstrated that a certain family of polymers could be given metallic properties through *doping*. In their pioneering article, they demonstrated a doped polymer with a conductivity of 38 S/cm, an increase by a factor of 10,000,000 compared to the pristine material.[4] Though this value is still low compared to metals, which typically conducts an additional 1,000 times better, this early work

still demonstrated a polymer that was far from an insulator. Today, doped conductive polymers reaching more than 1,000 S/cm are commercially available, such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), shown in figure 3f.[5] Scientific articles reporting higher values than this are commonplace, including reports of organic materials reaching superconductivity.[6, 7]

Many organic materials can, unlike metals and inorganic semiconducting crystals, be dissolved and processed from a solution.[8] Many important metals are also extremely rare, as demonstrated by the genuine interest in asteroid mining.[9] Organic materials in contrast comprise some of the most abundant and easily obtainable elements on earth. The Nobel Prize was certainly given with this in mind, envisioning a sustainable future with novel organic electronic materials lowering cost of consumer electronics through more efficient ink-based fabrication and cheaper constituents. However, this vision has yet to materialize, and organic electronics has remained an interesting novelty largely outperformed by its inorganic counterparts.

(a)



(b)

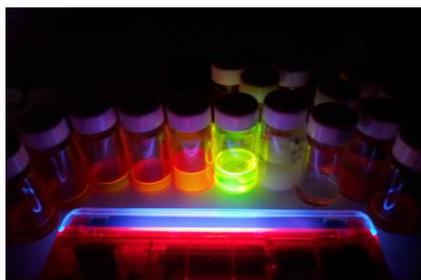


Figure 1. (a) A transparent LEC designed to display a message and (b) ink vials, with the dissolved semiconducting polymers photoexcited by UV light.

Organic light-emitting devices

The display technology is where organic electronics has been the most successful. This is because the organic light-emitting diode (OLED) has been able to compete with the liquid crystal display (LCD), as evident from the fact that OLED screens are found today in many of the most popular smartphones. However, the success of OLEDs is not attributed to simple low-cost fabrication. Instead, they exhibit superior display performance by offering vivid colors and high contrast ratios. Since no backlight is needed, OLED displays consume less power as well. However, the device structure of an OLED is often very complex, as is the method of manufacturing. High performance OLEDs require thin films, multilayered structures, and air

sensitive constituents, making them far from a low-cost alternative to inorganic technologies. A 55" TV using OLED technology is currently sold for approximately 7,000€¹, significantly more expensive than an LCD display of similar size.

This thesis is based on the light-emitting electrochemical cell (LEC), first realized by Pei and coworkers in 1995.[10] Compared to OLEDs, LECs offer a higher resilience towards surface roughnesses and film defects, allowing large area devices to be made using simpler and upscalable methods. A LEC can be made using air stable materials and does not critically rely on multilayered structures simplifying fabrication substantially.[11] Because of this, LECs might have a better chance in actually living up to the promises of organic electronics by being a practical and printable low-cost device.

Purpose of thesis

LECs are promising due to the advantages presented in the section above, but several issues have remained to be resolved. Efficiency and lifetime have traditionally been far from that achieved with other light-emitting technologies, and functional fabrication methods for large scale printing and coating processes have remained elusive.

This thesis will present pioneering breakthroughs in LEC design and fabrication, thus providing a path towards fully solution processable and efficient light sources made on a much larger scale than the state of the art prior to this work.

¹ Price lowered from 10,000€ to 7,000€ during the preparation of this thesis.

Materials

Device architecture

A LEC consists of two electrodes and an *active layer* comprising mobile ions and a light-emitting organic semiconductor, arranged to form a *device*. The most common device architectures are the surface cell and the sandwich cell, as schematically shown in figure 2. The sandwich cell (figure 2a) is the most practical, with a large light-emitting region defined by the overlapping area of the bottom and top electrode. In the surface cell (figure 2b), an open and large interelectrode distance is possible allowing direct electrical and optical probing of the electrochemistry taking place during LEC operation. However, devices with substantial light output have proven difficult to realize from surface-cell LECs.[10, 12] This thesis will employ the sandwich cell architecture when the LEC is tested in terms of performance (luminance and lifetime), while the surface cell will be used to directly observe the electrochemistry taking place. The combination of both architectures is thus valuable experimentally as they both, in different ways, help shed light on the complex physics and chemistry in play during LEC operation.

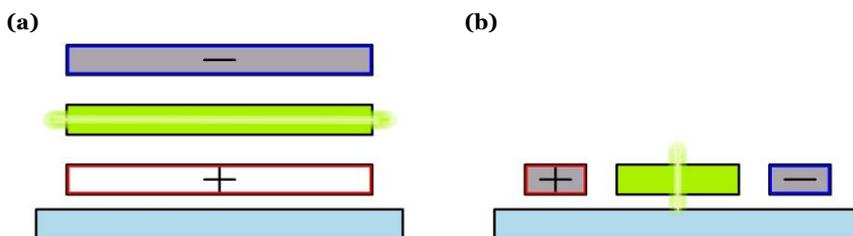


Figure 2. Schematic cross section of the two light-emitting electrochemical cell architectures employed in this thesis: (a) a sandwich cell and (b) a surface cell. Note the need for a transparent electrode in the sandwich cell, as light needs to pass through at least one of the electrodes to escape the device.

The active layer in a LEC always comprises a light-emitting semiconductor and an electrolyte, while the electrodes consist of electrochemically stable conductive materials. The sections below will present these in more detail, as well as the solvents employed for the preparation of inks.

Light-emitting organic materials

Organic semiconductors exist in many forms, and this thesis will focus on the poly(*p*-phenylene vinylene)-based co-polymer superyellow (figure 3a) and the polyspirobifluorene-based superblue (figure 3b). However, the LEC concept can be applied to non-polymeric materials as well, such as ionic transition metal complexes or small molecules, the latter being the most commonly employed in commercial OLEDs.[13, 14] Common examples of

small molecules are tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$) and tris(8-hydroxyquinoline)aluminium (Alq_3) shown in figure 3d and 3e, respectively. Small molecules offer several advantages over conjugated polymers, primarily during material fabrication due to their smaller size and simpler structure. However, fabrication of actual devices from solution has proven difficult, due to the typically poor film-forming abilities of small-molecule materials.[15]

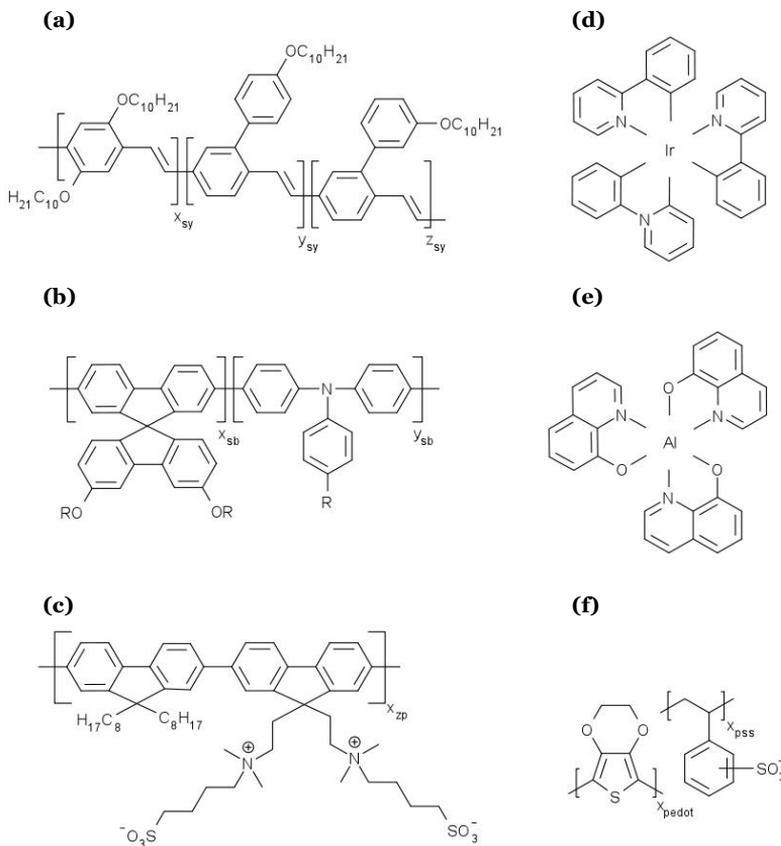


Figure 3. Examples of organic semiconductors: the conjugated co-polymers (a) superyellow, (b) superblue (note that R denotes a side chain with a structure not disclosed by the manufacturer) and the zwitterionic polymer (c) poly[(9,9-bis((N-(4-sulfonate-1-butyl)-N,N-dimethylammonium)-ethanyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]. The organometallic complexes (d) tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$) and (e) tris(8-hydroxyquinoline)aluminium (Alq_3). Finally, (f) poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS).

In all cases, the functionality of an organic semiconductor will depend on the energetic positions of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[16] The HOMO and

LUMO can be seen as the equivalences to the edges of the valence and conduction band of a crystalline inorganic semiconductor, respectively. Unlike inorganic materials, organic semiconductors can be easily *tuned*, by adding functional side groups or by creating co-polymers, where different organic semiconductors are combined into a co-polymer chain. This allows the HOMO and LUMO levels to be moved collectively, or the energy gap between them to be changed. Adding side chains can also influence solubility and film-forming abilities of the material.[17, 18] The relative ease with which this can be done is one of the major arguments in favour of organic electronics, as it offers an impressive versatility. However, the interactions between electronic orbitals which define the location of energy states are also dependent on the geometry of the polymer and its relation with other molecules. In a solution deposited film, a simple change of ink solvent can shift the HOMO and/or LUMO levels markedly, and the observed emission from an organic light emitting device does commonly exhibit a very broad spectrum due to the disordered nature of the resulting amorphous film. [19-22] This is in stark contrast to the highly ordered structure of, and more narrow emission from, inorganic semiconductors.

Superyellow is an example of a singlet emitter. As such, there is a limit to the efficiency that can be achieved in a LEC based on this material, as the formed triplets are lost as heat. It is often assumed that 25% of all excitons formed during charge recombination are singlets, which means that 75% of all charges injected into the device are wasted under otherwise ideal loss-free operation.[16] However, the validity of this statement is under debate, especially for long polymer chains, and the singlet-triplet fraction could be higher.[23] The formation of light-emitting singlets via *triplet fusion* is also an interesting concept that could increase the amount of singlets by 150%.[24, 25] Analysing the efficiency of the current generation of LECs should be done with this knowledge in mind, as a switch to a triplet-emitting material is anticipated to increase the device efficiency significantly. This is not an unsubstantiated claim, as the switch from singlet to triplet emitters has already been achieved in phosphorescent (i.e. triplet-emitting) OLEDs, and a subsequent increase in efficiency has been experimentally verified.[26]. Unfortunately, the triplet emission is often achieved using heavy atoms such as iridium or platinum (e.g. Ir(ppy)₃ in figure 3d), making phosphorescent materials expensive and less appealing from a sustainability viewpoint.[27]

An interesting LEC material is the zwitterionic conjugated polymer. This material combines the electronic properties of the organic semiconductor with the ion-providing properties of a salt, as the neutral molecule contains localized positive and negative ionic charges. The polymer employed in this thesis, shown in figure 3c, has the ionic charges separated by flexible carbon chains allowing some degree of ion mobility. In OLEDs, zwitterionic

polymers have been employed as electron injectors, as the achievable short-range ionic redistribution can be utilized to improve the charge injection from the cathode.[28]

Electrolyte materials

A good electrolyte provides high ion conductivity and is electrochemically stable over a large energy range encompassing the HOMO and LUMO levels of the organic semiconductor it is mixed with. The structures of the salts and the ion solvating materials employed in this thesis are shown in figure 4.

The salts (figure 4a and 4b) both have the same CF_3SO_3^- (triflate) anion, with either a Li^+ or a K^+ as the positive cation. Li^+ is the most commonly cation used, probably due to its long history as a part of lithium battery electrolytes, but it has been shown that K^+ is a better option for LECs as the turn-on time of devices with the larger cation surprisingly decreases, indicating a higher ionic conductivity.[29, 30] However, LiCF_3SO_3 is still used as it can be readily dissolved in the solvent tetrahydrofuran, commonly used for LEC fabrication, in which KCF_3SO_3 precipitates.

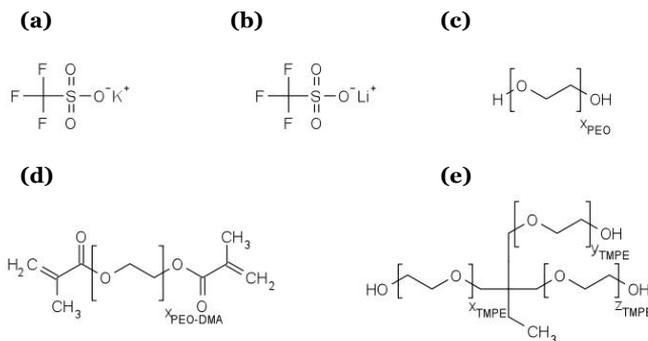


Figure 4. Employed electrolyte materials: (a) potassium trifluoromethanesulfonate, (b) lithium trifluoromethanesulfonate, (c) poly(ethylene oxide), (d) poly(ethylene oxide) dimethacrylate, and (e) trimethylolpropane ethoxylate.

