Organic light emitting devices (OLEDs) and structurally integrated photoluminescence based chemical and biological sensors excited by OLEDs

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Organic light emitting devices (OLEDs) and
Structurally integrated photoluminescence based chemical and biological sensors excited by OLEDs

by

Bhaskar Choudhury

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Electrical Engineering
Program of Study Committee:
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Iowa State University
Ames, Iowa
2005
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For the Major Program
to

ma-deuta-my parents,

and

phool mahi,

your love has brought me so far...

~*~
TABLE OF CONTENTS

Acknowledgements

Chapter 1. Introduction to organic light emitting devices (OLEDs) and OLED based integrated biochemical sensors 1
   1. Introduction to organic light emitting devices 1
      1.1 History of organic electroluminescence 1
      1.2 Advantages and disadvantages of OLEDs 3
      1.3 Basic OLED structure and operation 4
      1.4 Carrier injection
         1.4.1 Image force lowering 8
         1.4.2 Thermionic emission 9
         1.4.3 Field emission 11
      1.5 Carrier transport in OLEDs 11
         1.5.1 Field dependent mobility 12
         1.5.2 Space charge limited current 14
      1.6 Charge recombination and efficiency
         1.6.1 Charge recombination 16
         1.6.2 Efficiency 17
      1.7 Molecular doped guest-host system
         1.7.1 Energy transfer 18

2. Introduction to OLED based integrated biochemical sensors 19
   2.1 Fluorescence based biosensors 20

3. Dissertation organization 23

Chapter 2. Temperature dependence of electroluminescence spikes, turn off dynamics and charge traps in organic light emitting devices 29
   1. Introduction 29
   2. Theory 29
   3. Device structure and materials 32
   4. Experimental results and discussion 35
   5. Conclusion 38

Chapter 3. Luminescence chemical and biological sensors based on the structural integration of an OLED excitation source with a sensing component 41
   Abstract 41
   1. Introduction 42
   2. Experimental 46
   3. Results and discussion 47
      3.1 Oxygen sensor 47
      3.2 Immunosensor 51
   4 Conclusion 52
Acknowledgements

My sincere thanks to my advisors, Dr. Joseph Shinar and Dr. Vikram Dalal for guiding me through the thesis work.

A big thanks to Dr. Ruth Shinar for all her suggestions and help.

Thanks to all the committee members of my program of study.

Thanks to all the members of Dr. Shinar’s and Dr. Dalal’s group.

Thanks to my wife Sonia for her patience and help.

And finally, thanks to my brother-dada, for everything.
1. Introduction to organic light emitting devices (OLEDs)

OLEDs constitute a new and exciting emissive display technology. In general, the basic OLED structure consists of a stack of fluorescent organic layers sandwiched between a transparent conducting anode and metallic cathode [1,2]. When an appropriate bias is applied to the device, holes are injected from the anode and electrons from the cathode; some of the recombination events between the holes and electrons result in electroluminescence (EL).

1.1 History of organic electroluminescence

The first EL from an organic molecule, anthracene, was reported by Pope and coworkers in 1963 [5]. They reported EL from a thick anthracene crystal (10μm-5mm), when a bias of several hundred volts was applied across it. The achievement did not stimulate much interest as the applied bias was very high. However, P. S. Vincent et al [7] achieved bright blue EL from vacuum-deposited 0.6 μm thick anthracene crystal films with an applied bias of less than 100V.
The breakthrough was achieved by Tang and VanSlyke in 1987 [1], who made a bilayer structure by thermally evaporating the small molecular weight organic materials, N, N'-diphenyl-N, N'-bis(3-methylphenyl) 1, 1'-biphenyl-4, 4' diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq3) to achieve a total thickness of ~100 nm. They achieved a very bright green emitting OLED with a brightness higher than 1000 cd/m^2 and an external quantum efficiency of ~1% when a low bias of 10V was applied across the structure [1]. Following this achievement Adachi et al [8] succeeded in fabricating stable multilayer devices by inserting hole and electron transport layers between the two electrodes. In 1989, Tang et al [2] developed a laser-dye doped Alq3 multilayer structure, in which the fluorescent efficiency was improved and the emission color varied from the original green to the dopant emission color.

Following the success of fabricating small molecular OLEDs, Burroughs et al [9] discovered the first polymer LED (PLEDs) by spin coating a precursor polymer of the luminescent poly-(para-phenylene vinylene) (PPV) onto a indium tin oxide (ITO) coated glass. Compared to small molecular devices, polymer light emitting devices (PLEDs) have several potential advantages, e.g. , fabrication by spin coating [9,10] or inkjet printing [11] from solutions and subsequent thermal treatment.

Fluorescent emission of singlet excitons are the main mechanism of OLED light emission. As the probability of forming spin singlet states and spin triplet states are 25% and 75% respectively, the ideal maximum fluorescent yield is, therefore, limited to 25% by spin statistics. To overcome this theoretical limit M. A. Baldo et al [12] fabricated and
demonstrated phosphorescent OLEDs, by doping phosphorescent molecules, where the EL is due to triplet emission, into a fluorescent host layer.

1.2 Advantages and disadvantages of OLEDs

OLEDs are already commercialized and they are making ways to the display markets. Currently OLEDs are used in low information displays with limited size such as mobile phones, PDAs, MP3 players, digital cameras and some laptop cameras. The driving force behind this success is some advantages that the OLEDs enjoy.

Advantages:

Self-luminous- The efficiency of OLEDs is better than that of other display technologies without the use of backlight, diffusers, and polarizers.

Low cost and easy fabrication- Roll-to-roll manufacturing process, such as, inkjet printing and screen printing, are possible for polymer OLEDs.

Color selectivity- There are abundant organic materials to produce blue to red light.

Lightweight, compact and thin devices- OLEDs are generally very thin, measuring only ~100nm

Flexibility- OLEDs can be easily fabricated on plastic substrates paving the way for flexible electronics.
High brightness and high resolution- OLEDs are very bright at low operating voltage (White OLEDs can be as bright as 150,000 cd/m²)

Wide viewing angle- OLED emission is lambertian and so the viewing angle is as high as 160 degrees

Fast response- OLEDs EL decay time is < 1us.

Disadvantages:

- Highly susceptible to degradation by oxygen and water molecules.

Organic materials are very sensitive to oxygen and water molecules which can degrade the device very fast [21]. So the main disadvantage of an OLED is the lifetime. With proper encapsulation, lifetimes exceeding 60,000 hours have been demonstrated. In our laboratory itself, we have been able to increase the shelf life of green Alq₃ based OLEDs, from few days to almost a year.

- Low glass transition temperature $T_g$ for small molecular devices ($>70^\circ$C). So the operating temperature cannot exceed the glass transition temperature.

- Low mobility due to amorphous nature of the organic molecules.

1.3 Basic OLED structure and operation

The basic current structure of OLED has one low work function conducting transparent anode, one or more organic layers and a cathode. Small molecular organic materials are
normally thermally evaporated and polymers are spin coated on a transparent ITO coated glass substrate to a thickness of about 100 nm in case of small molecular OLEDs [3]. The basic device structure and the equilibrium energy levels are shown in Figure 1.1. When a forward bias is applied to this structure, holes \((h^+)\) are injected from the anode and the electrons \((e^-)\) are injected from the cathode. These injected carriers recombine, form excitons and some of them decay radiatively to give the EL. Thus, for injection EL the fundamental physical processes include carrier injection, transport, recombination and radiative exciton decay[3, 4]. Normal operating voltage is about 2-20 V, corresponding to average electric field of 0.1-2 MV/cm, which is very high compared to the typical fields \(\sim 10 \text{ kV/cm}\) of inorganic semiconductor devices. The resistivity \(\rho\) of the devices ranges over eight order of magnitude, with very high values of \(10^5-10^{13} \Omega \cdot \text{cm}\) in forward bias. In reverse bias, \(\rho\) is also very high \((10^9 \Omega \cdot \text{cm})\) [10,11].

The ITO, a wide band gap \((E_g = 3.5-4.3 \text{ eV})\) semiconductor, is composed of indium oxide \((\text{In}_2\text{O}_3)\) and a small amount of tin oxide \((\text{SnO}_2)\) \((\sim 5 \text{ wt\%})\). Most OLEDs use ITO as the anode due to its relatively high work function and high transparency \((90\%)\) to visible light [13]. The conductance and transparency of ITO are mostly dependent on the film thickness and composition ratio of two components. The resistivity of a 200 nm thick ITO is about \(10^3 \Omega \cdot \text{cm}\) with mobility \(\mu \sim 10 \text{ cm}^2/\text{Vs}\). With increased ITO thickness the conductance increases, but the transparency decreases. Another very important parameter is its work function \((\Phi_0)\) or Fermi energy \((E_F)\) relative to the organic materials [15]. Because the highest occupied molecular orbital level \((\text{HOMO})\) energies of organic materials are typically \(E_{\text{HOMO}} = 5-6 \text{ eV}\), a high \(\Phi_0\) is needed for the anode to efficiently inject holes to the organic layers.
Fig. 1.1. (a) Double layer device structure (b) equilibrium state energy level at \( V = 0 \) (c) energy level at a forward bias \( V = V_{\text{app}} \)
For the cathode, low work function materials such as Ca ($\Phi_0 \sim 3$ eV), Mg ($\Phi_0 \sim 3.7$ eV), Al ($\Phi_0 \sim 4.3$ eV) are used to minimize the energy barrier for e- injection from $E_F$ of the cathode to the lowest unoccupied molecular orbital (LUMO) level of organic materials. The problem of many low work function metals is extreme reactivity to oxygen and water, hence Ca and Mg should be protected by an additional layer, such as Al. Another way to minimize the barrier from electron injection is to insert a very thin (~1 nm) insulating layer of LiF, CsF or AlO$_X$ between the top organic layer and the Al cathode. These buffer layers generate a dipole layer and thus reduce the barrier for electron injection to the organic layers.

The hole and electron transport layers (HTL and ETL, respectively) are the layers favorable for hole and electrons respectively. When the applied bias $V_{app}$ is less then the built in voltage $V_{bi}$, the injected current is negligible and most of the current is caused by free carriers in the organic layers or leakage current. At high forward applied field the injected holes and electrons hop from site to site through the organic layers. Some of the carriers may accumulate in a specific area, called the charge accumulation zone, usually at the organic-organic interface of the multi-layer structure. If the density of electrons and holes are sufficiently high, then the distance between them becomes sufficiently low for recombination to radiative singlet excitons (SEs).