The ion-solvating materials employed in this thesis are all to some extent based on poly(ethylene oxide) (PEO) (figure 4c). The very first LEC made by Pei et al. used LiCF_3SO_3 and PEO for the electrolyte, so it is remarkable that the same material combination is still widely used in LEC systems, as well as in many other electrochemical applications e.g. polymer batteries.[31, 32] Unfortunately, PEO easily crystallizes, forming regions of fringed micells that repress ionic conductivity.[33, 34] The electrochemical stability is also far from ideal.[35]

This thesis has used the ion-solvating materials PEO (long chain, $M(\text{PEO}) = 600,000 \text{ g/mol}$ or $5,000,000 \text{ g/mol}$, figure 4c), poly(ethylene

oxide)dimethacrylate (PEO-DMA, $M(\text{PEO-DMA}) = 750 \text{ g/mol}$, figure 4d), and trimethylolpropane ethoxylate (TMPE, $M(\text{TMPE}) = 450 \text{ g/mol}$, figure 4e). PEO-DMA and TMPE possess low molar mass (shorter chain length) than PEO, which allows the materials to be molten and non-crystalline at room temperature, and thereby increasing the ion mobility. However, since approximately the same amount of electrolyte is needed independent of the length of the PEO chain, a shorter molecule will lead to an increased amount of end groups in the active layer. Stable end groups must therefore be identified. Standard PEO is capped by hydroxyl (-OH) end groups, which could be possible sites for undesired redox reactions. Yu et al. also demonstrated better device performance using PEO-DMA compared to standard long chain PEO, indicating that the methacrylate endgroup is more electrochemically stable than the hydroxyl endgroup.[19] Tang et al. solved this issue even more elegantly by instead introducing the mobile TMPE, simply described as three short PEO chains linked together. TMPE minimizes the problem of side reactions by allowing the ion-solvating material to coordinate with the ions and follow these towards the electrodes during ionic migration. This results in an ion and TMPE depletion in the light-emission center of the device, thus limiting the amount of unwanted redox sites in this sensitive region.[36]

Electrode materials

The conductivity of the electrodes in a LEC is obviously important, as a significant electrode resistance can lead to voltage drops along the electrode surface during operation, which in turn is concomitant with a lower efficiency and non-uniform light emission (see figure 5d). The electrodes must also be stable during the electrochemical reactions taking place, and one of them should be highly reflective (unless a transparent device is desired). This thesis has primarily employed aluminium as the reflective electrode.

Metal electrodes can be used as both the anode and cathode in surface cells, but at least one electrode must be transparent to allow the light to escape from a sandwich cell (figure 2). To achieve this, indium tin oxide (ITO) is most commonly used ($\sigma = 10,000 \text{ S/cm}$).[37] Though expensive, due to the scarce supply of indium and the need for vacuum assisted deposition methods, it still offers a superior combination of stability, conductivity, and transmittance. Finding a replacement for ITO is clearly not trivial as no obvious candidate has yet been identified even though significant research has been made on the subject.[38]

For LECs, where solution processability is a key, electrode materials should be made using organic materials and/or inks as well. Matyba et al. demonstrated that this is indeed possible, by designing and fabricating the first all-organic LEC, comprising PEDOT:PSS and graphene as the anode

and the cathode, respectively,[39, 40] Since then, more examples of solution-processable LEC electrodes have been demonstrated, with some results indicating better performance than achieved using sputtered ITO.[41, 42] This thesis work has employed several solution-processable electrode materials and combinations thereof, but only a few will be disclosed here. Nevertheless, it is important to note that LECs do indeed allow for a wide range of electrode materials to be used, making the technology highly adaptable.

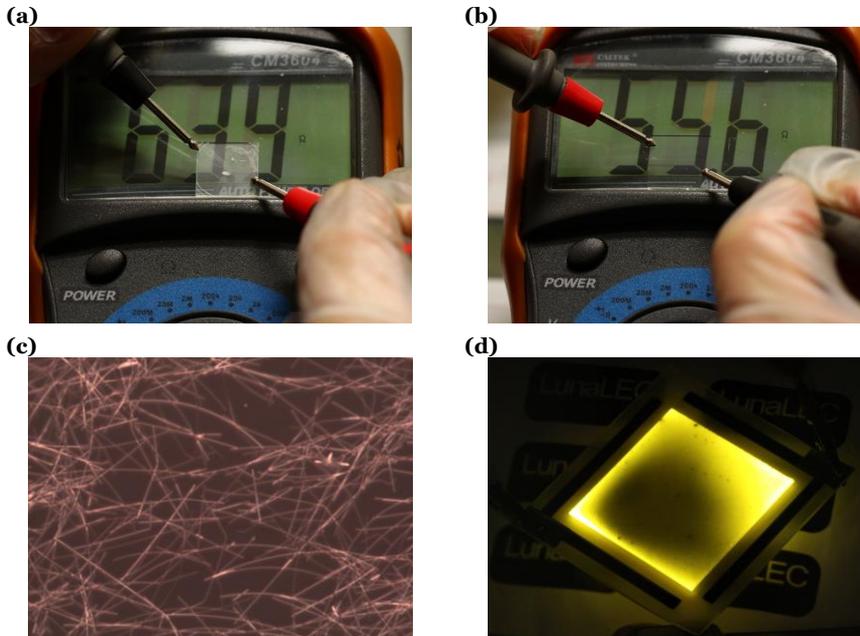


Figure 5. (a) The resistance measured on a thin layer of silver nanowires deposited from solution onto glass, and (b) the measurement performed on an ITO-coated substrate. The silver nanowires are almost as conductive as ITO, but note the milky appearance and uneven distribution of the silver coating compared to the higher transparency of ITO. (c) A microscope photograph of silver nanowires. (d) The emission from a device suffering from poor electrode conductivity.

Most extensively used is the aforementioned PEDOT:PSS (figure 3f). As a p-type charge-injection/planarizing layer on top of ITO, it improves LEC stability as first demonstrated by Fang et al.[43] However, the relatively high conductivity of optimized PEDOT:PSS has allowed it to also be used as a completely ITO-replacing anode for small devices, as in the all-organic LEC mentioned previously. PEDOT:PSS is commonly processed from a water dispersion, and careful drying is required to ensure that a deposited PEDOT:PSS film is completely void of moisture. This is typically done by drying at temperatures above the boiling point of water for several hours.

ZnO has been used as a transparent n-type charge-injection/planarizing layer on top of ITO. However, ZnO acts as an excellent and robust cathode interface, thus complementing the PEDOT:PSS anode nicely. Though not an organic material, ZnO can be deposited from solution using dispersions of the material.[44] However, the material cannot be used as a pure electrode due to its low conductivity, and only remain applicable as an electrode when combined with a more conductive material.

For large-area devices, high metallic-like conductivities are required for the electrodes to ensure homogeneous emission at high brightnesses. Here, silver nanowires (figure 5c), and hybrids combining them with e.g. PEDOT:PSS, have shown the most promising results. The nanowires employed in this thesis are delivered in an ethanol dispersion, and dilution and sonification are required prior to deposition to avoid agglomeration. Still, coating silver nanowires onto a surface and achieving a highly conductive network of wires without any clustering is extremely difficult. This thesis presents completely new deposition methods for the fabrication of patterned transparent top electrodes based on silver nanowire dispersions.

Solvents

Several difficulties in LEC fabrication stem from the mix of a hydrophobic organic semiconductor with a hydrophilic electrolyte. Finding solvents that can allow a homogenous blend solution to form is therefore important. Ideally, the same solvent should be used for all constituents but solvent blends have successfully been employed as well.

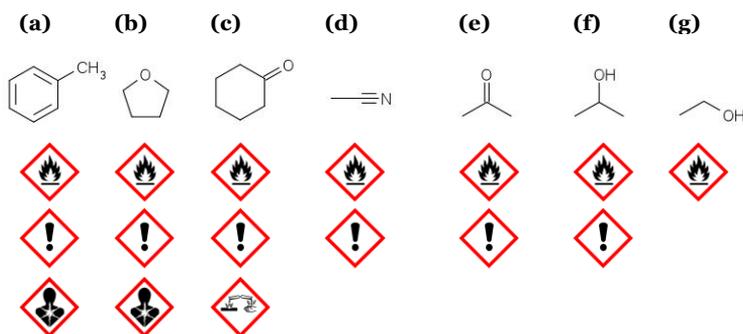


Figure 6. The solvents used in this thesis and their hazard symbols: (a) toluene, (b) tetrahydrofuran, (c) cyclohexanone, (d) acetonitrile, (e) acetone, (f) isopropanol, and (g) ethanol

The standard procedure when fabricating an ink is to first dissolve all constituents separately at a set concentration, typically 10 mg/ml, thus creating *master solutions* of each individual constituent. The active-layer ink

is subsequently made by mixing these master solutions, creating a *blend* with the desired constituent mass ratio.

The solvents that have been used to dissolve superyellow and superblue in this work are tetrahydrofuran (THF), cyclohexanone, and toluene. The electrolyte was dissolved in THF, cyclohexanone, or acetonitrile. Both THF and cyclohexanone can thus be used for the conjugated polymers as well, allowing the same solvent to be used for all constituents. Acetonitrile has been used in the opposite way, as it does not dissolve superyellow and superblue. This can be utilized to create layer-on-layer structures as an acetonitrile-based solution can be deposited on top of the conjugated polymers without dissolving them. Acetonitrile has also been used for cyclic voltammetry, as it is electrochemically stable and can dissolve a wide range of electrolytes. Ethanol and isopropanol have been used to dilute PEDOT:PSS and Ag-NW dispersions during electrode fabrication. Similarly to acetonitrile, these solvents do not dissolve the conjugated polymers allowing layer-on-layer fabrication from solution.

The electrochemical generation of light

The LEC creates light using electrochemistry, and a model for the processes taking place has been put forward and verified experimentally.[45-47] This model explains observed LEC characteristics, and it is presented here.

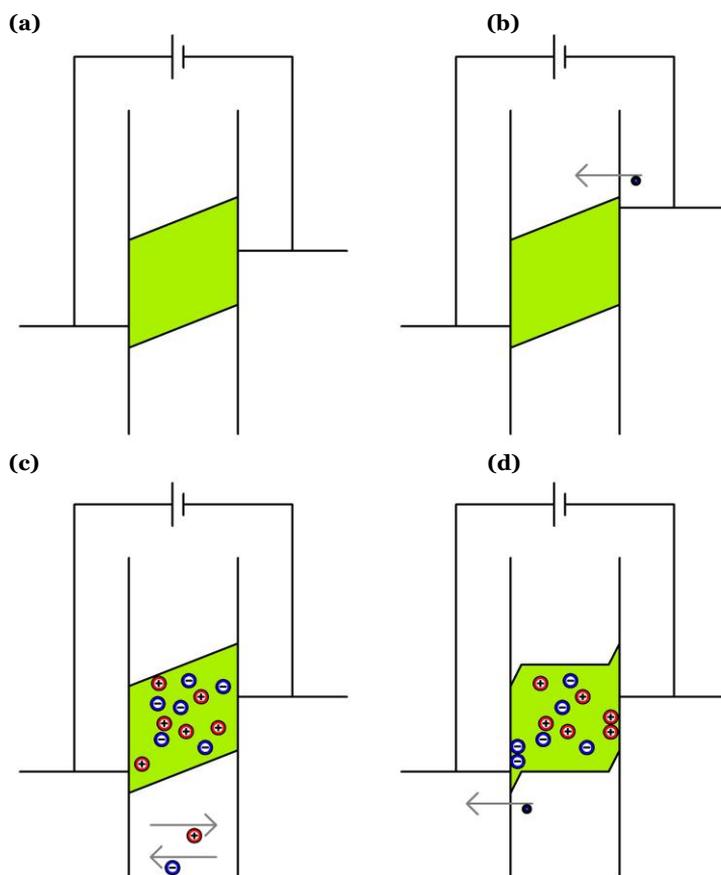


Figure 7. The formation of electric double layers. (a) An organic semiconductor with its HOMO and LUMO levels indicated, sandwiched by two electrodes with different workfunctions. An external power source provides an electric field between the two electrodes, but the energy barriers between the electrode/organic material interfaces prevent charge injection. No current flows. (b) A cathode with a low workfunction is introduced, allowing charge injection from the cathode. (c) A schematic picture of a LEC, with mobile ions blended with the organic semiconductor, as an external voltage is applied (d) The same system as shown in c, but under steady-state. Ions have redistributed and screen the electric field. Electric double layers have formed close to the electrodes, and charges can now tunnel through the thin barrier at the anode.

Charge injection

Finding electrode materials able to inject charge into undoped light-emitting organic semiconductors at a low voltage is not straightforward. Most metals have workfunctions similar to those shown in figure 7a, which means that there is a substantial energy barrier between charges in the electrode and the HOMO-LUMO levels of the semiconductor.[48] Exotic alternatives, such as alkali and alkaline earth metals, exhibit low workfunctions that can be used to improve charge injection simply by lowering the barrier between the LUMO and the cathode, as shown in figure 7b.[49] However, these materials are also very sensitive to oxygen and water making fabrication in air difficult. Moreover, thin organic layers, sensitive to short circuits, are required to promote tunneling through the small, but still existing, barrier.

The LEC solves this problem through its use of mobile ions. Charge injection is facilitated by the formation of electric double layers (EDLs) at the electrode interfaces. The EDLs form when mobile ions respond to an electric field induced by an externally applied voltage (figure 7c and 7d). This will cause a build-up of positive ions at the negative electrode and negative ions at the positive electrode. The formed EDLs are very thin, on the order of 1 nm, which results in a huge electric field gradient at the electrode interfaces independent on the active layer thickness. The validity of this has been observed experimentally, as functional LECs with air-stable gold electrodes and an interelectrode distance of 1 mm emitting light at 3 V have been reported, indicating the formation of *ohmic contacts* between the electrodes and the semiconductor.[46, 50]

Electrochemical doping

When a sufficiently high voltage bias is supplied between the two electrodes (figure 8a), EDL formation will allow electronic charges to be efficiently injected into the HOMO and LUMO levels of the charge transporting material (figure 8b). This voltage can be roughly estimated by the bandgap of the employed organic semiconductor. In devices with a very thin active layer, and small amounts of electrolyte, the formation of EDLs can in principle allow charge injection and light emission directly. However, if the film is a bit thicker and some free ions remain, the initial electronic charge injection will be compensated by an ionic migration (figure 8c).

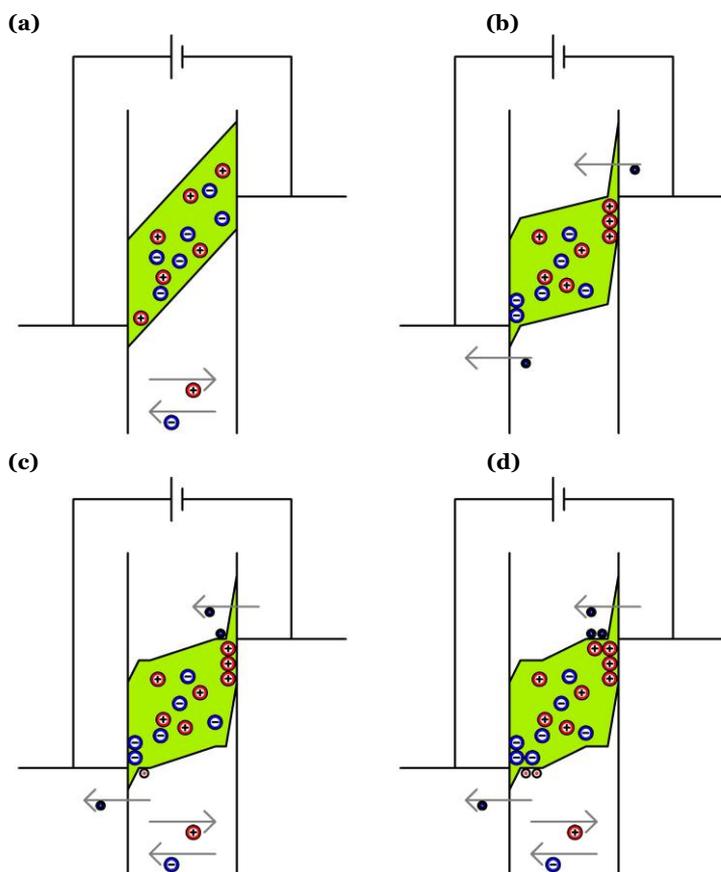


Figure 8. The electrochemical doping. (a) A schematic picture of a LEC at the moment an external power source is connected. (b) The electric double layers have formed, and the voltage bias is high enough to allow charge injection and extraction from both the LUMO and HOMO levels of the organic semiconductor. (c) An electron is injected into the LUMO and extracted from (hole injected into) the HOMO. (d) The injected electronic charges are compensated by ions of opposite charge creating neutral charge/ion complexes.

The injection of electrons at the cathode will thus attract positive cations causing the formation of *n-type doping*. The extraction of electrons (commonly referred to as injection of positive *holes*) at the anode will similarly be compensated by negative anions and cause *p-type doping* (figure 8d). The electrochemical doping is thus created during the initial operation, improving the electron (and hole) transport of the organic semiconductor. This is critical for thicker films, and it allows LECs with large interelectrode distances to transport electronic charge effectively at a low voltage.

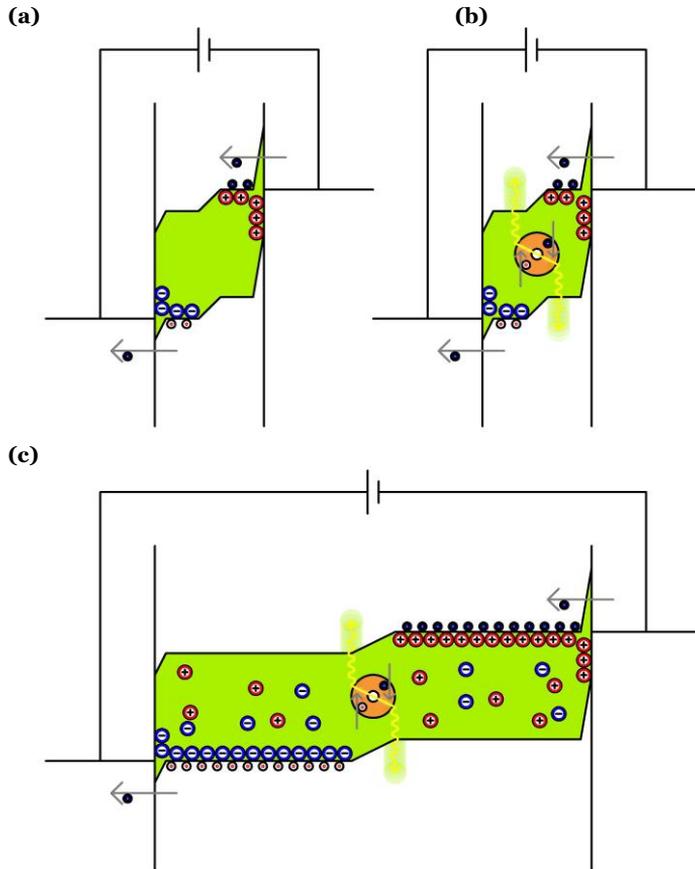


Figure 9. (a) The charge injection and ion compensation, continue to effectively doping the organic semiconductor, thereby increasing its conductivity and allowing charge to move further into the organic semiconductor. (b) The n-doped and p-doped regions meet, allowing electron/hole recombination and light emission through the formation of excitons. (c) The electrochemical doping increases the conductivity allowing thick films to be employed without significant resistive losses in the electron-transporting layers.

Formation of a pn-junction

The electrochemically doped regions will grow towards each other until they meet, as shown in figure 9a. When they meet, the p-type and n-type regions form a pn-junction, where electrons and holes can recombine forming excitons and subsequently light (figure 9b). This structure with two regions capable of efficient charge transport sandwiching a thin layer of intrinsic undoped material is very similar to the structure of an efficient multilayered OLED, where an electron transport layer (ETL) and a hole transporting layer (HTL) are used for the same purpose.[51] However, a LEC only requires one active layer during fabrication, as the multilayered

architecture is created by the device itself when subjected to a voltage bias that allows injection of charge into both the HOMO and LUMO of the organic semiconductor.

The resulting pn-junction can be controlled by the amount of electrolyte in the system. With an infinite amount of free ions, electrochemical doping will continue to occur after the doping fronts have met increasing the conductivity of the device and narrowing the pn-junction width. Unfortunately, this lowers the efficiency of the device, as the doped regions also act as effective fluorescent quenching sites.[52] However, having only enough ions to cause formation of EDLs, but no doping, will only allow thin film devices to work, as thick films will be severely limited by the poor electronic conductivity of organic semiconductors in their undoped state. However, since it is the amount of ions available in the system that dictates how far the doping fronts can progress, the final device structure under voltage bias can be designed by the mass ratio of the blend constituents. This understanding has resulted in very efficient LECs in recent years.[43, 53]

Degradation mechanisms

The LEC theory outlined above is only accurate if the electronic and ionic charges are “consumed” by the desired electrochemistry, i.e. the doping of the organic semiconductor and light-emission. Unfortunately, LECs are susceptible to side reactions, making the device operation far more complex.

The formation of the EDL does allow for efficient charge injection independent of the electrode material used, but the electrochemical stability of the electrodes is still important. An example of this electrode selection criterion is the aluminium electrode, which acts as an excellent cathode in a LEC. However, its limited anodic (oxidation) stability makes it unsuitable as an anode.[54, 55] Similarly, redox reactions involving the electrolyte must also be avoided. Unfortunately, it has proven difficult to identify an electrolyte that is completely inert over the range of potentials over which the electrochemistry of the light-emitting material takes place, i.e. the electrochemical window spanned by the HOMO and LUMO levels of the light emitting organic semiconductor. The LEC technology would benefit greatly from the discovery of such an electrolyte, as much of the instability problems arise from the limitations of the currently available options, e.g. PEO.

The mixture of a typically hydrophilic electrolyte and hydrophobic organic semiconductor makes LECs prone to phase separation.[34, 56] This is problematic, as high-performance LECs rely on a good composition of organic semiconductor and electrolyte. Phase-separated LECs can exhibit a spatially varying electrolyte concentration, causing inhomogeneous light-emission dominated by areas containing the largest amounts of electrolyte, as these offer the lowest electrical resistance by facilitating electrochemical

doping the most. The high current and the electrochemical instability of the very same regions lead to rapid degradation of the device.

External contaminants are also candidates for unwanted redox reactions. For light-emitting devices, oxygen (air) and water are obvious detrimental species that can seriously harm the function of the LEC, specifically the cathode and the n-doped organic material.[57] The reduction of water also creates hydrogen gas which has been put forward as the primary cause of the *black spots* commonly seen in air degraded OLEDs and LECs, as the escaping gas causes delamination of the cathode.[58, 59] Because of this, the LEC will depend on high quality encapsulation materials. Low cost alternatives of these must be found if cheap organic light-emitting technologies are to be realized. A lack of purity of the employed solids and solvents also constitute sources of contaminations, and these materials must be chosen with care.

LECs are sensitive to temperature, and device stability can be improved by cooling the LEC to lower temperatures.[60, 61] This also means that a poor efficiency will decrease lifetime, as the energy not emitted as light is lost as heat, which in turn increases the temperature of the device. Interestingly, a higher device efficiency is therefore expected to improve device stability.

Fabrication methods

The use of solution-processable materials, and the advantages of electrochemical doping outlined in the previous section, allow for the employment of many different fabrication methods.[62] Those utilized in this thesis will be presented below.



Figure 10. The two interconnected gloveboxes used for the fabrication and characterization of LEC and OLED devices. Note the large and small antichambers, with red handles, used to transfer materials and equipment into, and out from, the glove-boxes.

Glove boxes

To achieve high performance and limit the amount of contaminants, a nitrogen-filled glovebox system has been used. The oxygen and water levels are constantly monitored and typically <1 ppm. The system consists of two connected gloveboxes with independent purification systems. One is exclusively used for the fabrication of LECs (the wetbox), and the second for the thermal evaporation of electrodes and the device characterization (the drybox). The gas pressure inside the boxes are carefully monitored, and always kept approximately 4 mBar above the air pressure in the lab. If the pressure drops below a set value, a pressurized nitrogen source refills the

gloveboxes until the safe level is again reached. This prevents air from leaking into the glovebox. Both systems are also equipped with oxygen and water adsorbers, consisting of reactive small copper particles that easily react with (i.e. oxidize) the contaminations, and thus capture them. Unfortunately, the adsorber will saturate and lose its reactivity with time. A regular regeneration of the copperoxide back into copper is therefore required, using heat and hydrogen gas (typically mixed with nitrogen or argon). The regeneration procedure and the constant need for a pressurized nitrogen source make the glove-box system expensive to maintain.

Access to the glovebox is provided through antichambers connected to a vacuum pump (figure 10). Bringing material into the glovebox is a slow process, as antichambers containing air must be repeatedly evacuated and flushed with pure nitrogen before being opened to the inside of the glovebox. Rubber gloves, as seen in figure 10, allow the user to operate equipment and to handle solvents and materials inside the box. In terms of safety, a glovebox offers very good protection of the user.

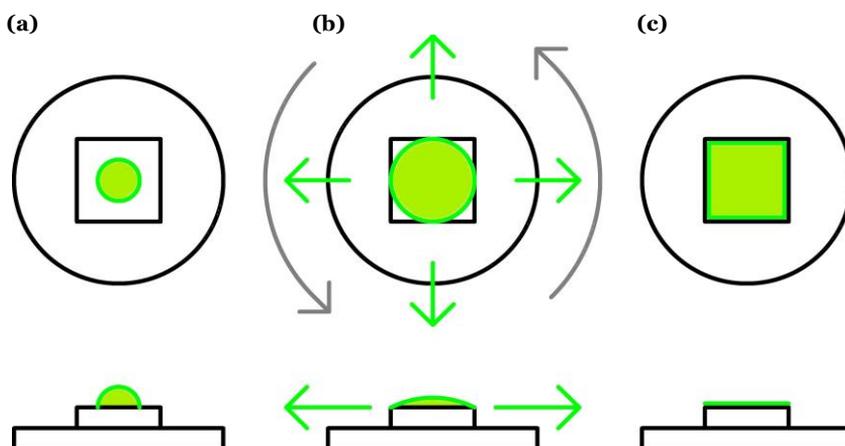


Figure 11. Schematic picture displaying (a) the positioning of ink on a substrate, (b) the rotation of the substrate, where most material is expelled from the surface, and (c) the resulting film.

Spincoating

The most common LEC fabrication process is spincoating, as schematically shown in figure 11. A thin film is created by covering a substrate with ink, and spinning it at a set rotational speed. By adjusting this speed, the thickness of the resulting wet film can be accurately controlled.[63] The spincoater can be small, and thus placed within a glovebox allowing fabrication under controlled atmosphere. Also, films can be made using only a few mg of solid content making it ideal for research where only small

amounts of sample material typically can be obtained. However, most of the ink (approximately 90%) is lost during coating as it is expelled of the edges of the substrate, making it unsuitable for upscaled fabrication. It is also difficult to deposit a film on top of another film without affecting (dissolving) the underlying layer. However, to achieve multilayered structures, a hydrophilic material can be coated on top of hydrophobic material, or vice versa. Each layer is thus prevented from dissolving the prior deposited layer. This thesis includes several examples of multi-layered structures achieved using such *orthogonal* solvent systems.

Spincoating does not alleviate phase separation, but experiments have shown that it can be less pronounced in comparison to other techniques, probably because the high rate of drying gives the blend less time to phase separate.[64]

Thermal evaporation

The most successful method for fabricating organic light-emitting devices in terms of efficiency and lifetime is thermal evaporation under high vacuum. This method can be used for both organic materials and metals, allowing electrodes as well as active layer constituents to be deposited. A quartz crystal can very accurately monitor the thickness of the deposited layer, and the solvent-free process allows several layers to be deposited onto each other. Very advanced multilayered architectures can thus be formed, optimized for effective and balanced charge injection, exciton confinement, light extraction, etc. The currently most efficient organic light-emitting devices make heavy use of this technique.[26, 65]

Thermal evaporation utilizes a heated source material, and thin films are formed when vapor released from the source condensates onto the cooler substrate. Unfortunately, the materials employed e.g. metals, require a high temperature before they begin to vaporize and the expensive tungsten crucibles usually break due to thermal stress after less than 10 uses. The power and time required to heat the crucible, and to achieve sufficient vacuum, also adds to the cost and complexity.