1.4 Carrier injection

In organic materials, disorder, low bandwidth, electron phonon interactions and temperature all work together to localize charge carriers. Thus, the primary injection event consists of a transition from an extended band-like state in the metal electrodes into a localized molecular polaronic state in the organic material. The highly insulating nature of most organic solids
coupled with low charge carrier mobility resulting from weak intermolecular interaction and disorder, make the standard the semiconductor techniques inapplicable to study their electronic properties [14]. Despite these difficulties, J. Kalinowski performed a thorough theoretical analysis of the mechanism of carrier injection. The possible mechanisms developed by various researchers over the time are briefly discussed in this section.

1.4.1 Image force lowering [15]

When carriers are injected from a metal electrode into the organic layers (Fig 1.2), they encounter the injection barrier \( q_{\text{injection barrier}} \), which is the energy difference between the Fermi level \( E_f \) of the metal and the LUMO level \( E_{\text{LUMO}} \) for electron injection. Similarly, holes encounter a barrier, which is the difference between \( E_f \) and \( E_{\text{HOMO}} \). Following the injection, many electrons remain on the surface of the organic layer at distance \(+x\) from the metal-organic interface. These electrons induce equivalent hole charges in the metal layer at \(-x\). The hole charges are referred to as the image charges. As a result of these image charges, the new potential of the metal-organic interface system becomes

\[
\Psi(x) = \phi_m - \chi - \frac{q^2}{16\pi\varepsilon x} - qFx = \phi_m - \frac{q^2}{16\pi\varepsilon x} - qFx
\]

\[\varepsilon = \varepsilon, \varepsilon_0\]

We get the effective potential barrier height as:

\[
\phi_{\text{eff}} = (\phi_m - \chi) - \sqrt{\frac{q^2F}{4\pi\varepsilon}}
\]  

where \( \phi_m \) is metal work function, \( \chi \) is electron affinity, \( F \) is electric field and \( q \) is electron charge.
Fig. 1.2. Image force of the barriers for electron injection at the metal-organic interface. The energy barrier at the interface is lowered by an amount $q\Delta \varphi$ from $q\varphi_m$ to $q\varphi_B$.

Therefore, the barrier lowering is

$$\Delta \varphi = \sqrt{\frac{q^3 F}{4\pi \varepsilon}}$$

(3)

The above treatment holds for neutral contact between metal and wide gap intrinsic semiconductors, which is the case for organic semiconductors.

1.4.2 Thermionic emission

The current voltage characteristics of OLED depend critically on the electronic states at the metal-organic interface. Charge injection at low applied bias is primarily due to thermal
emission of charge carriers over the interface potential barrier when the barrier is not too high for thermal injection. Emtage and O’Dwyer [18] solved drift-diffusion equation for the injection from metal into wide-gap intrinsic semiconductor, in which the depletion width is infinite without injection. Emtage and O’Dwyer derived that:

(a) in the low field limit, \( E \ll 4\pi e kT^2/q^3 \)

The thermionic injection current density \( (J) \) over the barrier is given by

\[
J = N_0 q \mu E \exp\left(-\frac{q\phi_H}{kT}\right)
\]  \hspace{1cm} (4)

and

(b) in the high field limit

\[
J = N_0 \mu \left(\frac{kT}{q}\right)^{1/2} (16\pi e q E^3)^{1/4} \exp\left(-\frac{q\phi_H}{kT}\right) \exp(f)^{1/2}
\]  \hspace{1cm} (5)

Although not explicitly shown, the backflow current is present. The origin of the backflow in wide bandgap organic semiconductors is disorder.

The existence of disorder in organic semiconductors adds an obstacle to the injected carriers. Due to disorder, a distribution of site energies is created, and carriers injected occupy the molecular sites in contact with electrodes and also at the low-energy end of the distribution. To move further into the organic materials, the carriers must overcome random energy barriers in addition to the image potential. For this reason, most injected carriers will backflow into the electrode at low applied field strength. When the electric field is increased, the efficiency of injection increment will be more significant than in the case when only image force is considered. This thermal injection process has been proved both by Monte Carlo simulation [20] and experiment [23].
1.4.3 Field emission [22]

Field emission is the process whereby carriers tunnel through a barrier in the presence of a high electric field. When the barrier is triangular, the tunneling is called Fowler-Nordheim (FN) tunneling. When the forward field across the 100nm thin OLED is increased, the triangular energy barrier becomes shallower (Fig. 1.1c) [22]. It is typically ~2 nm wide at an applied field of 2 MV/cm, in which case the width is sufficiently thin for tunneling. For a triangular barrier, the FN current density is given by

\[ J_{FN} = A F^2 e^{-F_0/F} \]

where parameter A and F_0 are related to the potential barrier and are given by

\[ A = \frac{m q^3}{8 \pi \hbar m \phi_b}, \quad F_0 = \frac{8 \pi \sqrt{2 m \phi_b^3}}{3 q \hbar} \]

The barrier \( \phi_b \) itself is a function of field F through the image-force lowering effect. Typically, for low fields (<2 MV/cm), the thermionic current dominates; for high fields (>2 MV/cm), the tunneling current prevails [23].

1.5 Carrier transport in OLEDs

Unlike inorganic semiconductors, the transport properties in OLEDs are determined by intersite hopping of charge carriers between localized states [31]. If two molecules are separated by a potential barrier, a carrier on one can move to the other either by tunneling through the barrier or by moving over the barrier via an activated state. The latter process is called hopping [32]. The actual transit rate from one site to another depends on their energy difference and on the distance between them. The carriers may hop to a site with a higher energy only upon absorbing a phonon of appropriate energy [33]. This decreases the
probability of transit to a localized state with higher energy. The energetically allowed hops to a distant site are limited also by the localized length [34]. The energy states involved in the hopping transport of holes and electrons form narrow bands around the HOMO and LUMO levels. The width of these bands is determined by the intermolecular interactions and by the level of disorder [34].

1.5.1 Field dependent mobility

In most organic semiconductors, the carrier mobility is a strong function of applied electric field, unlike inorganic semiconductors where mobility is, in general, independent of the applied field. Over a reasonable range of fields, the time-of-flight (TOF) measurement gives the mobility in organic semiconductors as

\[
\mu = \mu_0 \exp(-\frac{\Delta\theta}{kT}) \exp[\beta F^{1/2}(\frac{1}{kT} - \frac{1}{kT_0})]
\]

or simply, \( \ln \mu \propto S \times F^{1/2} \), where \( S \) is a constant and \( F \) is electric field.

The dependence of \( \ln \mu \) on \( F^{1/2} \) is of Poole-Frenkel type. The Poole-Frenkel effect describes the electric-field assisted detrapping phenomenon. When a field is applied, the trap-potential in which a carrier is trapped will be deformed into an asymmetric shape. The situation is very similar to Schottky barrier lowering due to image force with the difference being that one is in the bulk and the other is in the interface. Both cases result in the \( F^{1/2} \) dependence.

Although the Poole-Frenkel mechanism predicts a field-dependence in agreement with experiment [35], it is not possible to have a high concentration of charged traps in all organic materials, as is necessary for the usual application of Poole-Frenkel theory. The temperature
The coefficient of the mobility was found to be independent of the chemical composition, which is clear evidence against the dominance of impurity effects. In addition, a deviation of both the magnitude of $S$ and its temperature dependence from the prediction of Poole-Frenkel theory is observed [35].

Gaussian disorder models [34] and most recently, a theory based on the spatial correlation of energetic disorder [33] have been suggested. Spatial correlation can be caused by molecular density fluctuations. In the case of $\pi$-conjugated polymers, additional energetic
disorder arises from the distribution of the conjugation length. The existence within the polymer of more crystalline and less crystalline regions also suggest spatial correlations.

1.5.2 Space-charge limited current

Given ohmic contact, the current-voltage relation of an organic semiconductor is linear at low fields but becomes nonohmic at higher fields. This behavior is, in general, due to two effects: i) At the higher current densities corresponding to higher values of field, a relatively large concentration of charge carriers in transit to the collector electrode is present between the electrodes. These carriers constitute the space charge. ii) The existence of traps [28] which are due to the disorder within the organic semiconductor, gives rise to highly localized energy states within the energy gap. The traps filled by injected charge carriers become electrically charged centers, thus contributing to the formation of the space charge as well [30].

The trap-free SCL current is given by Mott and Curney equation

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3}$$  \hspace{1cm} (8)

At low applied voltage, if the density of thermally generated free carriers (say $p_0$) is predominant, i.e. $qp_0 \frac{V}{d} \gg \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3}$, the J-V characteristics will be ohmic and the transition voltage is

$$V_\Omega = \frac{8}{9} \frac{qp_0 d^2}{\varepsilon}$$

With traps confined in discrete energy levels, the SCL current becomes
where $p_t$ is the trapped carrier density.

\[
J = \frac{9}{9} \varepsilon \mu \theta \frac{V^2}{d^{3/2}}
\]

\[
\theta_a = \frac{p}{p + p_t}
\]

Starting from the Ohmic region, as the applied voltage is increased, the density of free carriers resulting from injection can increase to such a value that the quasi-Fermi level $E_f$ moves down below the shallow hole trapping level $E_t$, and most traps are filled. The traps filled limit $V_{tf}$ is the condition for the transition from the trapped J-V to the trap-free J-V characteristics.
1.6 Charge recombination and efficiency

After carrier injection and transport, both electrons and holes can recombine to form various excited states such as singlet excitons, triplet excitons and charge transfer excitons. In fluorescence devices, the emission is due to the radiative decays of singlet excitons (SEs), as radiative triplet exciton (TE) is forbidden.

1.6.1 Charge recombination (Langevin recombination)

If the oppositely injected holes and electrons are statistically independent of each other and the recombination process is random, then it can be treated by the Langevin formalism [30,47]. The necessary condition for recombination is that the separation $X_{h,e}$ between the hole and the electron must be less than the Coulomb capture or Onsager radius $r_c$ (see Fig. 1.5). Onsager radius is the distance where the Coulomb attractive energy and the thermal dissociation energy are equal [3], i.e.,

$$r_c = \frac{q^2}{4\pi\varepsilon_0 kT}$$

Since $\varepsilon \approx 3\varepsilon_0$ for most organic materials, the typical capture radius is ~17 nm at room temperature. Hence, the charge carrier densities should be greater than $10^{17}$ cm$^{-3}$ as the recombination requires $X_{h,e} \ll r_c$.

The bimolecular recombination rate between electrons and holes are given by

$$R = \gamma pn$$

Where $p$ and $n$ are hole and electron densities respectively and $\gamma = e(\mu_h + \mu_e)/\varepsilon$ is the bimolecular recombination coefficient.
Fig. 1.5. Mean separation $\lambda_{h-e}$ and Coulomb capture of a hole and electron pair. If $\lambda_{h-e} < \lambda_C$, then the pair can form various excites such as singlet, triplet or charge transfer exciton.