The maximum size of the substrate is limited by the thermal evaporation technique, due to the need for a vacuum chamber. The method is also sensitive to the source-substrate separation distance. Figure 12d demonstrates the film variation using three different distances r using a simple $1/r^2$ dependency, demonstrating how the deposited layer thickness on a flat substrate will vary. In this context, a large r is preferred, but this unfortunately leads to large material loss as a majority of the vaporized material will miss the substrate and instead condensate on the walls of the vacuum chamber. For large substrates, a dynamic solution can solve this problem, e.g. by moving the substrate or source during the deposition. However, this adds to the complexity of the system. Thermal evaporation

also requires care, as a too fast deposition rate will cause heating and possibly damage to an organic film.[66]

Though solution-processable electrodes are more interesting from a practical and commercial standpoint, they currently lack the conductivity, purity, and/or smoothness of thermally evaporated materials. This thesis therefore relies mostly on the use of thermally evaporated (or sputtered) electrodes, i.e. ITO and aluminium, when characterizing a solution-processed active layer. A photograph of the thermal evaporator, with the source and substrate holder visible, is shown in figure 12e.

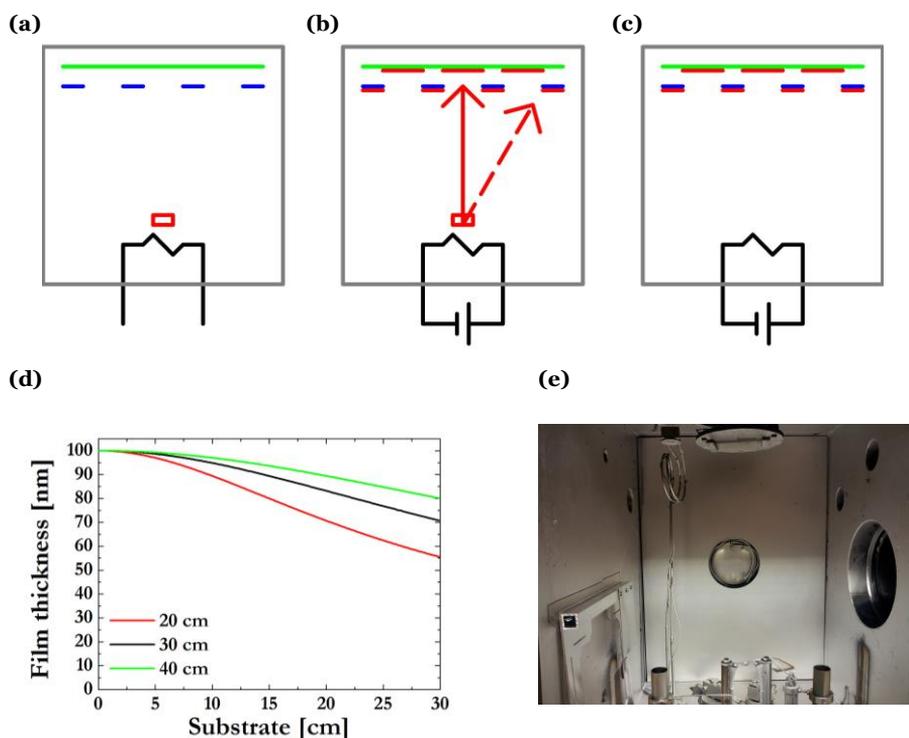


Figure 12. Thermal evaporation. (a) The electrode material (red) is placed in a tungsten crucible and the chamber containing material and substrate (green) is evacuated. (b) A power source is connected to the crucible, which is heated, causing the formation of a material vapor that condensates on the substrate positioned above the source. (c) A thin patterned film of material has formed, facilitated by the use of a (blue) shadow mask. The source is now empty and the thermal evaporation is complete (d) Film thickness variation, assuming a $1/r^2$ dependence, using three different source-substrate distances. (e) A photograph of the employed evaporation chamber employed in this thesis, with substrate holder and source.

Slot-die coating

The slot-die comprises a coating head with a small slit and an ink reservoir. The ink is supplied at a constant rate by an external pump, and delivered onto the substrate through the slit by lowering the head assembly towards the substrate until a meniscus is formed between them, as shown in figure 13a-b. By moving the head and substrate relative to each other at a set speed, a loss-free material coating is achieved (figure 13b). The ink transfer via the formation of a meniscus allows the coating to be made onto soft materials without the risk of mechanical scratching. [67]

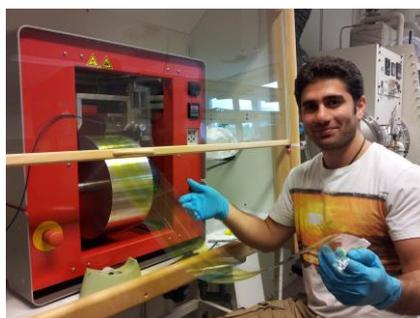
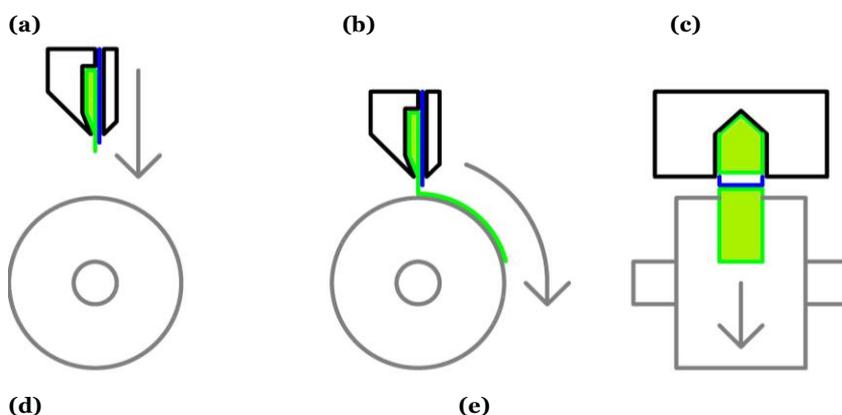


Figure 13. Slot-die coating. (a) The slot-die is moved towards the roll on which a substrate is attached. (b) The distance between slot-die and substrate allows a meniscus to form, and the substrate to be coated by rotating the roll with substrate. (c) Front view of the coating, demonstrating the use of a meniscus guide (blue) to control the coating. (d) Photograph of slot-die with a meniscus guide designed to coat six parallel stripes from one slot. (e) Photograph of the roll coater utilized in this thesis.

Slot-die coating is common in roll-to-roll (R2R) processes, as the substrate, or web, can be supplied to the slot-die head at a constant speed using rollers. If the supplied ink can be filtered prior to use, the performance can be enhanced as the risk for clogging is minimized. However, dust already

on the substrate is hard to remove and could potentially cause defects in the coated film.

The use of an external pump and tubing imply that there is always a dead volume of ink that cannot be used. There is also normally a start-up loss, as an even film is not immediately achieved due to the initial adjustment needed to create a stable meniscus. For obvious reasons, only flat substrates can be used, and the distance between the slot-die and the substrate must be kept within the limit where the meniscus can be maintained. The slot-die used in this thesis also employs a *meniscus guide* (figure 13c) that improves the control of the width, and thus the layer thickness and homogeneity, of the coated layer. This allows for a small degree of patterning and a larger variation in distance between slot-die and substrate (figure 13d).[68]

This thesis uses the roll coater shown in figure 13e, for which the substrate is fed to the slot-die using a large roll with a circumference of 1 m. This machine combines the functionality of a large scale R2R process with that of the small material consumption of a sheet-fed machine, and it is the first of its kind to be produced commercially.[69]

Spray coating

Spray coating is done by transferring the ink to the substrate in the form of small droplets i.e an *aerosol*. These are commonly formed by an atomizing nozzle, through which ink or a combination of ink and a carrier gas, is forced under pressure as shown in figure 14a. Several advanced methods for forming an aerosol exist, e.g. electrospray and the ultra-sonic atomizer.[70-72] This thesis has employed the most common method in which the ink is atomized using pressurized gas. The employed nozzle, depicted in figure 14d, uses internal mixing and pressurized nitrogen as carrier gas. Standard handheld airbrushes have been used as well.

The method is somewhat reminiscent of thermal evaporation, in that the material is ejected from a point source onto a substrate positioned at a defined substrate-source distance with patterning being possible using a shadow mask, though with a lower resolution (figure 14b). Large area coatings typically rely on nozzle movement relative to the substrate in order to achieve an even film thickness. An example of an employed nozzle movement, typically called a *sweep*, is shown in figure 14c. Since spray coating can be done under ambient air conditions, this can be easily achieved by manually moving an airbrush, or by using a computer-controlled spray coater. Figure 14e displays a custom-built machine that was designed for this purpose. Spray coating is highly suited for material deposition on non-flat surfaces, and the method is typically employed in industry for high quality coating of e.g. cars.

The method commonly employs a dilute ink to avoid clogging the nozzle and to improve the uniformity of the deposited film. Because of this,

significant amounts of solvent and time can be consumed during the coating process. A substantial amount of carrier gas is also required.

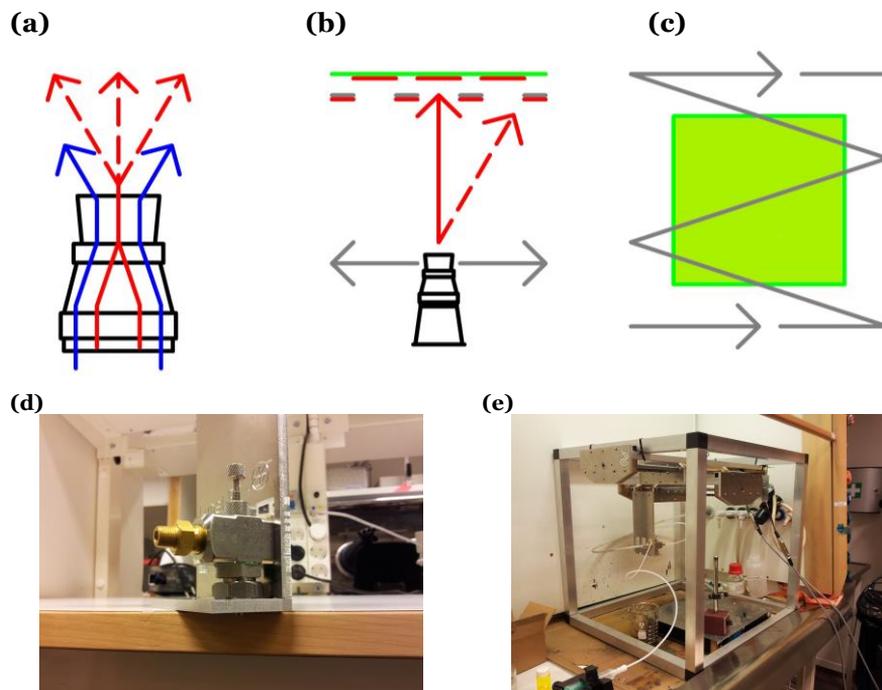


Figure 14. Spray coating. (a) Schematic picture of the atomizing nozzle. A carrier gas (blue arrows) is fed to the nozzle under pressure, and mixed with the ink (red). (b) The nozzle is moved back and forth over the substrate to ensure an even film formation. A shadow mask can be used for (low) resolution patterning. (c) Top view of a spray coating sweep. Typically, several sweeps are done to create the final layer. (d) A close up of the spray nozzle used for automatic coating. (e) The custom-made machine allowing computer-controlled movement of the spray nozzle.

Characterization methods

Measuring luminance

The SI-unit for luminance, the brightness of a surface, is cd/m^2 . Interestingly, this unit takes human physiology into account, by being dependent on the varying color sensitivity of the human eye. Specifically, blue, green, and red devices having a luminance of $100 \text{ cd}/\text{m}^2$ will all be perceived equally bright by a human eye. However, as can be seen in figure 15, the human eye is far more sensitive to wavelengths close to 555 nm, corresponding to green light, than deep red and blue. Because of this, the maximum theoretical efficacy varies for different colours, with green having the highest possible theoretical efficacy ($683 \text{ lm}/\text{W}$ at 555 nm) while dark blue at 460 nm can only reach a maximum of $198 \text{ lm}/\text{W}$.

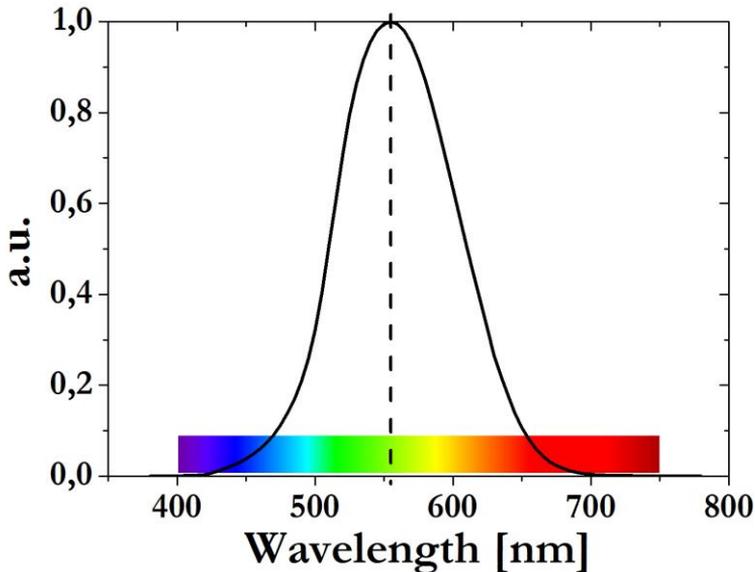


Figure 15. The CIE 1931 luminosity function, which is used to measure luminance. The eye-response maximum is located at a wavelength of 555 nm (green light), which means that the human eye is the most sensitive at this wavelength.