1.6.2 Efficiency

If we assume that the probability of recombination of $e^\cdot - h^+$ pairs in the singlet spin configuration to SEs is equal to the probability of recombination of pairs in the triplet spin configuration to TEs, then only a quarter of the pairs will recombine to the radiative SEs. So the internal EL efficiency or internal quantum efficiency ($\eta_\text{EL}^{\text{int}}$) will be limited to a maximum of 25% when there is no other quenching of SEs, and the hole-electron density is ideally balanced, i.e., $c_{h-e} = 1$. Typically, SEs are quenched by various processes such as charge transfer to another molecule, traps and defects. In electrical excitation, the internal EL quantum efficiency is written as

$$\eta_\text{EL}^{\text{int}} = c_{h-e} \eta_R \eta_{PL}$$

where $\eta_R$ is the fraction of recombination events that result in SEs.

1.7 Molecular doped guest-host system

Molecular doped guest-host (G-H) blends have been studied extensively to improve the efficiency [2,52] or to modify the emission color [53,54] of OLEDs. The requirement for an
effect G-H system is that the energy gap of the guest molecule should be small than that of the host molecule and at least one of guest HOMO or LUMO level should be located inside host HOMO-LUMO level. Examples of red emitting efficient guest molecules are 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl aminostyryl)-4H-pyran (DCM1) and [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene] – propane-dinitrile (DCM2).

Since at least one of the guest energy levels is located inside the energy levels of host, the guest molecules act as strong charge trapping sites. They are also very efficient fluorophore if doped at a low concentration. It is possible to change the emission color of the OLED by carefully controlling the concentration of the guest molecules. Schematic energy level diagram of a G-H system is shown in Fig 6.

![Diagram](image)

Fig.1. 6. Schematic energy level diagram of guest-host system with hole and electron trap

### 1.7.1 Energy transfer

A donor SE, or a host fluorophore, can transfer its energy to an acceptor, guest fluorophore nonradiatively and the emission from the guest is usually due to Förster or resonant energy transfer from the host to the guest. The energy transfer rate from donor to the acceptor is given by
where $\tau_0$ is the average donor exciton lifetime and $R_0$ is the energy transfer radius.

Besides Förster energy transfer, guest emission can also be generated by the recombination between an electron and a hole trapped on the guest. For example, DCM2 molecules are traps for both holes and electrons in Alq3, NPD and DPVBi hosts. Thus the guest molecule acts as a trap recombination center [2] to emit its own color. If the trapped charge density is very high for both charges, then the recombination of trapped charges on guest molecules can generate efficient emission.

2. Introduction to OLED based integrated biochemical sensors

Biosensors are defined as an analytical device incorporating a biological sensing element which translates the chemical parameters of a system into an optical or electrical signal. Biosensors offer small, selective, and portable diagnostics for key biological substances. Such diagnostics could improve management of patients and allow testing in the home or at convenient outpatient clinics. While most biosensors are in the development stage, current research promises to meet several of the important measurement goal for selected metabolites, drugs and other important clinical molecules. Enzyme technology was exploited as early as 1950s with the development of an enzyme test strip [42] for the simple analysis of solutions, and the enzyme electrode is still the classic and most commercially marketed biosensor. The first example of this technique is the combination of the enzyme, glucose oxidase and an oxygen electrode, which measures glucose by detecting the reduction in oxygen when the oxidation of glucose is catalyzed by the enzyme [52].

$$K_{\mu\rightarrow \lambda} = \frac{1}{\tau_0} \left( \frac{R_0}{R} \right)^6$$

(12)
2.1 Fluorescence based biosensor [41]

During the past 15 years there has been a remarkable growth in the use of fluorescence in the biological sciences especially in development of biochemical sensors. Fluorescence is now used in environmental monitoring, clinical chemistry, DNA sequencing, and genetic analysis. Because of the sensitivity of fluorescence detection, it has increasingly become a major technique for sensing biochemical analytes.

Luminescence is the emission of light from any substance and occurs from electronically excited states. Luminescence is formally divided into two categories, fluorescence and phosphorescence, depending on the nature of the excited states. In excited singlet states, the electrons in the excited orbital are paired (of opposite spin) to the second electron in the ground-state orbital. Consequently, return to the ground state is spin-allowed and occurs rapidly by emission of a photon. The emission rates of fluorescence are typically $10^8 \text{ s}^{-1}$, so that a typical fluorescence lifetime is near 10 ns. Because of the short time scale of fluorescence, measurement of the time resolved emission requires sophisticated optics and electronics.

Phosphorescence is emission of light from triplet excited states, in which the electron in the excited orbital has the same spin orientation as the ground-state electron. Transitions to the ground state are forbidden and the emission rates are slow ($10^3-1 \text{ s}^{-1}$), so that phosphorescence lifetimes are typically in microsecond to seconds. Following exposure to light, the phosphorescent substances glow for long time as the excited phosphors slowly return to the ground state. It is very hard to see phosphorescence in a concentrated solution as there are many deactivation processes which compete with emission, such as nonradiative decay and quenching processes. Transition-metal-ligand complexes (MLCs), which contain
a metal and one or more organic ligands, display mixed singlet-triplet states. These MLCs display intermediate lifetime of 400ns to several microseconds.

The processes, which occur between the absorption and emission of light, are usually illustrated by Jablonski diagram. A typical Jablonski diagram is shown in fig.1.7.

Fig. 1.7. One form of Jablonski diagram

The intensity of fluorescence can be decreased by a wide variety of processes. Such decreases in intensity are called quenching. Quenching can occur by different mechanisms. Collisional quenching occurs when the excited state fluorophore is deactivated upon contact with some other molecules in solution or gas, which is called the quencher. Collisional quenching is illustrated on the modified Jablonski diagram in Fig.1.8 In this case, the fluorophore is returned to the ground state during a diffusive encounter with the quencher.
The molecules are not chemically altered in the process. For collisional quenching, the decrease in intensity is described by the well known Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K[Q] = 1 + k_q \tau_0 [Q]$$  \hspace{1cm} (13)

In this expression $K$ is Stern-Volmer quenching constant, $k_q$ is the bimolecular quenching constant, $\tau_0$ is the unquenched lifetime and $[Q]$ is the quencher concentration. A wide variety of molecules can act as collisional quenchers, such as, oxygen, halogens, amines and electron-deficient molecules like acrylamide. The mechanism of quenching varies with the fluorophore-quencher pair.

![Jablonski diagram with collisional quenching and FRET.](image)

Fig. 1.8. Jablonski diagram with collisional quenching and FRET.

The collisional quenching property of oxygen has been used extensively in this study to develop fluorescence based biosensor. The light source to excite the fluorophore molecules, which are either ruthenium or platinum based metal ligands, is either a DPVBi based blue OLED or Alq3 based green OLED. The spectrum which enables us to use these light sources effectively are shown in Fig. 1.9.
Fig. 1.9. PL spectrum of metal ligan Ru(dpp) and DPVBi OLED. (1) PL of Ru(dpp), (2) excitation in air (3) absorption spectra of Ru(dpp), (4) EL of blue DPVBi OLED, (5) EL of violet OLED

3. Dissertation organization

This dissertation consists of seven chapters. The first chapter is the introduction to the Organic Light Emitting Devices and OLED based biosensors. In the second chapter, the decay mechanism following a voltage pulse of DPVBi based blue OLED, is described. Chapter 3 is a published work on the new technology of integrating OLED to the sensing film. In chapter 4, results of this new sensor technology on gas and solution phase monitoring of oxygen is discussed. Chapter 5 is a published work on monitoring glucose using the integrated OLED approach. Chapter 6, covers the results and discussion on anthrax sensor using the same integrated approach. Finally chapter 7 gives the general concluding remarks of this dissertation.
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Chapter 2. Temperature dependence of electroluminescence spikes, turn off dynamics and charge traps in organic light emitting devices

1. Introduction

Since the first bilayer Alq3 OLED was reported by Tang et al [1], extensive studies have been conducted to improve device brightness, efficiency and long term stability. Transient EL, i.e. light emission from the OLED operated under short pulsed bias, is attracting considerable interest to study the basic processes in OLEDs and for applications that require a pulsed source. The turn off dynamics following a bias pulse has been studied very actively to get some insight into the carrier dynamics and to explore the recombination mechanism in the organic layers. [4,5]

Energetic disorder, structural disorder and impurities in the organic semiconductors create traps, which controls the transport properties of the organic semiconductors. These traps reduce the number of mobile carriers and detain the charges for a long time and so the traps become charge storage sites. [7]

2. Theory

When a bias is applied to an OLED, the independent carriers are injected from their respective electrodes and they drift/hop to the recombination zone, which is the interface between the hole transport layer (HTL) and the electron transport layer (ETL). These injected carriers can (1) form excitons and (2) form correlated charge pairs (CCPs) for light emission or (3) remain as independent charges. All these different species exist in the recombination zone immediately after the bias is turned off at \( t = 0 \). Hence, the emission decay following
turn off is due to (i) decay of excitons generated at $t < 0$, (ii) recombination of CCPs, and (iii) recombination of initially ($t = 0$) independent holes and electrons. The turn off decay follows some general characteristics, which are discussed briefly in the following paragraph.

(i) The decay of the preexisting singlet excitons is exponential if their dynamics is governed by monomolecular processes.

(ii) The main mechanism of CCP decay [7, 8] is closely related to random walk diffusion under Coulomb interaction [8]. Let $W(r_0, t)$ be the probability so that the CCPs, with separation $r_0$ at $t = 0$ will remain separate at time $t$. then their recombination rate $R_{\text{ccp}}(t) = -dW/dt$ for a Gaussian-like distribution of separations $g(r_0)$ is given [8] by

$$
R_{\text{ccp}}(t) = \frac{\sqrt{4\pi}}{D_{\text{ccp}}^{3/2}} \int_0^\infty g(r_0) \exp\left(-\frac{r_0^2}{4D_{\text{ccp}}t}\right) \exp\left(-\frac{r_c}{r_0} \left[1 - \text{erf}\left(\frac{r_0}{\sqrt{4D_{\text{ccp}}t}}\right)\right]\right) dr_0
$$

where

$$
g(r_0) = \exp\left[-\frac{(r_0 - \bar{r})^2}{\sigma^2}\right] \frac{1}{4\pi^{3/2} \sigma^{3/2}}
$$

$D_{\text{ccp}}$ is the CCP diffusion coefficient.

$r_c = e^2/(4\pi\varepsilon_0 kT)$ is the Onsager radius ($r_c \approx 17\text{nm}$ at room temperature)

$\text{erf}$ is the error function.

The CCP characteristic time for recombination is defined by

$$
\tau_{\text{ccp}} = \bar{r}^2 / 4D_{\text{ccp}}
$$

Where $\bar{r}$ is the median separation.