To accurately measure the luminance, one must thus consider the emission spectrum. A typical method is to use a standard photodiode, and convert the resulting data to luminance during later analysis or by calibrating the diodes using commercially handheld luminance meters, such as the Konica Minolta LS-110. A more elegant solution is the use of photodiodes with eye response filters, which mimic the responsivity of a

human eye. This allows all colors to be accurately and directly measured with the correct luminance, without the need for recalibration. Complete LEC measurement setups, including amplifying electronics for the diodes and the software controlling the data acquisition and power sources, have been designed and built by the author. These setups have been used in the majority of our LEC-related publications since 2010.[11, 36, 73-76] To convert measured efficacy values to luminous power, this thesis have assumed that the LEC is a perfect Lambertian emitter. This allows the luminance to be converted to luminous power (lm/W) using the formulas in [77].

The light exiting the device (and detected by the setup) is actually only a small fraction of the light emitted by the organic semiconductor. This is due to poor light outcoupling, as only approximately 20% of the light created in the pn-junction typically escapes through the ITO-glass substrate.[26, 78, 79] The rest is lost through e.g. wave-guiding modes in the active layer and substrate. Extracting light, using internal and external outcoupling schemes, could potentially increase output by a factor of five. Several interesting methods exist, and reported data suggest that a huge improvement in efficiency can be achieved through outcoupling architectures, some of which are surprisingly simple.[80-82] This thesis does not take these losses into account, and the presented efficacy values therefore underestimate the actual light-creating abilities of the LECs significantly.

Measuring doping concentration

Doped regions demonstrate strong fluorescence (photoluminescence) quenching, and this allows for an *in situ* observation of doping fronts progressing through the device. The material is typically excited using UV light, as the high energy photons are easily absorbed by the organic semiconductor and invisible to the detector/observer, allowing for minimized light contamination.[10]

This feature has been extensively exploited when studying surface cells as a method of calculating the doping concentration of the organic semiconductor. The doping concentration is defined as the amount of injected charge per organic semiconductor repeat unit.

The experimental data were recorded using a source-measure unit (Keithley 2400) and a camera equipped with a macro lens. This resulted in a graph of the current vs time and a set of photographs depicting the movement of the doping fronts (figure 16). By using the photos, times t_0 and t_1 , corresponding to the onset of doping fronts and the formation of pn-junction respectively, could be determined. The total amount of injected charge is now readily found by integrating the current (figure 16c) from time t_0 to t_1 .

The thickness of the active layer was measured using an atomic force microscope (AFM) in tapping mode, while interelectrode distance was defined during fabrication using thermal evaporation through a shadowmask. The electrode width was measured using a caliper. From the photograph depicting the formation and position of the pn-junction (also used to establish t_1), the correct volume ratio corresponding to the p-doping and the n-doping could be established and from this the calculation of doping concentration is straight forward. In the example shown in figure 16, the p-doped volume occupies 60% of the interelectrode width.

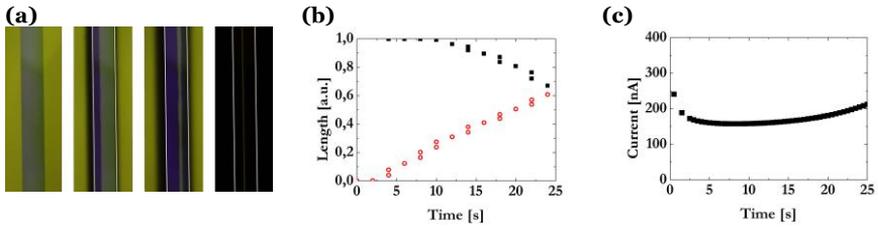


Figure 16. (a) Photographs used for the calculation of doping concentration. The light-green regions correspond to the two electrodes, the dark green to undoped active material, and the black regions to electrochemically doped active material. Note the earlier onset of p-type doping at the anode (left electrode). (b) The position of the doping fronts with respect to time extracted from a set of such photographs. (c) The current as a function of time which was correlated to the progression of doping fronts for the calculation of doping concentration,

Results

Light-emitting electrochemical cells with record performance

Electrochemical side-reactions caused by the presence of an electrolyte with an inadequate electrochemical stability window can be minimized by using a low electrolyte concentration in the active layer. This was experimentally verified by Fang et al. using MEH-PPV as the emitting species in 2009.[43] However, MEH-PPV is a red emitter with a relatively small bandgap, so it is of interest to experimentally verify that materials with wider bandgaps, capable of emitting green and blue light, can be used as well.

The cyclic voltammetry (CV) measurement in figure 17a shows the electrochemical stability window of the PEO-KCF₃SO₃ electrolyte versus the yellow-green light-emitting conjugated co-polymer superyellow.[35] The data indicates that the oxidation of the electrolyte will compete with the p-doping of superyellow and that the reduction of the electrolyte is the thermodynamically preferred reaction compared to n-doping. A surface cell study is of great value at this point, as the observed formation of moving doping fronts would indicate that p-type and n-type doping of the conjugated polymer can dominate over, or co-exist with, the electrolyte side reactions. As can be seen in figure 17c-f, doping fronts are formed at both electrodes. However, a slight delay in the n-doping onset indicates that electrolyte reduction is initially favored at the cathode/active layer interface, in agreement with the CV data. Still, a pn-junction is formed close to the middle of the interelectrode gap, slightly closer to the cathode due to the initial delay of the n-type doping. However, a comparison with results using MEH-PPV reveals that the formation of a pn-junction in superyellow requires a substantially higher voltage. This is an indication that there is an increased amount of side-reactions in superyellow-based devices, possibly due to the combination of the PEO-based electrolyte and the wider bandgap of superyellow in comparison to MEH-PPV.

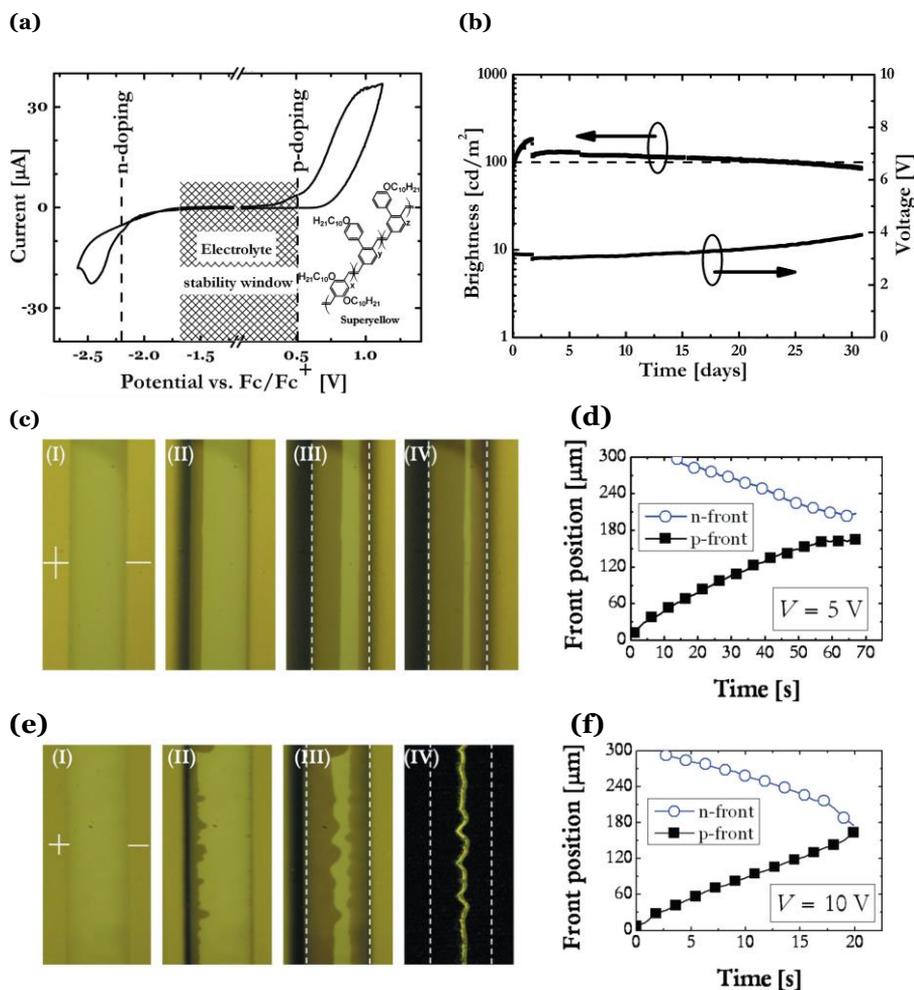


Figure 17. (a) Cyclic voltammetry data, demonstrating the oxidation and reduction potentials of the conjugated co-polymer superyellow used as the light-emitting organic semiconductor. Oxidation and reduction levels of the electrolyte is shown as well, demonstrating the poor compatibility with especially n-type doping of superyellow. (b) A lifetime measurement of a LEC using superyellow as the emissive organic semiconductor. A high initial constant current was used, and subsequently lowered. Lifetime is defined as the time a device is emitting at above 100 cd/m^2 (the dashed line). (c) Sequential pictures demonstrating the formation of positive and negative doping fronts using a 5 V constant voltage bias, and (d) a plot of the front positions vs time. (e) Similar data collected using a higher constant voltage bias of 10 V, at which a light-emitting pn-junction is successfully formed. (f) Plot of the front positions vs time for the 10 V measurement, during which a light-emitting junction is formed after 20 s.

The final test is to make a sandwich cell. The surface cell data could be used to calculate an optimal electrolyte concentration, allowing for a minimization of unwanted electrochemical side reactions.[53] A constant current density was used to further alleviate side reactions, as demonstrated by Fang et al.[83] With respect to the poor electrochemical stability of the electrolyte, it is remarkable that a sandwich device exhibited a luminance of $>100 \text{ cd/m}^2$ for >25 days at a maximum efficacy of 6 lm/W , three times better than observed for MEH-PPV (2 lm/W)! However, it must be emphasized that achieving a higher brightness with a yellow-green device is easier than achieving it with a red or blue device, due to the higher responsivity of the human eye in the yellow-green region, as discussed in the “Characterization methods” section. In fact, the measured lifetime was slightly inferior compared to MEH-PPV, even though the latter was driven at a four times higher current density and thus under a higher stress. Later work, using ion solvating materials and salts with similar combined CV-responses as PEO-KCF₃SO₃, indicates that blue devices suffer even more from the poor electrochemical stability window of the electrolyte, reaching lifetimes of only 25 h under similar operational conditions.[74]

Separating ion and electron transport

LEC operation is dependent on an efficient migration of both electrons and ions, which is normally achieved by using a single active layer where electrolyte and organic semiconductor are blended together. Since the electrolyte typically is hydrophilic, and the organic semiconductor hydrophobic, phase separation can easily occur. This can potentially cause poor performance, and alleviating phase separation is often stated as a method of improving the characteristics of the LEC.[35] However, we have brought forward the hypothesis that a carefully designed phase separation could potentially allow for an improvement in device performance, especially for electrochemically unstable electrolyte materials. In general, a system where the interaction between the semiconducting organic material and an electrochemically unstable electrolyte, e.g. PEO-KCF₃SO₃, is minimized should alleviate the formation of side reactions in LEC devices. The key question is then if such a system, in which ions are not in intimate contact with the organic semiconductor, can still allow for electrochemical doping.

This phase-separated architecture was achieved using a surface cell. The hydrophobic superyellow was coated on top of gold electrodes, and subsequently coated with a hydrophilic layer of electrolyte. An orthogonal solvent system could be employed, which allowed the two layers to be successfully coated on top of each other by spincoating. The resulting bilayered LEC is shown in figure 18a. This surface cell minimizes the contact between the ionic and electronic phases, while still allowing both ionic and electronic charge to move throughout the entire interelectrode distance.

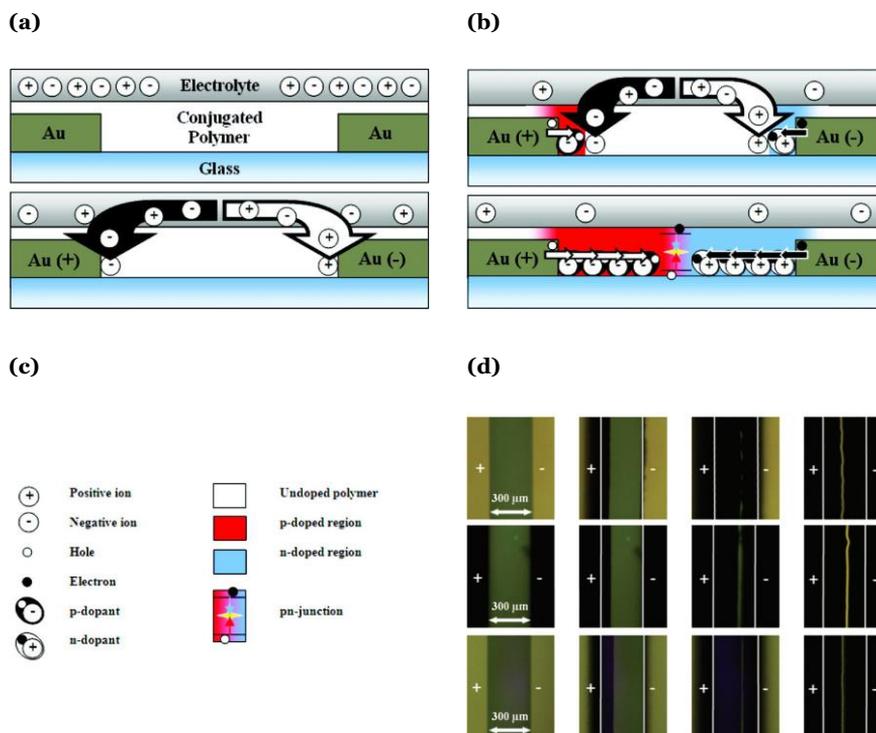


Figure 18. (a) A schematic picture of the bi-layered light-emitting electrochemical cell and the initial ion redistribution and formation of electric double layers. (b) The onset and growth of doping, and the subsequent formation of a pn-junction where exciton formation takes place. (c) Glossary of symbols. (d) Three different devices demonstrating successful doping progression: (*top*) a standard blend cell, (*middle*) a bilayered cell, as observed through the glass substrate, and (*bottom*) a bilayered cell as observed through the electrolyte.