The recombination $R_{\text{ccp}}(t)$ has a peak at $t = \tau_{\text{peak}}$. This peak is due primarily due to the maximum value of $g(r_0)$ at $r_0 = \bar{r}$. It should be noted that $\tau_{\text{peak}} \neq \tau_{\text{ccp}}$, but rather $\tau_{\text{ccp}} \sim 2\tau_{\text{peak}}$. 


At $t \sim \tau_{ccp}$, $R_{ccp}(t)$ is roughly proportional to $t^2$, but this dependence evolves to $t^{3/2}$ for $t \gg \tau_{ccp}$.

(iii) At $t=0$, there is also some population of independent or uncorrelated charges. They can diffuse away from the charge accumulation zone, or pair up with counter charges to form CCPs and/or excitons. Net diffusion occurs only normal to the layers of the device. Let $N_h$ be the number of holes per unit area localized at the center of the thin recombination zone at $t = 0$. Then the time dependent number of holes $p(x,t)$ is given by the Gaussian expression [9]

$$p(x,t) = \frac{N_h}{\sqrt{4\pi D_h t}} \exp\left(-\frac{x^2}{4D_h t}\right)$$

(3)

Where $D_h$ is the hole diffusion coefficient. The distribution of electrons $n(x,t)$ with initial concentration $N_e$ and diffusivity $D_e$ satisfies the same relation.

The recombination rate $R_{h-e}(t)$ of the initially independent charges is given by Langevin equation

$$Rh-e(t) = \gamma \int_0^{\Delta x_0} p(x,t)n(x,t)dx$$

$$= \frac{\gamma N_h N_e}{2\sqrt{\pi(D_h + D_e)}} \times \begin{cases} t^{-1/2}, & \text{if } t << \tau_{h-e} \\ \frac{\Delta x_0 \sqrt{\pi D_{eff}}}{\sqrt{\pi D_{eff}}}, & \text{if } t \gg \tau_{h-e} \end{cases}$$

(4)

Where $\gamma$ is the bimolecular rate constant, $\Delta x_0$ is the width of the recombination zone or charge accumulation zone, and $D_{eff} = (1/D_h + 1/D_e)^{-1}$ is the effective diffusion coefficient of the holes and electrons. The characteristics recombination time of these initially independent charges $\tau_{h-e}$ is defined as $\tau_{h-e} = \Delta x_0^2/4D_{eff}$. $R_{h-e}(t)$ is proportional to $t^{-1/2}$ for $t << \tau_{h-e}$ and to $t^1$ fro $t \gg \tau_{h-e}$. In order to observe the $t^1$ behavior the charges must be localized in a specific region $\Delta x_0$ such as the recombination zone of the OLEDs.
3. Device structure and materials

The chemical structure and full names of the materials used in this device is shown in Fig. 2.1. The generic structure of the DCM2 doped DPVBi multiplayer small molecular OLED that has been fabricated, is shown in Fig. 2.2. All organic materials and the cathode metals were evaporated by conventional thermal evaporation in a vacuum chamber (<10⁻⁵ Torr) installed inside argon filled glove box; the oxygen and water levels were normally below 1 ppm. The thickness of each layer was monitored by a Maxtek TM-100 thickness monitor. Typical deposition rates were 0.1-2 Å/sec for the organic materials, and 2-3 Å/sec for the Al cathode.

To fabricate the devices, 2"×2" ITO substrates were aqua regia and ozone-treated to improve the hole injection. On the treated ITO, a ~5 nm thick layer of the blue pigment copper phthalocyanine (CuPC) was deposited. The ~5.3 eV HOMO level of CuPC is close to the ~5.1 eV Fermi level of ITO (see the energy diagram in Fig. 2(b)), therefore, efficient hole carrier injection from ITO in CuPC layer is expected. In addition, CuPC is known to be good hole conductor, with mobility 0.02-0.04 cm²/Vs at room temperature.

Following the deposition of CuPC, a 40 nm thick hole transport layer (HTL) of N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (α-NPD) was deposited. The hole mobility of α-NPD is ~3×10⁻⁴ cm²/Vs at typical operating voltages.

For emission, a layer of highly efficient blue fluorescent 4,4'-bis(2,2'-diphenyl-vimyl)-1,1'-biphenyl (DPVBi) was evaporated on the α-NPD. To enhance the concentration of traps between HTL and ETL a very thin layer of DCM2 doped DPVBi was co-evaporated between α-NPD and DPVBi layer. Thickness of this co-evaporated layer was 1 nm and the DCM concentration was 5 wt %.
Fig. 2.1. Molecular structure and full name of the materials used in this work.
Fig. 2.2. (a) Typical multiplayer device structure studied in this study. (b) Energy level diagram of the structure. CsF lowers the electron injection barrier, but the degree of lowering is unknown.

To protect the DPVBi layer from the relatively high temperature during the subsequent Al evaporation, a 10 nm thick electron transport Alq₃ layer was evaporated between the DPVBi and the Al layer, since Alq₃ has a very high glass transition temperature $T_g > 170^\circ$C, in
contrast to the $T_g = 64^\circ$C of DPVBi. The thickness of Alq3 layer was limited to 10 nm to avoid emission from that layer.

On the top of the Alq3 layer, a very thin 1 nm-thick CsF layer was deposited to improve the electron injection from the ~150 nm thick Al layer. The Al was deposited for external contact through a 2"×2" mask containing 21×21 circular pixels; the circles were ~1.5 mm in diameter.

4. Experimental results and discussion

The experimental results of the decay of the DPVBi OLED at 4 different temperatures are shown in Fig. 2.3. Fig. 2.4 shows that the experimental results fit well with the sum of the three terms corresponding to the three mechanism mentioned above: (i) an experimental term due to the prompt excitation decay, (ii) the term due to CCP recombination $R_{ccp}(t)$, which is responsible for the overshoot (due to the complexity of the graph only the sums of the exponential decay and CCP recombination $R_{ccp}(t)$ are represented by solid lines), and (iii) the term due to $R_{he-e}(t)$ (dashed line, which is responsible for the long emission tail following the overshoot.

The important information that can be gathered from Fig 2.3 and 2.4 are:

(a) At room temperature, the exponential decay of the OLED shows a decay time constant of 35 ns and with higher temperature the decay time constant decreases to 22 ns. This value is not the intrinsic singlet exciton decay time, which is <10 ns for Alq3 and DPVBi devices [12]. The source of this higher decay time constant is the RC time constant of the device.

(b) The overshoot shown in Fig. 2.3 and 2.4 increases with increasing temperature. The overshoot amplitudes, relative to the quasi-steady state EL are 1.08, 2.3, 3.7 and 5.1
respectively. The reason is that the DCM2 molecules, while being fluorophores, is also an electron

![Normalized intensity vs. time graph](image)

Fig. 2.3. EL decay of DPVBi OLED following a pulse for four different temperature and hole trapping sites. In a Förster resonance energy transfer, the electrons and holes in the LUMO and HOMO levels of the host come down to the guest LUMO and HOMO levels and the rate of this transfer increases with temperature and hence increasing the electrons and holes in the guest’s LUMO and HOMO level. As the number of CCPs now increases, so does the overshoot.

(c) The longer lifetime of the decay, which is due to the uncorrelated charge pair recombination decreases with temperature. As the temperature increases, probability of finding a hole/electron, for an uncorrelated electron/hole, increases because, the diffusion of
these carriers increase as $T^{-1/2}$ (see equation 4). So the decrease in the long lifetime with temperature is due to the higher recombination rate of the uncorrelated carriers.

Fig. 2.4 EL decay (log-log scale) after external field turns off in DPVBi OLED. The open symbols are experimental data. The solid lines are the sum of the exponential decay and $R_{ccp}(t)$. The dashed lines are the predicted emission due to initially independent charges $R_{h-e}(t)$.

The $1/t$-tail originates from strong charge accumulation in the recombination zone formed around the internal organic/organic interface. Without doping, the recombination zone width $\Delta x_0$ is $\sim 5$ nm, [13] but the 1-nm-thick DCM2 doping reduces the trapped charge zone width to the thickness of the doped layer. Indeed, at a doping level heavier than 1 wt%, the 1 nm thick-doped layer yields almost pure DCM2 emission (i.e., almost no DPVBi emission). Thus the recombination zone is well confined around the doped layer.
The emission following the bias pulse is mainly due to $R_{ccp}(t)$ and $R_{h-e}(t)$. Hence, the area under the emission curve should be proportional to the total number of photons $Q_{\text{tot}}$ emitted after the pulse, i.e.

$$Q_{\text{tot}} \propto \int_0^\infty \left[R_{ccp}(t) + R_{h-e}(t)\right] dt$$

Although Eq. (5) cannot be solved analytically due to the divergent integral of $1/t$, it can be estimated experimentally. $Q_{\text{tot}}$ is related to the total number of trapped holes $P_t$ and electrons $N_t$ at $t = 0$ in the recombination zone. Specifically, $Q_{\text{tot}} < \min \{P_t, N_t\}$. Since not all of the recombination events result in EL, the observed $Q_{\text{tot}}$ only provides a lower bound for the number of charges trapped on the DCM2 molecules and on intrinsic DPVBi trap sites. Since in the sample almost all of the emitted photons come from DCM2 molecules, the total number of possible trap sites generated by the DCM2 molecules is estimated to be $\sim 2.5 \times 10^{11}$ in the 1.5 mm diameter pixel, assuming a simple cubic structure with a 1 nm lattice constant.

(5) Conclusion

In this work we have studied the behavior of EL spikes and overshoots at the turn off of a voltage pulse in OLED containing a narrow DCM2 doped DPVBi recombination zone, when the OLED is subjected to higher temperature. The overshoot increases as the temperature increases and the long lifetime decay constant of the recombination of uncorrelated charge pair decreases as the temperature increases.
Acknowledgement

This work was supported by the Ames Laboratory, operated by Iowa State University for the US Department of Energy.

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Chapter 3. Luminescent chemical and biological sensors based on the structural integration of an OLED excitation source with a sensing component

A paper published in SPIE proceedings 5214, 64(2004)

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ABSTRACT

A new platform for luminescent chemical and biological sensors, integrating the excitation source, an OLED, with the sensing component, is described. The utility of the platform is demonstrated for an oxygen sensor and its potential is demonstrated for antibody-antigen immunoassays. The oxygen sensor is operable in two modes, i.e., photoluminescence (PL) intensity mode and lifetime mode, where changes in the PL intensity and lifetime, respectively, are correlated with the oxygen level. In the life time mode, the need for sensor calibration, which remains a challenge in real-world sensing applications, is eliminated. Attributes and issues related to sensor performance, including design and stability, are discussed.

Keywords: Organic Light Emitting Device, OLED, photoluminescence, PL, oxygen sensor, immunosensor
1. INTRODUCTION

The field of photoluminescence (PL)-based chemical or biological sensors is growing rapidly [1,2]. Such sensors are typically composed of a sensing element, whose PL is monitored before and during exposure to an analyte, a light source which excites the PL, and a photodetector (PD). Current light sources such as lasers and inorganic LEDs are bulky or require intricate integration procedures [3]. In contrast, the structural integration of an OLED with a sensing element is simple, resulting in small-size devices [4,5] which are attractive for developing miniaturized sensor arrays for medical and environmental applications, including for high throughput, multianalyte analysis [4,5]. This paper describes the first steps towards the realization of this new sensor platform.

The viability of the proposed structurally integrated OLED/luminescent sensors results from the intrinsic advantages of OLEDs as low-voltage, miniaturizable [6], flexible [7,8] and efficient light sources, and the dramatic improvements in OLEDs achieved over the past decade, which has led to their emergence in commercial products [9]. These improvements include external quantum efficiencies and lifetimes which exceed 18% and 20,000 hours, respectively, for green emitters, 10-12 and 6% and 1,000 hours, respectively, for blue emitters [13-15].

Motivated by the need for miniaturized sensors and multianalyte sensor arrays, and the above-mentioned OLED attributes, we have recently explored this new sensor platform by fabricating a structurally integrated PL-based oxygen sensor [5]. The basic structure of the platform is shown in Fig. 3.1, where the OLED excitation source is deposited on one side of a glass substrate, while the sensing component is deposited on the other side of the substrate.
Equivalently, the OLED and sensing components can be fabricated on separate substrates and attached back-to-back.

For complete integration of a compact sensor device, the position of the PD is of importance as well. One possible PD position is “in front” of the volume containing the analyte (“front-detection”), i.e., the analyte is between the sensing element and the PD (see Fig. 3.2a). If the OLED consists of a single opaque pixel, this front-detection geometry is the obvious geometry. If, however, the OLED is transparent, or consists of an array of pixels, the PD can monitor the PL that passes through the transparent OLED or between the gaps of the OLED array. In this geometry, therefore, the PD is positioned “behind” the transparent OLED or OLED array (“back-detection;” see Fig. 3.2b).

![Fig. 3.1. Basic structure of an integrated OLED/fluorescence-based chemical and biological sensor.](image-url)
Fig. 3.2. Sensor device geometries: (a) front detection mode and (b) back detection mode using an array of OLED pixels.

Note that the “back detection” geometry is clearly preferable not only for integration and miniaturization purposes, but also for the development of such sensors for *in vivo* operation.

For the oxygen sensor demonstrated in this work, the sensing element was a film consisting of ruthenium tris(4,7-diphenyl-1,10-phenanthroline) chloride [Ru(dpp)_3] dye (see Fig. 3.3), [16,17] embedded in a sol-gel matrix; the strong red PL of Ru(dpp)_3 is quenched by collisions with O_2. The dependence of the PL intensity (I), as well as its lifetime (τ), on the oxygen partial pressure [O_2], is described by the Stern-Volmer equation

\[ \frac{I_0}{I} = \tau_0/\tau = 1 + k\tau_0 [O_2], \]

where the subscripts 0 denote values in the absence of a quencher and k\τ_0 is known as the Stern-Volmer constant. Experimental Stern-Volmer plots of 1/I or 1/τ vs [O_2] should
therefore be linear with identical slopes for a single type of luminophores in a given host, equally accessible to the quencher. Indeed, in solution, this predicted linear dependence was confirmed [17].

![Figure 3.3](image.png)

**Fig. 3.3.** Structure of tris (4,7-diphenyl-1,10-phenanthroline) Ru(II).

In this work, we demonstrate oxygen sensor devices fabricated with both front and back detection geometries and discuss some of their properties (see Figs. 4 - 6). The devices were calibrated by monitoring the PL intensity as a function of the oxygen level. In addition, we demonstrate the operation of the sensor devices in a lifetime mode, where the effect of the oxygen level on the PL lifetime was monitored. This mode of operation is advantageous over the intensity mode, as it eliminates the need for re-calibration, which remains a challenge in developing sensors operable in real-world environments. Preliminary assessment of the utility of OLED-based integrated devices for immunosensing is also described.
2. EXPERIMENTAL

Blue OLEDs were fabricated by vacuum evaporation of the organic layers, the CsF buffer layer, and the Al cathode, on Applied Films Corp. 20 Ω/square indium tin oxide (ITO)-coated glass, as described previously [5,18-20]. The hole transporting layer was N,N′-diphenyl-N,N′-bis(1-naphthyl phenyl)-1,1′-biphenyl-4,4′-diamine (α-NPD), and the emitting layer was either 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl (DPVBi) [5,19,21] or perylene-doped 4,4′-bis(9- carbazolyl) biphenyl (Pe:CBP) [22]. The OLEDs were prepared as either an unencapsulated 21×21 matrix array of ~1.5 mm diameter Al disc electrodes evaporated onto the organic layers for front detection (as the wire contacts did not enable back-detection) [20], or as a smaller encapsulated matrix array of ~2×2 mm² square pixels resulting from perpendicular stripes of etched ITO and evaporated Al for back-detection.

The oxygen sensing films were prepared by immobilizing Ru(dpp)₃ in a sol-gel matrix. First, Ru(dpp)₃ was blended with a sol, prepared from a methyltriethoxysilane precursor mixed with water and ethanol. The Ru(dpp)₃-doped sol was spin coated onto cleaned, silanized glass slides and then aged at 70°C. The resulting sensor films were optically transparent and crack free.

The EL of the OLEDs used in this study, which peaks at ~470 nm, strongly overlaps the broad PL excitation and absorption bands of Ru(dpp)₃. However, there is minimal overlap between the EL and the PL of the Ru(dpp) dye, which peaks at ~600 nm. This situation is ideal for the OLEDs/sensing film combination of this study.

The measurements on the Ru(dpp) sensor films excited by integrated DPVBi- or Pe:CBP-based OLEDs were performed in a flow cell with flowing oxygen/argon mixtures. Mixing was achieved by means of mass flow controllers, where the flow rates of the oxygen and
argon varied, while maintaining a constant total flow rate of 500 sccm, thus, generating varying oxygen partial pressures.

For intensity measurements the OLEDs were operated in a dc mode with a forward bias of 9 -20 V, or in a pulsed mode; for lifetime measurements, they were operated in a pulsed mode. The PD was a photomultiplier tube (PMT).

3. RESULTS AND DISCUSSION

3.1 Oxygen sensor

Fig. 3.4 shows the response of a typical oxygen sensor device, fabricated in a front-detection geometry, to alternating flow of 7 psi Ar and O\textsubscript{2}. As clearly seen, the PL intensity in pure O\textsubscript{2} was only 27\% of that in pure Ar (equivalently, the PL increased by a factor of 3.7 when the O\textsubscript{2} was replaced by Ar). The response time is 1 - 4 sec for a change in the PL intensity by a factor of 2.5 - 4.

![Graph showing response time of an integrated, OLED-excited oxygen sensor, fabricated with a front-detection geometry.](image-url)
Fig. 3.5. Shows the response of a device fabricated in back-detection geometry. The response is weaker than that of the front-detection device used to obtain Fig. 3.4: The PD response of the back-detection device increased by only a factor of ~2.5 when the gas was switched from O₂ to Ar, as compared to a factor of ~3.7 obtained with the front detection device shown in Fig.4. However, neither device was optimized with respect to the thickness of the sensor film, the OLED intensity, or any other structural or dynamical parameters. Such an optimization procedure is clearly necessary before any conclusion on the relative performance of front- and back-detection devices can be reached.

Fig. 3.6 shows Stern-Volmer plots of $I_0/I$ and $\tau_0/\tau$ as a function of oxygen level, measured using a typical sensor device with front-detection geometry. As clearly seen, in this device the PL intensity decreased by a factor of ~2.5 and the lifetime by a factor of ~2.3 when the oxygen level increased from 0 to 100%. Note that behavior of $I_0/I$ and $\tau_0/\tau$ agrees well with the Stern-Volmer Equation.

The results shown in Fig. 3.6 indicate that the effect of oxygen on $\tau$ can be used to measure the oxygen concentration with a structurally integrated OLED-excited sensor. As mentioned above, this approach is advantageous, as the need for re-calibration due to issues associated with OLED and/or dye stability (as long as both are still functional) is eliminated.

Dye photostability is critical for its application in chemical sensors. It has been shown that photoexcitation of Ru(dpp)₃ results in dissociative decomposition of that material. This dissociation is enhanced in the presence of singlet oxygen, which is a product of Ru(dpp)₃ PL quenching by oxygen. The reactive singlet oxygen may photooxidize the dye by reacting with ground state molecules. This is particularly problematic when high photon doses, such
as in long-term monitoring or fiber optic sensors are utilized, and when the dye is embedded
in a polymer matrix [17].

![Graph](image1.png)

**Fig. 3.5.** Response time of an integrated, OLED-excited oxygen sensor, fabricated with a
back-detection geometry. The applied bias was 9 V; the PMT voltage was 750 V.

![Graph](image2.png)

**Fig. 3.6.** $I_0/I$ and $\tau_0/\tau$ as a function of oxygen concentration. The sensor device was fabricated
in a front-detection mode; the OLED was operated in a pulsed mode. The pulse length was
100 µs and the repetition rate 20 Hz. The total Ar and O2 flow rate was 500 sccm.
The advantage of using OLED excitation, in particular in pulsed operation, in comparison to laser excitation, is demonstrated in Fig. 3.7, which compares Ru(dpp)$_3$ stability under 3 mW laser excitation at 488 nm and under pulsed DPVBi OLED excitation. As seen, the intensity of the Ru(dpp)$_3$ PL decreased by a factor of 5 following ~6 h of the laser excitation, but only by ~5% under the pulsed OLED excitation over the same period. The DPVBi OLED was biased to yield an average brightness of 40 Cd/m$^2$; the pulse width was 100 µsec, and the repetition rate was 1 kHz (i.e., a duty cycle of 10% and OLED brightness of 400 Cd/m$^2$ during the bias pulse).

![Graph showing Ru(dpp)$_3$ stability](image)

Fig 3.7. Ru(dpp)$_3$ stability under 3 mW laser and pulsed DPVBi OLED excitation. The OLED was biased to yield an average brightness of 40 Cd/m$^2$; the pulse width was 100 µsec, and the repetition rate was 1 kHz (i.e., a duty cycle of 10% and OLED brightness of 400 Cd/m$^2$ during the bias pulse).