The fabricated bi-layered device was tested using a constant voltage bias of 5 V, and doping and light-emission were observed with a performance surpassing that of the standard blend system (*top*, figure 18d). This includes a twice as fast turn-on time, which is attributed to the increased mobility of the ions in the pure electrolyte phase, and a higher maximum current, similarly attributed to the pure superyellow phase where electronic charge transport can take place in a more densely packed doped organic semiconductor not diluted by an ion solvating material. However, a faster turn-on time can also be attributed to less side reactions. A calculation of doping concentration (i.e. injected charge per co-polymer repeat unit) indicated that less than half the amount of charge is needed to form a light emitting pn-junction in the bi-layered structure. This means that less ion redistribution is required to compensate for the injected charge, thereby decreasing the turn-on time. This is a strong indication of successful

alleviation of side-reactions, assuming that the lower value is closer to the actual doping concentration while the higher also can be attributed to side reactions involving reduction or oxidation of the electrolyte. The latter value is thus an artifact stemming from the inadequate electrochemical stability window of the PEO-KCF₃SO₃ electrolyte.

The designed phase separation has been implemented in subsequent work, further indicating the validity of the results presented here. Using a bi-layered surface cell, Tang et al. successfully demonstrated electrochemical doping and formation of a light-emitting pn-junction using non-ionic small molecules as the organic semiconductor.[73] Though commonly used in OLEDs, neutral small molecules are traditionally not used in LEC research and their applicability in this field was unclear prior to this work. However, the result is also significant in that the HOMO level of the small molecules investigated was found to lie outside that of the electrochemical stability window of the employed electrolyte, a fact which previously has been shown to severely limit the chances of achieving a light emitting pn-junction in surface cells. This strongly supports the hypothesis that designed phase separation improves LEC stability.[35]

An interesting bi-layered sandwich cell has been reported by Youn et al.[84] The device they investigate acts as an OLED at the anode, and as a LEC at the cathode. PEDOT:PSS is used to facilitate positive charge injection into a pure SY layer while an electrolyte mixed with ZnO nanoparticles is placed between an aluminium cathode and the conjugated polymer to improve the negative charge injection via ion redistribution. Ambient fabrication of the active layer could be performed, and a respectable maximum efficacy of 5.3 cd/A was achieved.

Multilayered device structures

Charge recombination in close proximity to an electrode causes lower efficiency due to exciton quenching. In OLEDs, this is solved through the use of a multilayered structure able to confine electrons and holes, and subsequent exciton formation, to the center of the device.[26, 85] In a LEC, doped regions facilitate the charge transport but not charge trapping. Unfortunately, doped regions also quench fluorescence, and limits efficiency in a similar way as electrodes do.[86, 87] Creating an efficient pn-junction, both in terms of position and width, is therefore a challenge in a single-layer LEC.

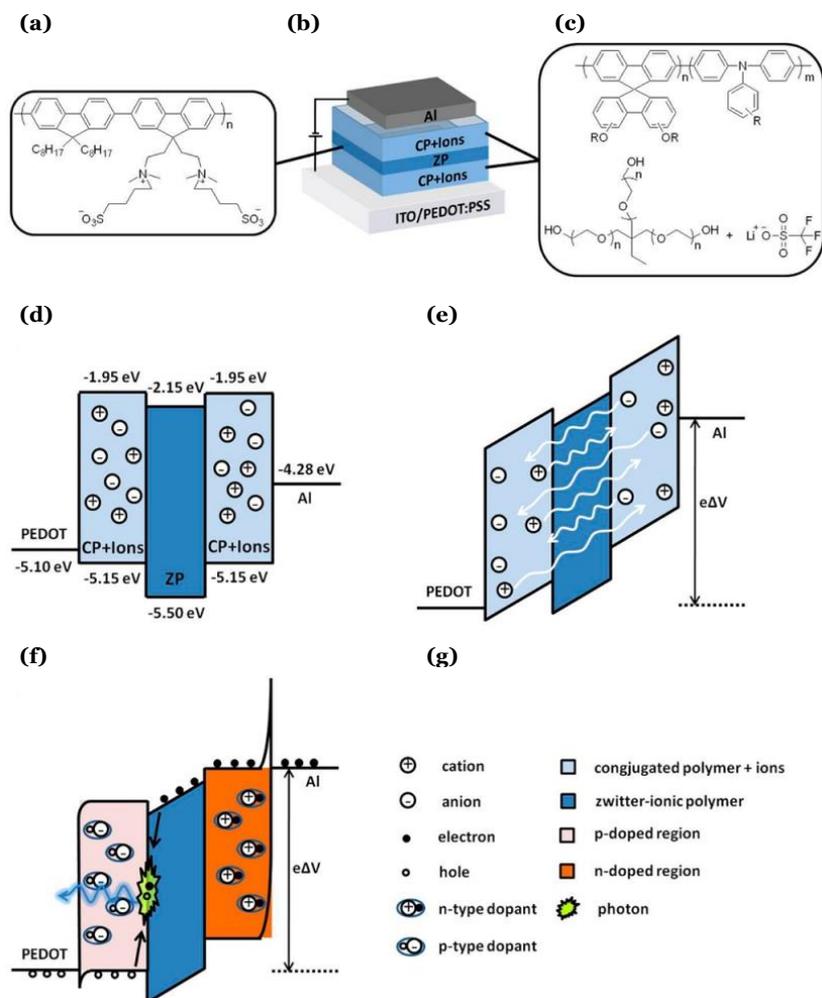


Figure 19. (a-c) A schematic figure of the trilayered device and molecular structures of the constituents. (d) Energy diagram of the trilayered device. (e) The device reacting to an external voltage bias, and (f) the device after electrochemical doping. (g) An explanation of the symbols used.

Degradation processes are also accelerated within the pn-junction, as this is where the most energy is released in the LEC system.[88] Moreover, exciton formation should ideally occur in an electrolyte-free region to minimize unwanted side-reactions.[36]

Finally, the emission spectrum from an organic compound can exhibit a significant overlap with its absorption spectrum. This self-absorption effect also causes a drop in efficiency of LEC devices comprising the same organic compound for both charge transport and light emission.

In an attempt to limit the effects mentioned above, a tri-layered approach was employed. The device structure is schematically shown in figure 19b. Two layers comprising a conjugated polymer and an electrolyte (figure 19c) were deposited in contact with the two electrodes, while a thin layer of zwitterionic conjugated polymer (figure 19a) free from electrolyte separated the two. This layer was made very thin and porous to allow ion migration. The hydrophobic blend layers, and the hydrophilic zwitterionic polymer, allowed the three layers to be fabricated via spin-coating from orthogonal solvent systems.

The best result with the tri-layered structure demonstrated an emission peak at 450 nm, making the device bluer than a device comprising only the conjugated polymer as the emitting species. The efficiency increased from 3.5 cd/A for a device based solely on the conjugated polymer to 5.3 cd/A for the trilayered structure.

However, the structure used in this experiment has several flaws, with the most apparent being that the zwitterionic conjugated polymer has a wider bandgap than the encompassing conjugated polymer. The emission from the zwitterionic polymer will therefore be strongly absorbed by the (doped) conjugated polymer. The charges are also not confined on the middle layer, but rather at the conjugated/zwitterionic polymer interface as depicted in figure 19d. A material with energy levels confined within the bandgap of the “host” materials should be more suitable. However, the substantial improvement made with this non-ideal system is nevertheless promising.

Encapsulation

Figures 17c and 18d display two identical blend LECs being driven by a 5 V bias. However, only one of the LECs manages to form a pn-junction with detectable light-emission. The most likely cause for this discrepancy is the higher vacuum (and smaller evacuated volume) in the experimental setup where light emission was detected. This indicates that small trace amounts of oxygen and water remaining in the vacuum chamber can attack the n-doped conjugated polymer, destroying its electronic properties. LECs are often characterized in a glove box with oxygen and water levels below 1 ppm, or in a high vacuum with pressures below 10^{-5} mBar. However, this might not be a

sufficiently inert atmosphere to completely avoid ambient-induced detrimental side effects as indicated by the above mentioned discrepancy.

Through encapsulation, as schematically shown in figure 20, LEC operation can be performed in an almost ideal atmosphere as air contaminants are effectively blocked from entering the device by the barrier materials. Furthermore, by performing the encapsulation in a glove box with ppm levels of oxygen and water, it is very likely that any trace amounts of oxygen and water trapped in the device will be completely consumed during the initial operation.

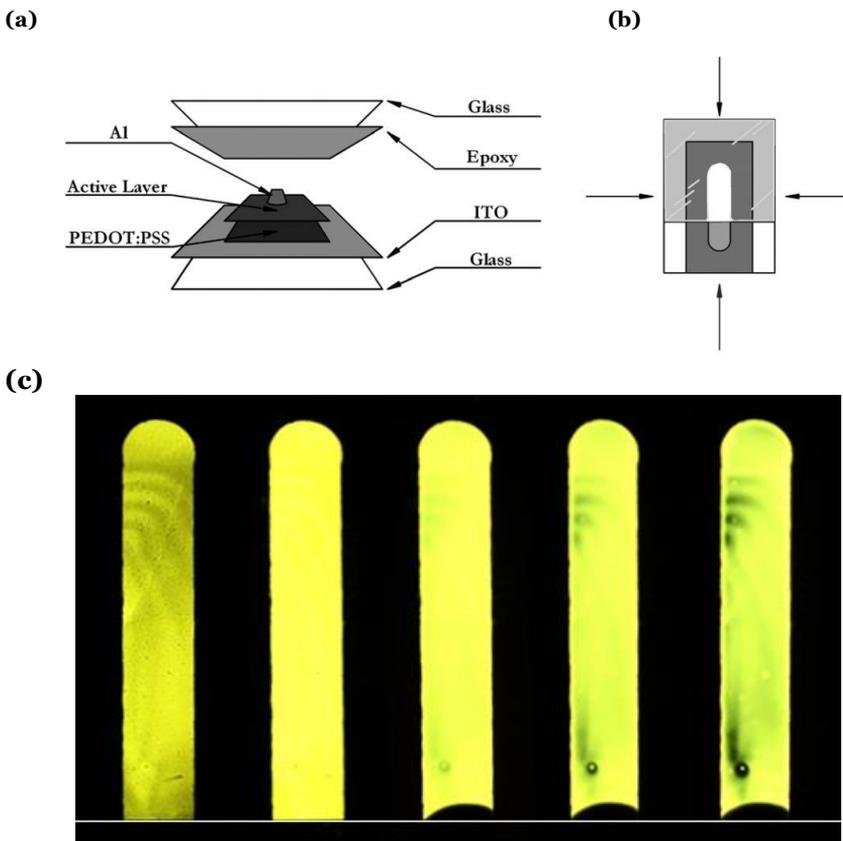


Figure 20. (a) A schematic picture of the encapsulation and device architecture employed. (b) Schematic top view of an encapsulated device. The arrows indicate the most likely leakage paths through the epoxy (light gray) and the active layer (dark gray) that could allow air to enter the light emitting region. (c) Sequential photographs of an encapsulated light-emitting LEC, with a fresh device on the left, demonstrating the device degradation due to leakage through the active layer (dark region first seen in third photograph).

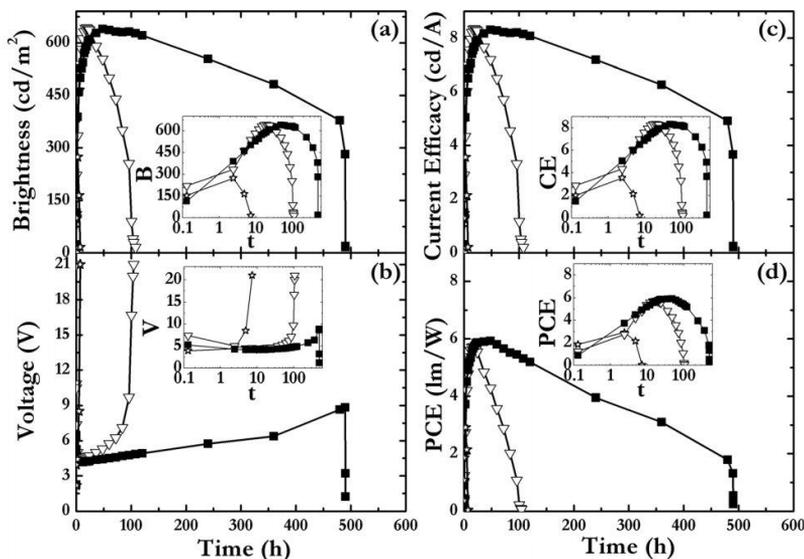


Figure 21. Data for a non-encapsulated LEC during operation in air (open stars), a non-encapsulated LEC during operation in the N₂-filled glove box (open downward triangles), and an encapsulated LEC during operation in air (solid squares) all driven at a constant current density of 7.7 mA/cm². (a) Brightness vs time, (b) voltage vs time, (c) current efficacy vs time, and (d) power conversion efficiency vs time.

Results of such an experiment are shown in figure 21. Compared to a device tested in a glovebox, the encapsulated device exhibited a five times longer lifetime! The naïve use of the term “inert glove-box atmosphere” in prior works has thus clearly underestimated the actual lifetimes of LECs, especially for the low-electrolyte concentration devices where “intrinsic” side reactions between the active layer constituents are minimized. This work also identified a substantial leakage path through the active layer (see figure 20c), which suggests that the results can be further improved using better encapsulation procedures.

Ambient fabrication

The efficacy values reported for small spincoated LECs are close to what is theoretically achievable with the singlet-emitting materials used. Assuming complete triplet harvesting using phosphorescent materials, and perfect internal and external light outcoupling, currently available LECs could reach highly impressive efficiency values of 300 lm/W. Continued work focusing on optimizing the active layer composition in singlet emitting LECs can therefore be anticipated to primarily address the problem of degradation, while significantly improved efficacy values are not to be expected.