The difference in the photostability of the Ru(dpp)$_3$ under laser excitation vs pulsed OLED excitation is very significant for commercialization purposes. It demonstrates clearly that the
stability of the OLEDs is much greater than that of Ru(dpp)_{3}. In other words, while the stability of current blue OLEDs may be insufficient for many display purposes, it is sufficient for Ru(dpp)_{3}-based sensors, because it is much greater than that of the Ru(dpp)_{3} sensing element, and results in oxygen sensors which are as long-lived as any current commercial oxygen sensor. The use of more stable oxygen-sensitive dyes is currently being studied.

In addition to the enhanced dye stability under pulsed OLED excitation, OLEDs are also advantageous due to reduced heat generation, which may be crucial for heat-sensitive analytes. This issue was treated in detail elsewhere [5].

3.2 Immunosensors

Immunosensors involve antibodies or antibody fragments as capture elements, often immobilized on a solid support, which bind specifically to antigens. In one approach, i.e., “sandwich” format, a primary antibody, which is attached to a surface, interacts with an antigen. The bound antigen is then allowed to interact with a secondary antibody, labeled with a fluorophore. This interaction results in a surface immobilized structure in which the antigen is “sandwiched” between the primary and secondary antibodies. The labeled secondary antibody enables monitoring of the bound fluorophore PL that depends on the antigen concentration.

As a preliminary test to assess the potential utility of OLEDs as excitation sources in such structurally integrated immunosensors, we monitored the PL of a Pierce rhodamine-tagged rat IgG (host: goat) antibody to evaluate the detectable concentration range. An aqueous solution of the labeled antibody (3 μL) was placed in wells produced in a thin transparent poly(dimethylsiloxane) (PDMS) slab. The PDMS slab was attached to the opposite side of the
OLED glass substrate, i.e., it replaced the sensor film shown in Fig. 1.

Fig. 3.8 shows our preliminary results, which indicate that the current antibody level that can be detected is ~0.3-0.4 μg, which, for an antibody with a molecular weight of ~150,000, corresponds to an antibody/antigen level of ~2 pmol, although the dynamic range is limited. Studies are underway to improve the dynamic range and to evaluate structurally integrated OLED/immunosensors on solid supports.

![Plot](image.png)

Fig 3.8. The PL (in arbitrary units) of a rhodamine-labeled antirat antibody as a function of the labeled antibody concentration. The line is a guide to the eye only.

4. CONCLUSIONS

Photoluminescence-based sensors that consist of structurally integrated OLEDs and sensing components show great promise for sensing various chemical and biological analytes. We have demonstrated the utility of such sensors for detection of oxygen in the gas phase using a dye embedded in a sol-gel matrix. Both the PL intensity and lifetime modes are usable for monitoring oxygen. In using the lifetime mode, issues associated with OLED and dye
instability, which require frequent calibration, are minimized. Moreover, the dye stability is improved by using pulsed OLED excitation, while the strong coupling between the OLED and the sensing component enables the use of small-sized pixels with negligible Joule heating. We have also shown that the OLED can be integrated with a sensing component in solution. This was demonstrated for a solution of rhodamine-labeled antibody placed in μL wells generated in a PDMS slab structurally integrated with the OLED. The utility of the integrated sensors for liquid analytes, which will be described in a future publication, was demonstrated recently also for glucose samples. For both, solid state sensing films or solutions, the response time of the sensor device was ~2-3 sec.

The compact OLEDs replace bulky and costly lasers or inorganic LEDs that require optical fibers and their structural integration is more complex. Future fabrication of microarrays for multianalyte detection should be achieved by utilizing OLED pixels emitting at different bands and integrated with various sensing components. The ability to generate small-sized pixels should enable the use of such sensors in microfluidic architectures for combinatorial analysis.

ACKNOWLEDGEMENTS

Ames Laboratory is operated by Iowa State University (ISU) for the United States Department of Energy (USDOE) under Contract W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences, USDOE, the National Aeronautics and Space Administration (NASA), and the Institute for Physical Research and Technology (IPRT) of ISU.
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Chapter 4: Structurally integrated organic light emitting device based sensors for gas and solution phase oxygen

1. Introduction

There is a growing need for low-cost compact chemical and biological sensor platforms for commercial, including biomedical, applications. This need has resulted in efforts to develop structurally integrated oxygen sensors as well as platforms suitable for multianalyte detection that are efficient and easily fabricated [1-6].

A well-known approach for gas-phase and solution O2 sensing is based on the dynamic quenching of the photoluminescence (PL) of oxygen-sensitive dyes such as Ru complexes and Pt or Pd porphyrins [1-16]. Collisions with increasing levels of O2 result in a decrease in the PL intensity I and PL lifetime $\tau$. In a homogeneous matrix, the concentration of O2 can be determined ideally by monitoring changes in I under steady-state conditions or in $\tau$ using the Stern-Volmer (SV) equation:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2]$$

(1)

Where $I_0$ and $\tau_0$ are the values in the absence of oxygen and $K_{SV}$ is the SV constant.

Despite the established sensing approach, in particular for gas phase measurements, extensive studies of optical O2 sensors are still continuing in an effort to enhance sensor performance, reduce sensor cost and size, simplify fabrication, and develop an O2 sensor that is compatible with in vivo biomedical monitoring [17].

Fast and reliable measurement of dissolved oxygen (DO) in water is important for biological, medical, environmental, and industrial monitoring [18,19]. Most commercial DO sensors are based on electrochemical techniques that suffer from shortcomings related to
oxygen consumption, solution stirring, and electrode poisoning. PL-based DO sensors, which do not suffer from such shortcomings, have also been studied [16,20-22]. For example, a Ru-complex was used in a porous sol-gel silica film [11] and quenching responses of 56% and 80%, which depend on the sol-gel nature, were obtained. These quenching responses correspond to detection sensitivities $S_{DO}$, defined for DO sensing as the ratio of the PL intensity or lifetime in a de-oxygenated solution to the corresponding value in an oxygen-saturated solution, of ~2.3 to 5. A submicrometer optical fiber DO sensor, also based on a Ru dye, showed a sensitivity of 3.2 when the dye was embedded in an acrylamide polymer [9]. Pt octaethylporphyrin (PtOEP) in polymer matrices have been studied mostly for $O_2$ monitoring in the gas phase with fewer studies for DO. An SV plot for a PtOEP dye embedded in a fluorinated polymer was recently obtained for DO in water [16]. The plot was close to linear at $O_2$ concentrations < 10 mg/L (i.e., 10 ppm by mass); it deviated from linearity (downward curvature) at higher concentrations. The sensitivity at 20°C was ~1.8. Large sensitivity (overall quenching response of 97%, i.e., $S_{DO} \sim 33$) and linear response over the entire concentration range were reported recently for a PtOEP-based nanosensor [15]. The enhanced sensor performance was attributed to high porosity, hydrophobicity, and a larger surface-to-volume ratio of the sensing element.

Detection of DO in aqueous and organic media were also reported using an oxygen-sensitive dye in a sol-gel matrix and a Ru-based dye immobilized in a Nafion membrane [12]. In the latter, membrane swelling was a key factor in the quenching process. Solvents that penetrated the membrane (e.g., methanol and water) resulted in linear SV plots with large responses, whereas solvents such as toluene, which do not penetrate the Nafion, resulted in poor sensitivity and nonlinear SV plots.
Development of field-deployable, compact sensors is expected to be beneficial for the varied needs of gas phase and DO monitoring. We therefore tested the use of an organic light emitting device (OLED)-based sensor for such applications. OLED-based sensors with tris(4,7-diphenyl-1,10-phenanthroline) Ru II (Ru(dpp)) embedded in a sol-gel film and PtOEP and PdOEP embedded in PS were used for gas phase O₂ detection. A PtOEP-doped PS film was used for O₂ detection in water and ethanol. Though the PS matrix may not be the ideal host for sensing of DO [23], our results, discussed below, demonstrate the viability of the OLED-based sensor platform for high sensitivity O₂ monitoring.

The structure of the integrated sensor has been discussed in chapter 3. The rise and fall time of the electroluminescence (EL) of appropriate OLEDs operating in a pulsed mode, typically < 100 ns, is much faster than τ of the O₂-sensitive dyes used for monitoring gaseous or dissolved oxygen, which is typically 0.5 – 1000 μs. Hence the OLEDs can be used to monitor oxygen through its effect on I or τ. For monitoring I, the OLEDs are excited continuously, while for monitoring τ, they are operated in a pulsed mode. The advantage of using OLED excitation, in particular in pulsed operation, in comparison to laser excitation, was demonstrated in chapter 3. For example, over 6 hours, I of a typical Ru(dpp)-doped sol-gel film and a PtOEP-doped polystyrene (PS) film decreased by 80% and 50%, respectively, under 3 mW laser excitation at 488 and 515 nm, respectively. I of these dyes decreased only by < 5% under pulsed blue and green OLED excitation at 400 Cd/m² and 10% duty cycle of a 100 μs pulse. This situation, together with the OLED attributes described above, demonstrates the potential viability of OLEDs as excitation sources for compact, commercial sensor devices, as the stability of the OLEDs is greater than that of either dye under laser
excitation. Thus, the utility of pulsed OLED excitation is advantageous for improving long-term sensor stability and, in addition, for protecting heat-sensitive sensing elements and/or analytes due to reduced heat generation by OLED excitation [2].

In this work we describe the development of structurally integrated oxygen sensors in which the light sources are OLEDs suitable for excitation of oxygen-sensitive dyes. The advantage of the OLED-excited sensors is presented through their small and flexible size, ease of fabrication, potential low cost, and promise as efficient light sources in sensor (micro)arrays for multianalyte detection, including in real-world applications. The performance of the sensors in the gas phase and in solution is evaluated in terms of the dynamic range and the detection sensitivity at different temperatures, the effect of the temperature on \( \tau_0 \) and \( \tau(100\% \text{ O}_2) \), and the effect of the preparation procedure of the sensing elements on these metrics. In the gas phase, \( S_g = \tau_0 / \tau(100\% \text{ O}_2) \); in solution, as mentioned, \( S_{do} \) is the ratio of \( \tau \) measured in a de-oxygenated solution to that of an oxygen-saturated solution. The utility of the OLED-based platform for detection of \( \text{O}_2 \) at various levels using different sensor films in a single, small-size array is also discussed.

2. Experimental procedure

2.1 The OLEDs

OLED arrays were fabricated by thermal vacuum evaporation of organic layers on 150–200 nm-thick, Applied Films Corp. 20 \( \Omega \)/square, indium tin oxide (ITO) (the anode)-coated glass, as described in chapter 3. The organic layers consisted of a 5 nm-thick copper phthalocyanine (CuPc) hole injecting layer that is also believed to reduce the surface
roughness of the ITO [36] and a 50 nm-thick \( N,N'\)-diphenyl-\( N,N'\)-bis(1-naphthyl phenyl)-1,1”-biphenyl- 4,4”-diamine (\( \alpha \)-NPD) hole transport layer. For blue OLEDs, with peak emission at \( \sim 470 \) nm, a 40 nm emitting layer was either blue-emitting 4,4”-bis(2,2”-diphenylvinyl)-1,1”-biphenyl (DPVBi) layer, or perylene-doped 4,4”-bis(9-carbazolyl) biphenyl (Pe:CBP) [33-35,37], typically followed by a 4 - 10 nm-thick tris(8-hydroxy quinoline) Al (Alq3) electron transport layer (see Fig. 4.1 for the molecular structures). For green OLEDs, with peak emission at \( \sim 530 \) nm, the \( \sim 40 \) nm thick emitting and electron transport layer was Alq3. In all cases, an 8 – 10 Å CsF buffer layer was deposited on the organic layers [33-35,39], followed by the \( \sim 150 \) nm thick Al cathode. The total thickness of the OLEDs, excluding the glass substrate, was < 0.5 \( \mu \)m. For measurements in the “front detection” geometry, the OLEDs were initially prepared as unencapsulated 21×21 matrix arrays of \( \sim 1.5 \) mm diameter Al disc electrodes evaporated onto the organic layers [36]. For measurements in the “back-detection” geometry, the OLEDs were prepared as an encapsulated matrix array of \( \sim 2 \times 2 \) \( \text{mm}^2 \) square pixels resulting from mutually perpendicular stripes of etched ITO and evaporated Al [3,5]. Encapsulation was achieved by lining the glass substrate with epoxy, and binding a top glass cover to the substrate. Initially, a common 5 min epoxy was used. The stability and operating lifetime measurements described in Sec. III.1 were performed using such a common epoxy. However, it appears that a high-vacuum epoxy would improve the stability and operating lifetime beyond the results shown in Sec. III.1.

For \( I \) measurements, the OLEDs were operated in a dc mode with a forward bias of 9 - 20 V. For \( \tau \) measurements, they were operated in a pulsed mode with a bias of 10 - 15 V, a pulse width of 100 \( \mu \)s, and a repetition rate of 20 - 50 Hz.
Fig. 4.1. Molecular structures of (a) tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) [Ru(dpp)],
(b) Pt octaethyl porphyrin (PtOEP), and the materials used to fabricate the OLEDs: (c)
copper phthalocyanine (CuPc), (d) (N,N'-diphenyl-N,N'-bis(1-naphthyl phenyl)-1,1'-
biphenyl-4,4'- diamine (α-NPD), (e) 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi),
and (f) tris(8- hydroxy quinoline) Al (Alq3).
2.2 The sensing element

Ru(dpp) was embedded in a sol-gel film. The sol-gel was prepared from 1 mL methyltriethoxysilane (MTEOS) precursor mixed with 0.18 mL water and 1 mL ethanol [2-4]. The mixture was sonicated for 1 hour and then kept at 4°C in the dark for 24 hours; 10 - 30 mg Ru(dpp) were mixed with the sol-gel. Films were prepared by spin coating at 2000 - 4000 rpm or drop casting. The resulting films were dried in air at 70°C for 5 – 6 hours or at room temperature for 2 – 3 days.

PtOEP-based sensing elements were prepared by dissolving 0.005 - 2.5 mg/mL of the dye and 1 - 100 mg/mL polystyrene (PS; Aldrich PS, molecular weight 45,000) in toluene. Films were fabricated by spin coating the solution at 2000 - 4000 rpm or drop casting 5 - 100 μL of the solution and evenly spreading it onto cleaned glass slides. The resulting films were allowed to dry for several hours in air in the dark at ambient temperature or at 60°C. Free standing PtOEP/PS films, which were removed from the glass substrate and glued to the opposite side of an OLED glass substrate, were also tested, but they did not show an improved performance.

Solution-based sensing elements (i.e., a dye dissolved in an appropriate solvent) were contained in wells generated in glass or in PDMS slabs.

For all spin-coated films, the effect of the spin rate in the range used was very small, resulting in slightly increased change in I for a given oxygen level with decreasing spin rate, probably due to an increased film thickness. As expected, the spin-coated films were visibly more homogeneous than the drop-cast films. However, the latter exhibited larger detection sensitivities. For PtOEP-based sensors, we observed detection sensitivities of ~37 and ~50
(see below), for similarly prepared sensor films fabricated from two different batches of the commercial dye.

2.3 The detection system

The sensor PL was monitored with a Hamamatsu R6060 photomultiplier (PMT) tube operated at 900 V. All of the results presented in this work, except for Ru(dpp), were obtained using the "back-detection" geometry, where two OLED pixels were typically used for excitation. The PL lifetimes were obtained by collecting the sensor response following the application of the OLED pulse. For Ru(dpp), the lifetimes were calculated from the exponential decay from 0.5 to 13.2 µs. For PtOEP the range was 1.0 to 150 µs. The data was successfully fitted to a single exponent, when allowing for the background current of the PMT. The experimental error in I and τ was smaller than 5%. The use of the sensor films for a period of 3 months for measurements in the gas phase did not reveal significant changes in the sensing films. The use of films in water and methanol was for shorter periods, as fluid motion induced separation of the films from the substrate. During these measurements, possible dye leaching did not appear to present a problem, probably due to the sensors’ operation in the τ rather than the I detection mode.

2.4 Gas phase measurement

Gas phase measurements on the oxygen sensor films excited by integrated DPVBi, Pe:CBP, or Alq3 OLEDs were performed in a flow cell with flowing oxygen/argon mixtures. Mixing was achieved by means of mass flow controllers, where the flow rates of the oxygen and argon varied, while maintaining a constant total flow rate, thus generating varying oxygen
partial pressures. The effect of the flow rate in the range 25-500 sccm was evaluated; there was no effect to the flow rate in this range for any of the oxygen levels studied. For example, for 10% O₂, τ was constant at 37.2 μs across the whole range for one film.

Measurements at temperatures above ambient were performed using a Fisher Scientific Isotemp incubator. The incubator housed the sensing element and flow cell, the gas carrying tubing, which was extended to assure its temperature equilibration, the OLED excitation source, and the PMT, which was thermoelectrically cooled and suitable for operation up to 60°C.

2.5 DO measurement

Measuring oxygen in water in an open cell, while bubbling the gas through the solution, was dependent on the flow rate of the bubbled gas mixture. τθ, measured after flowing pure Ar for ~7 min, generally increased with increasing flow rate (e.g., from ~35 to ~77 μs when the flow rate increased from 25 to 500 sccm). This behavior may indicate the presence of Ar (micro)bubbles at the surface and internal surfaces of the sensor film, in particular at high flow rates, which would result in a longer τ that is not due to DO. This situation can also stem from the need for a high flow rate to remove the DO and minimize dissolution from air. To overcome flow rate and cell configuration related issues, experiments were performed in a closed cell with a narrow gas inlet and outlet using two approaches. To ensure an equilibrium concentration, the gas mixture was bubbled at 50 or 100 sccm for 15-30 min prior to the measurement, well beyond the 7 min of gas bubbling that appeared to be sufficient to obtain a constant τ. In one approach, gas bubbling was continued during the measurement and care
was taken to introduce the gas mixture sufficiently above the sensing films to minimize possible (micro)bubble formation at the films' surface. Using this approach, the results were independent of the gas flow rate, which varied from 15 to 500 sccm; \( \tau_0 \), obtained by flowing 100% Ar, was \( \sim 77 \) \( \mu \)s; \( \tau(100\% \text{ O}_2) \) was \( \sim 2.5 \) \( \mu \)s. The latter value, however, is suspect to be due to \( \text{O}_2 \) (micro)bubbles at the sensing element.

In the second approach, the cell was sealed following the bubbling of the gas mixtures used to obtain the desired oxygen levels in the cell gas and solution phases. The gas phase in the sealed cell was then allowed to equilibrate with the solution. This approach appears to be the most promising in determining DO, as the value of \( \tau \) measured when the solution was in equilibrium with ambient air was similar to the value measured for the solution exposed to 21% \( \text{O}_2 \) in Ar. These values were also verified using a commercial Omega model DOH247 DO sensor; 21% bubbled \( \text{O}_2 \) corresponded to \( \sim 8 \) ppm. Thus, the results shown for DO were obtained using this approach.

2.6 Reagents

\( \alpha \)-NPD, DPVBi, Alq3, PtOEP and PdOEP were obtained from H. W. Sands, Ru(dpp) from GFS Chemicals, and MTEOS and the other solvents from Aldrich. All chemicals were used as received.
3. Results and discussion

In testing the OLED-based sensor platform, we monitored τ, and evaluated SV plots for various films under different experimental conditions. Effects of film preparation procedure, gas flow rate, and measurement temperature for both, gas phase and DO, were monitored.
3.1 Gas phase sensing

[DPVBi OLED]/[Ru(dpp-doped sol-gel] Sensors

The SV plot of a [DPVBi OLED]/[Ru(dpp)-doped sol-gel] sensor is shown in Fig. 4.2 [4,5]. As clearly seen, the sensor exhibited the linear SV relation throughout the entire 0 – 100% O₂ range. The sensitivity, however, was only ~2.3. Since the PtOEP- and PdOEP-based sensors exhibited much higher sensitivities, this work focuses on these more sensitive sensors.

Effects of film preparation conditions on PtOEP- and PS sensors

In optimizing $S_g$ and the dynamic range of the sensing elements using the OLED-based sensor platform, we varied the solution concentrations of the dye and the PS, and their ratio (see Sec. II). The best results in terms of $S_g$ and the dynamic range for the porphyrin-based sensing elements were obtained for films prepared by drop casting 40-50 µL of solutions containing 0.5-1.5 mg/mL dye and 20-50 mg/mL PS in toluene, at a dye:PS ratio of 1:25 to 1:50 (See table 4.1). The effect of the PS concentration in the solution used to generate the sensing film for a PtOEP concentration of 1 mg/mL is shown in Fig. 4.3. As clearly seen, for 1 mg/mL PtOEP, PS levels of ~30 mg/mL or higher resulted in the highest $\tau_0$. The use of dye concentrations exceeding 2 mg/mL, in particular with PS levels lower than ~10 mg/mL, resulted in shorter $\tau_0$ and reduced sensitivity. This situation is believed to stem from aggregation of dye molecules in the film and consequently, self-quenching.