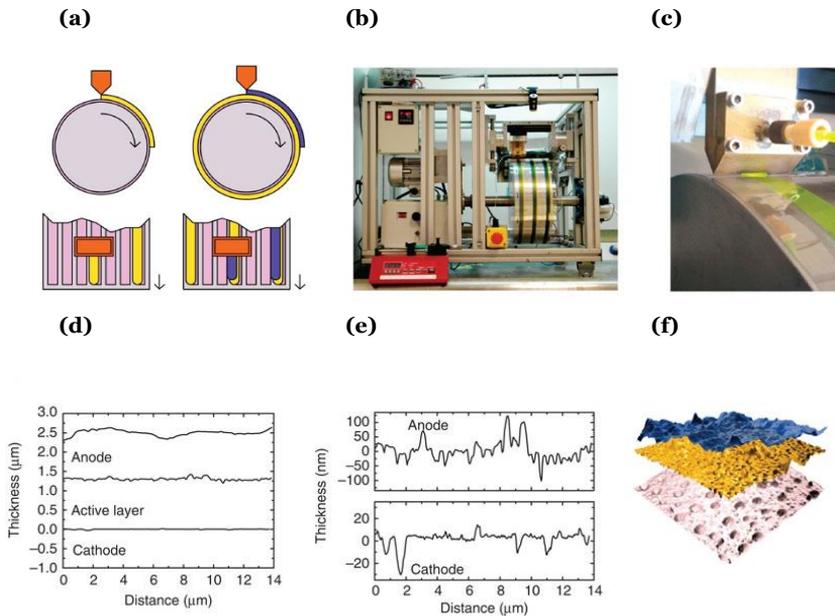


Figure 22. (a) A schematic picture of the application of the active layer and the top PEDOT:PSS anode. (b) The prototype roll coater used for slot-die coating. (c) A close up of the slot-die during active layer deposition. (d) The surface roughness in relation to layer thicknesses. (e) A close up of the surface roughness. (f) 3D height maps of the three coated layers.

Moreover, the LECs that have reached these impressive results are all based on small-scale expensive and slow fabrication methods, notably spincoating in low-oxygen atmospheres and thermal evaporation under vacuum. The obvious question is thus if it is possible to achieve the same high efficacy by employing scalable solution-based methods under ambient air, and thus truly take advantage of the strengths of the LEC technology.

Figure 22a-c displays a roll coater, a slot-die coating head applying ink to a flexible substrate, and a schematic picture demonstrating the coating of the active layer and the top electrode (PEDOT:PSS). The flexible poly(ethylene terephthalate) (PET) substrate comprised patterned ITO precoated with a thin layer of ZnO from solution.[89] The LEC, comprising the ZnO cathode, the PEDOT:PSS anode, and the active layer, was thus fabricated solely from solution onto a flexible ITO on PET substrate. Figure 22d-f demonstrates the high surface roughness of the constituent layers, which implies that a thick active layer is necessary in order to limit the formation of e.g. short circuits and non-uniform light emission. The active layer composition (SY:PEO:KCF₃SO₃=1:1.35:0.25) was chosen based on previous work by Matyba et al., which demonstrated functional LECs with PEDOT:PSS as the

anode and graphene as the cathode.[40] As can be seen in figure 23a-b, the fabricated devices exhibited homogeneous bidirectional light emission and respectable light output, proving that LECs indeed can be fabricated under ambient air conditions using a R2R compatible process.

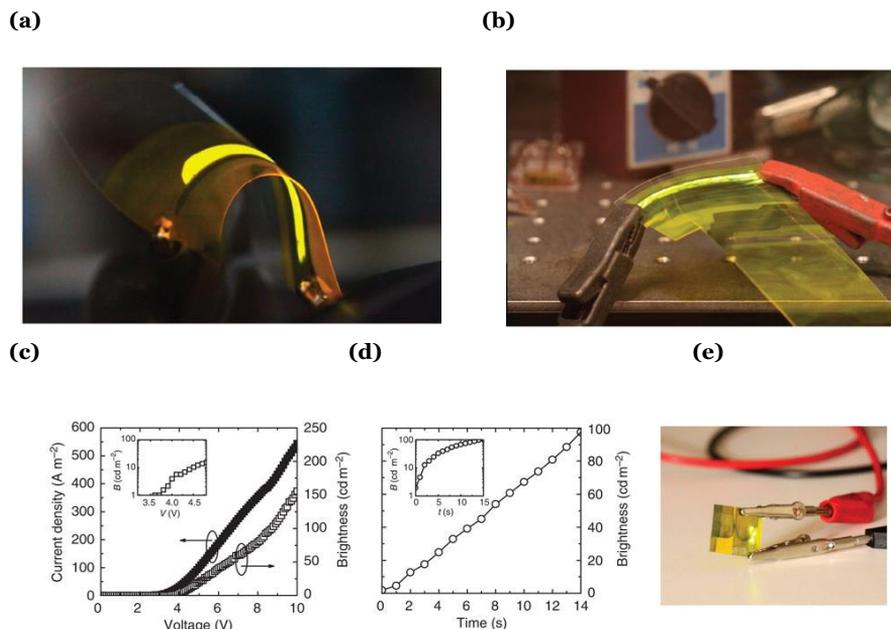


Figure 23. (a) A flexible slot-die coated LEC, demonstrating homogeneous bidirectional emission. (b) Photograph of a device after 6 months storage in a glove box. (c) Voltage sweep, indicating low voltage onset of light emission and significant light output above 100 cd/m². (d) Turn on time for a device driven in galvanostatic mode at $j = 770$ A/m². (e) A small encapsulated device, demonstrating operation in air.

However, the efficiency and lifetime of these R2R-fabricated devices were far from those achieved by earlier spincoated LECs, but this was expected due to the high electrolyte concentration employed.[43] The slot-die R2R-fabrication technique was also observed to be sensitive to dust particles, as the wet film was warped substantially by foreign particles. Short circuits and black non-emissive regions, larger than the actual particles causing them, were commonly observed from large-area devices. Phase separation was also observed to be more pronounced than for equivalent spin-coated devices, making uniform emission very difficult to attain from larger devices.

Large-area fabrication using spray coating

The phase-separation issue is very pronounced for large-area LECs. Since the electrolyte controls the electrochemistry, and thus factors like efficiency, lifetime, and turn-on time, concentration gradients should ideally be completely avoided. Failing in achieving a homogeneous electrolyte

distribution throughout the film can be directly observed as poor device aesthetics, i.e. uneven emission colour and intensity. Early tests, using Meyer rods as ink applicators, resulted in the devices shown in figure 24a-b.

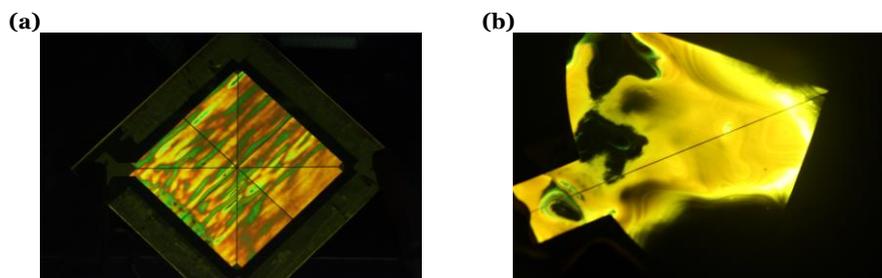


Figure 24. (a) a Meyer-rod-coated large-area LEC, demonstrating significant emission-color variation. (b) Close up of a large-area LEC, demonstrating the effects of phase separation and severe electrolyte crystallization.

Spray coating using a *dry* carrier gas is an excellent method for limiting the issues of phase separation, as the gas efficiently removes the evaporating solvent from the droplets/deposited film. The forced convection thus increases the rate at which the film/droplet dries. By using a low ink flow rate, volatile solvents, and a dynamic coating process, in which the substrate or nozzle is constantly moved, the deposited droplets can be allowed to dry significantly before an additional drop is deposited in its vicinity. This limits the maximal phase separation to the size of the individual droplets deposited. If the drops are sufficiently small, and several are deposited on top of each other, the resulting emission will appear completely homogeneous to the eye.

This concept has been examined using a Dektak XT profilometer and an optical microscope, and the results are shown in figure 25. Two different thin SY coatings on glass are shown, differing by the two different solvents employed during ink fabrication. Figure 25a-b resulted from the use of an ink containing a 5 mg/ml concentration of superyellow in toluene. Individual drops can be seen overlying each other, showing that solvent communication between deposited drops is minimized. However, the height map is very flat indicating that each drop adds very little to the resulting film thickness. In contrast, replacing toluene with the more volatile THF resulted in an overall smaller drop size and the more distinct height map seen in figure 25c-d. Based on these observations, it is reasonable to infer that some solvent evaporates as the drops travel from the nozzle towards the substrate, and that this effect is more pronounced for the more volatile THF. The impinging drops thus decrease in volume, and contain a higher concentration of

polymer as they land on the substrate, creating a thicker layer, but with a smaller footprint, than seen when using the less volatile toluene.

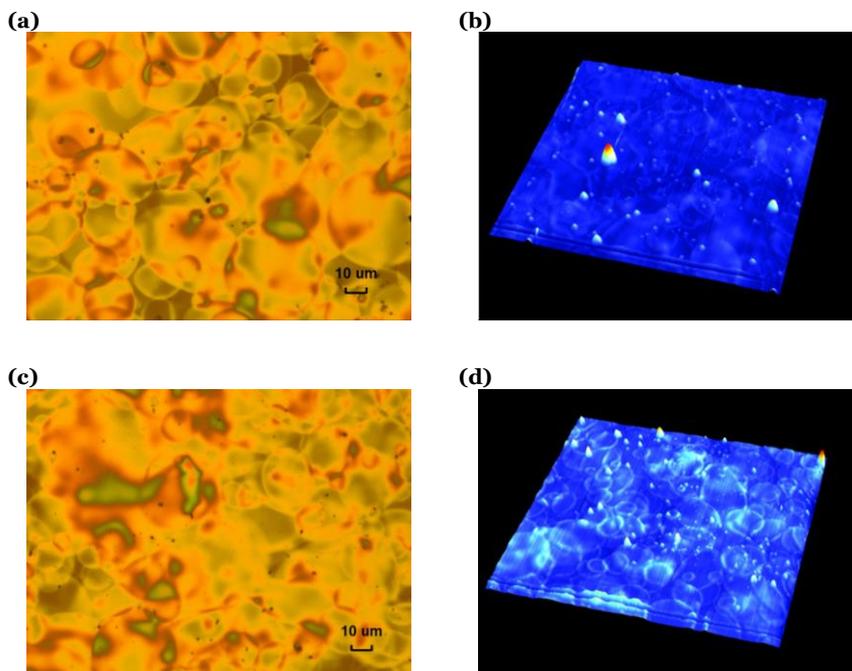


Figure 25. (a) A thin layer of airbrush-deposited conjugated co-polymer superyellow from toluene. Drops can be seen overlapping others, indicating limited solvent communication. (b) A 3D height map of the same layer made using a surface profilometer. (c) The resulting layer when tetrahydrofuran was used as the solvent. The formed drops are smaller, indicating that the impinging drops have dried before hitting the substrate and (d) the corresponding 3D height map, demonstrating a more distinct surface morphology.

Figure 26a-d summarizes the concept of the dry spray coating. The use of toluene corresponds to figure 26a-b, as the solvent evaporation occurs primarily on the substrate surface. Thick layers can be achieved by moving the nozzle back and forth to slowly build up several layers. This allows each deposited drop to dry on the substrate before the next drop lands in its near vicinity, and thus be less affected by the impinging drops. Figure 26c-d describes the situation using a more volatile solvent such as THF. The small drops have dried substantially before hitting the substrate, and the coating can be made continuously as the rate of drying is faster than the rate solvent is added to the substrate. However, the smaller footprint of the individual drops increases the risk of short circuits, as pinholes are more likely to form.

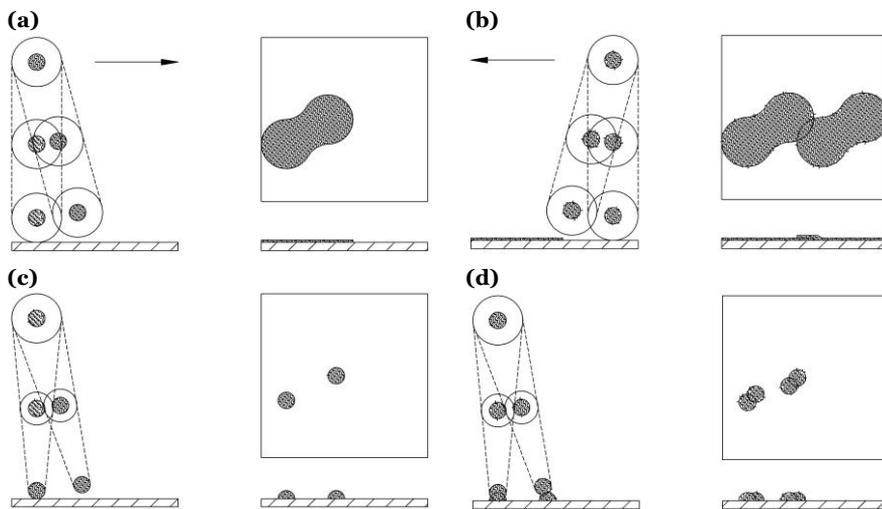


Figure 26. (a) Two drops impinge on the surface and combine to create a thin and spatially defined wet film. The spray nozzle is moved to allow the film to dry. (b) The nozzle is returned and two new drops are deposited. The solvent evaporates before the underlying layer is dissolved. (c) Two drops containing dissolved material travels towards the substrate and dries significantly before impinging on the surface. (d) Subsequent droplets land on top of the previously deposited material, but does not contain enough solvent to dissolve the material already deposited.

To achieve repeatability and simplify optimization, a custom-made coating machine was fabricated in-house, with which ink flow, nozzle movement, and nozzle-substrate separation could be accurately controlled via a computer. Using this coater, efficient LECs have been made using TMPE and KCF_3SO_3 as the electrolyte constituents. A SY:TMPE: KCF_3SO_3 =1:0.1:0.03 mass ratio was used, which has previously been shown to reach high efficacy values for active-layer thicknesses of approximately 120 nm.[19, 36, 43] ITO-coated glass substrates were used as received, without any prior cleaning. Toluene was used as the primary solvent in the active-layer ink, which featured a concentration of 2.5 mg/ml. As discussed above, the less volatile toluene allows the drops to spread over a larger area as they land. The low ink concentration further corroborates this effect, which in turn decreases the film roughness.[72] The spray-coated active layer was dried at 343 K under nitrogen atmosphere (O_2 , $\text{H}_2\text{O} < 1$ ppm), and an aluminium electrode was subsequently deposited on top of the stack using a thermal evaporator. The device was characterized using an accelerated lifetime test, during which a 3.85 mA/cm^2 constant current density was applied. The result is shown in figure 27a. The LEC reached a maximum efficacy value of 6 cd/A at 210 cd/m^2 . This is equal to the LEC peak efficacy value in 2010, and not far from the best results achieved using TMPE-based electrolytes.[36, 58, 75].

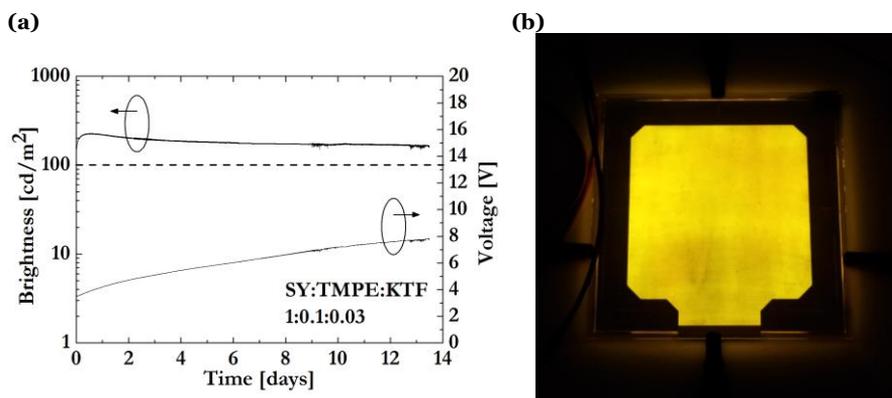


Figure 27. (a) Accelerated lifetime measurement of a LEC where the active layer has been deposited by spray coating in ambient air. (b) Large-area LEC, on a 400 cm^2 substrate, fabricated in air exhibiting uniform emission. This is attributed to the employment of an optimized spray-coating process.

Wet coatings are normally very sensitive to dust particles, as these can severely deform the drying film and result in severe light emission defects and short circuits. Fortunately, the dry spray coating outlined above has proven to be very resilient towards dust contamination, as particles can be clearly observed in devices that still exhibit homogeneous emission. This is e.g. seen in the large 400 cm^2 device shown in figure 27b. Spray coating is also a very versatile coating method. Early experiments employed a hand held airbrush (figure 28a) by which coating was done manually. However, the large device-to-device variation caused by this manual procedure did not allow for device optimization, although several promising device architectures and electrode materials were tested, as described below.

Figure 28b displays a large transparent LEC in which all layers were fabricated using the airbrush. The electrodes were made from a dispersion of silver nanowires in an ethanol-isopropanol mixed solvent system, and the active layer comprised PEO-DMA and KCF_3SO_3 . The bottom anode was coated with a thin layer of planarizing PEDOT:PSS to limit the amount of protruding nanowires that could potentially cause short circuits through the active layer film. A further improvement of this concept utilized an aluminium plate as the substrate. Initially, the aluminium was directly coated with an active layer and sequentially a cathode consisting of silver nanowires as previously described, but the device demonstrated poor light emission. However, by first coating the aluminium with a thin planarizing layer of PEDOT:PSS, light output was vastly improved. Figure 28c-d display two devices with and without the PEDOT:PSS layer. This concept allows the substrate to also function as both electrode and protective barrier, thus simplifying the overall device architecture. The photograph in figure 28e

demonstrates the same concept, but on a non-flat substrate. Finally, figure 28f proves that bi-layered structures can be made without the need for orthogonal solvent systems, as the blue and yellow material were both dissolved in toluene.

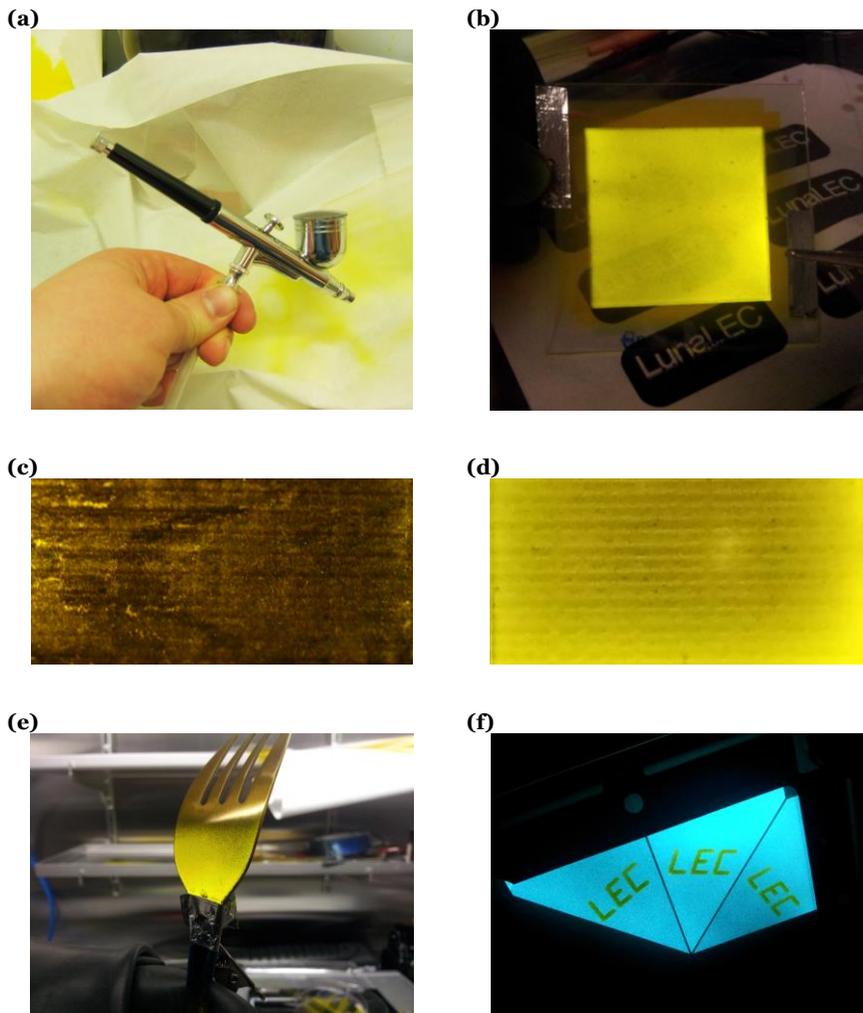


Figure 28. (a) A handheld airbrush for manual spray coating. (b) A LEC made from spray coating solely, using a silver nanowire/PEDOT:PSS hybrid electrode as the anode, a thick active layer comprising SY, PEO-DMA, and KCF_3SO_3 , and a cathode made from silver nanowires only. (c) A LEC fabricated directly on aluminium and (d) with an added thin layer of PEDOT:PSS improving light output. (e) A metal fork used as a non-flat substrate exhibiting light-emission. (f) A LEC where a superblue, PEO-DMA, and KCF_3SO_3 layer has been coated on top of thin spray-patterned SY demonstrating the realization of multi-layered device architectures without the need for orthogonal solvent systems.

Discussion and outlook

The LEC efficiencies reported in paper I and IV, and in the work by Yu et al.[19] and Tang et al.[36], are indeed impressive considering the singlet-only emission and the poor light outcoupling. Equally interesting are the pioneering results in paper III, where the process of solution fabrication in air using a R2R-compatible process, based on slot-die coating, is presented. The fabrication of LECs via spray coating is also presented, and shown to be a very robust method with respect to dust contamination, phase separation, and emission quality. Devices with spray-coated active layers fabricated in air have in fact demonstrated efficiency values on par with the best devices fabricated using conventional (and expensive) spin-coating under inert environment.

The major issue with LEC has, however, been the device stability. The 25 days of uninterrupted operation presented in paper I constituted a notable improvement at the time of publication (in 2010), but is still low compared to the stability of most CFLs and LEDs, which feature operational lifetimes of >500 days. However, papers I, II, IV, and V demonstrate how the LEC stability has been further improved during recent years via the employment of new materials and improved device architectures. Paper IV projects a lifetime of approximately 5600 h, corresponding to more than 230 days of continuous operation at a luminance higher than 100 cd/m².

In conclusion, this thesis has demonstrated LEC fabrication and operation under ambient conditions, and devices that feature high efficiency and improved stability. The gap between LECs and the lighting technologies of today has become smaller, which indicates that LECs could become a competitive lighting technology in the future. Further development should primarily address the still limited lifetime by identifying new electrolytes with wider electrochemical stability windows, and improve efficiency using light outcoupling structures and triplet-emitting materials. Moreover, successful implementation of cost-efficient R2R production methods could allow LECs to become an ultra low-cost lighting alternative for various short-lived application, such as plastic packaging and medical-treatment applications. Moreover, for such applications, biodegradability might be desirable, with short lifetimes and benign materials then turning into an advantage.

A major bottleneck for the further development of the LEC is the fringe technologies on which it depends. The development of a simple and cost-efficient fabrication of LEC layers will not be of great value if electrode and encapsulation materials remain expensive and complex to handle. Metals and glass remain integral components in LECs today, as organic alternatives

to conductive electrodes and encapsulation materials are still under development and remain difficult and expensive to obtain.

Summary of appended articles

Paper I

A. Sandström, P. Matyba, and L. Edman.

Yellow-green light-emitting electrochemical cells with long lifetime and high efficiency

Applied Physics Letters, 96(5) 053303 (2010)

Contribution: Device fabrication and characterization of sandwich cells. Data analysis. Manuscript preparation.

The conjugated co-polymer superyellow is used to fabricate light-emitting electrochemical cells. The employed electrolyte is shown to have an electrochemical stability window that does not encompass the HOMO and LUMO levels of superyellow, but both surface and sandwich cells are nevertheless functional. The sandwich cells are also shown to have a high efficacy and long operational lifetimes.

Paper II

A. Sandström, P. Matyba, O. Inganäs, and L. Edman.

Separating ion and electron transport: the bi-layer light-emitting electrochemical cell

Journal of the American Chemical Society, 132(19) 6646-6647 (2010)

Contribution: Device fabrication and characterization. Data analysis. Manuscript preparation.

Surface cells are made using a bi-layered architecture, where electronic and ionic transport channels are completely separated. The devices are fabricated by first spin-coating a pure light-emitting polymer layer onto the anode and cathode, followed by a layer of pure electrolyte. Orthogonal solvent systems are used to avoid dissolution of the underlying layer. The results demonstrate a much better device performance for the bi-layer architecture, with more light emitted and an improved conductivity of the active layer. A lower calculated doping concentration also indicates that a lower rate of side-reactions is in effect in the bi-layered LEC.

Paper III

A. Sandström, H. F. Dam, F. Krebs, and L. Edman.

Ambient fabrication of flexible and large-area organic light-emitting devices using slot-die coating

Nature Communications, 3, 1002 (2012)

Contribution: Ink formulation, device characterization, data analysis, and manuscript preparation.

A first functional R2R-compatible fabrication process of LECs is presented, where all layers are coated from inks under ambient air; the inks were in addition prepared under air. Three layers are coated in succession on ITO-coated poly(ethylene terephthalate) (PET) substrates. The exposure to oxygen and water during fabrication is shown to not affect the devices to a high extent, and the R2R-fabricated devices are demonstrated to emit significant light at a low voltage.

Paper IV

A. Asadpoordarvish, **A. Sandström**, S. Tang, J. Granström, and L. Edman

Encapsulating light-emitting electrochemical cells for improved performance

Applied Physics Letters, 100(19) 193508 (2012)

Contribution: Device characterization, data analysis, manuscript preparation

A functional encapsulation method of LECs, using glass as the barrier material and a UV-curable epoxy as the adhesive, is demonstrated and shown to increase the operational lifetime by a factor of five. The stability of encapsulated devices is shown to be limited by the intrinsic degradation of the active layer, and by edge leakage through the active layer. By simply removing the active layer from the edge of the device, and using full encapsulation, very promising stability results are achieved.

Paper V

S. Tang, **A. Sandström**, J. Fang, and L. Edman

A Solution-Processed Trilayer Electrochemical Device: Localizing the Light Emission for Optimized Performance

Journal of the American Chemical Society, 134(34) 14050-14055 (2012)

Contribution: Device characterization, data analysis, manuscript preparation

A novel tri-layered LEC architecture is fabricated, using a zwitterionic polymer as an intermediate layer positioned between two charge-transporting layers comprising a blue conjugated co-polymer blended with an electrolyte. The resulting device is critically dependent on the zwitterionic layer thickness, but an increase in device efficacy is achieved if the intermediate layer is made very thin. It is further demonstrated that the the exciton formation zone is pinned at the interface between the p-doped conjugated co-polymer and the zwitterionic layer.

Acknowledgements

This thesis is the result of almost five years of research, and more than 28 years of support from colleagues, peers, friends, and family. This section is dedicated to these people, who truly deserve credit for the realization of this work.

First and foremost, this thesis would not have been if not for my supervisor Ludvig Edman. I am in awe of his literally enlightening work, and words can not express my gratitude for letting me be a small part of it.

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