Fig. 4.4 shows SV plots at 23°C of two different films, using PtOEP from two different commercial batches, similarly prepared by drop casting 50 µL of solutions containing PtOEP:PS at a ratio of 1:50, and evenly spreading the drop. As seen, the use of different
commercial batches of PtOEP resulted in different sensor responses, with one batch resulting in $S_g$ values of $\sim 50$, while the other showed lower values, typically of $\sim 37$.

| PS Concentration (mg/mL) | Fig. 4.3 Effect of PS concentration in solutions used to generate the sensing films on $\tau_0$ in the gas phase. The PtOEP concentration was 1 mg/mL. The line is a guide to the eye. |
Fig 4.4. Stern-Volmer plots obtained at 23°C (○, □) for two different films prepared by drop casting 50 μL of solutions containing PtOEP:PS at a ratio of 1:50. The PtOEP originated from two different commercial batches. The SV plot for one film at 45°C (▲) is also shown. The line represents a best quadratic fit.

Variations in the thickness and homogeneity of drop cast films are also suspected to contribute to variations in Sg in similarly prepared films. As seen, the SV plots for such films are typically nonlinear. While films with dye:PS ratio of 1:50 are better in terms of Sg, a 1:10 ratio was still usable, exhibiting a slightly lower sensitivity, but a linear SV plot. Film drying conditions (i.e., in air at ~23°C or 60°C, under vacuum conditions, or in an Ar atmosphere) did not affect sensor performance appreciably, and AFM and SEM images did not reveal any significant differences between the various films.

**Detailed evaluation of SV Plots, Sg, and dynamic range at room temperature.**

The strong red PL of Ru(dpp) and PtOEP is quenched by collisions with O₂; ideally, the quenching process is described by Eq. (1). Based on this equation, it is expected that for a given homogeneous matrix with a single type of luminophore molecules equally accessible to
the quencher, the SV plots of \(I_0/I\) (under steady state conditions) or \(\tau_0/\tau\) vs \(O_2\) partial pressure will be linear with identical slopes and unity intercept.

For an \(O_2\)-sensitive dye in solution, the predicted linear SV dependence was confirmed. It was also observed for the solid matrix of the [DPVBi OLED]/[Ru(dpp) sensor film] [4,5]. But as shown in Fig 4.4 which shows SV plots of PtOEP-based sensors prepared from solutions containing a dye:PS ratio of 1:50 and excited by an Alq3 OLED, that is not always the case.

The Ru(dpp) PL was excited by the blue DPVBi-based OLED, as the OLED’s emission at ~470 nm strongly overlaps the broad PL excitation and absorption bands of Ru(dpp). The large Stokes shift between the absorption band of Ru(dpp) and the emission band at ~610 nm is advantageous for OLEDs, since a long-pass filter positioned in front of the PD blocks the emission from the OLED, resulting in a low background signal. The need for such a filter was eliminated when monitoring changes in \(T\) for sensor evaluation. We observed a linear dependence of \(T_0/T\) and \(I_0/I\) on the oxygen concentration (see Fig. 4.2) with detection sensitivities of ~2.3 – 4 [4,5]. The data points for \(I_0/I\) and \(\tau_0/\tau\) as a function of \([O_2]\) could be presented by a common straight line, even though the environments of the dopant dye molecules were not necessarily identical (i.e., some were probably at an internal surface, while others were embedded in the bulk of the sol-gel host matrix). The linear dependence is advantageous for calibration and analysis. However, the PL decay time of Ru(dpp), which is only ~8 µs in the absence of oxygen, is relatively short and therefore results in a lower detection sensitivity than that of dyes with longer PL lifetimes, such as PtOEP. Indeed, the SV plots shown in Fig. 4.4 demonstrate that an Alq3 OLED together with a sensing element
based on a PS film doped with PtOEP results in much higher sensitivities than a silica sol-gel film doped with Ru(dpp).

The emission band of Alq, which peaks at 530 nm, overlaps a small absorption band of the porphyrin dyes. The strong red shift of the PL of the dyes, which peaks at ~635 nm, is advantageous in resulting in a very low background. Moreover, $\tau_0(\text{PtOEP}) \approx 100$ μs. Clearly, these long PL lifetimes are responsible for the higher detection sensitivities. The Alq/PtOEP sensors exhibited sensitivities of typically ~37 or ~50. These sensitivities are ~10 to ~20 times larger than those of the DPVBi/Ru(dpp) sensors [4,5].

The nonlinear behavior of $1/\tau$ vs $[\text{O}_2]$ for Alq/PtOEP, where the slope increases with increasing $[\text{O}_2]$ is unusual, and currently not clear. It may be speculated that oxygen induces local changes in the PS morphology, which enhance accessibility to the PtOEP molecules. The deviation of the SV plots from linearity, which is often observed [6,11,12,16], is a potential disadvantage in using the porphyrin dyes. In some cases this deviation does not complicate calibration, as it is possible to fit the experimental data to a polynomial (see Fig. 4.4). Additionally, it is sometimes possible to obtain linear SV plots by modifying the sensing film. Such films showed close to linear SV plots with somewhat reduced sensitivities.

To monitor O₂ levels accurately over the entire 0-100% O₂ range, an array of sensors with various PtOEP films can be used simultaneously. By preparing the films under different conditions (e.g., PS:dye ratio, film thickness), different SV plots and detection sensitivities are expected. For example, one such simple array could comprise two sensing films: a 1:10 PtOEP:PS film that exhibits near linear SV plot over the whole 0 – 100% range, and a Ru(dpp) film, which is very sensitive to low levels of O₂ and exhibits a linear behavior up to
~30% O₂ (Fig. 4.2). By using the OLED-based sensing platform, it is possible to easily fabricate a small-size array of OLED pixels, where 2-4 pixels correspond to a given sensing film in the sensor array. Thus, through consecutive excitation of such small groups of OLED pixels, O₂ can be detected by different sensing films that exhibit linear calibration plots and sensitivities suitable for different regions of O₂ levels. This approach will also result in redundancy in determining the O₂ level, thus providing a more accurate and reliable result. Moreover, it will provide the basis for sensor (micro)arrays for multianalyte detection, using an array of OLEDs emitting at various wavelength. Such arrays were recently fabricated using combinatorial methods [41].

**Stability and Operating Lifetime**

In a 30 day test, the [Alq3 OLED]/[PtOEP-doped PS film] module was biased continuously for 1 month at 8 V dc; the PtOEP-doped PS film, prepared by drop casting a toluene solution containing 1 mg/mL PtOEP and 15 mg/mL PS, was exposed to air and excited continuously by the OLED. This brightness level was comparable to the average brightness of the OLED in the pulsed mode during the measurement. Once every 24 hours, the bias to the OLED was switched to a pulsed mode, and ô (corresponding to the 21% O₂ in air) was determined. In this pulsed mode, the pulse amplitude, width, and repetition rate were 20 V, 100 μs, and 50 Hz, respectively. The displayed value of ô was determined by averaging the decay curves over 1000 sweeps. As Fig. 9 clearly shows, ô slowly decreased from 20.2 ± 0.1 to 19.7 ± 0.05 μs during this 30 day test. In other words, the relative error actually decreased with time, from ~0.5% to ~0.25%. Thus, the results demonstrate clearly that the lifetime of this sensor module is well beyond the 30 day test.
Fig. 4.5. PL lifetime $\tau$ of a PtOEP-doped PS film in ambient air; the PL was excited by an Alq3 OLED. The OLED was biased continuously at 8 V for 30 days, and $\tau$ was measured once every 24 hours by switching the bias to a pulsed mode. See text for details.

In summary, the structurally integrated OLED-based sensors, using the PL lifetime detection mode, exhibited responses comparable to those obtained using other excitation sources and more elaborate experimental designs. Porphyrin-based dyes showed large sensitivities over a wide dynamic range. In addition to their long PL lifetimes, the advantage of the porphyrin-based sensors is their ~530 nm absorption band, which is suitable for excitation with the more stable and efficient green Alq3 OLED. The larger PtOEP and PdOEP sensitivities together with the OLED stability make the Alq3/PtOPE and Alq3/PdOEP sensors very attractive for future realworld applications. In particular, the long PL lifetime eases sensing using the PL lifetime mode, which unlike the intensity mode, does not require frequent sensor calibration. The compact sensor platform is promising for sensor
(micro)arrays based on various sensing elements with dedicated, individually addressable OLED pixel excitation sources.

### 3.2 Dissolved oxygen

PtOEP-doped PS films, similar to those used to monitor gas-phase oxygen, were used to monitor DO in water and ethanol.

![Fig 4.6 SV plots for DO in water and ethanol](image)

Fig. 4.6 shows SV plots of DO in water and ethanol. The sensitivities are ~4.5 and 5.8 for water and ethanol, respectively. In water, the values of $\tau$ increased from ~18.2 $\mu$s in O2-saturated solution to ~80 $\mu$s in Ar-saturated solution; in ethanol, they increased from ~17 $\mu$s to ~87 $\mu$s. The lower values of $\tau_0$ for DO relative to the value in gas phase probably reflect solvent-related PL quenching, as the PL of the polymer-embedded dye was reported to be
quenched also by hydroxyl vibrations of water [16]. The larger values of $\tau$ in the O2-saturated water and ethanol in comparison to that in the gas phase may indicate the more limited solubility of oxygen in the former. The similarity of the responses and detection sensitivities for water and ethanol, despite the larger solubility of oxygen in ethanol (~8 times higher at 25°C) [43], may indicate that the oxygen concentration in the PS host, which is in equilibrium with the DO, is comparable for both liquids. We note that the detection sensitivities of DO in water measured with the OLED-based sensors is among the highest reported to date.

4 Conclusion

Based on the performance of the oxygen sensors described in this work, the use of OLEDs as excitation sources in PL-based chemical and biological sensors is promising. The ease of OLED fabrication and OLED/sensing component structural integration result in compact devices, which are expected to be inexpensive and suitable for real-world applications. The example of oxygen sensing demonstrates the viability of the approach in using the PL lifetime detection mode, where small changes in the intensity of the excitation source, dye leaching, or stray light have a minimal effect on the sensor response. The availability of OLEDs with EL spectra covering a wide spectral range makes them attractive for use with various fluorophores. In particular, OLED arrays with different color pixels that are individually addressable have been developed. Such arrays are attractive for developing small-size sensor arrays for multianalyte detection. Current studies focus on such studies and on a structural integration of not only the OLED/sensing component, but also the photodetector.
ACKNOWLEDGEMENTS

This work was supported by NIH Grant 1 R43 EB001513-01A1, NASA Grant NAG-1-02098, NSF Grants CHE-0345189 and ECS-0428220, the Institute for Physical Research and Technology of Iowa State University (ISU), and by the Director for Energy Research, Office of Basic Energy Science, USDOE. Ames Laboratory is operated by ISU for USDOE under Contract W-7405-Eng-82.

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[26] www.universaldisplay.com - active in OLED research


Chapter 5. Glucose biosensors based on organic light-emitting devices structurally integrated with a luminescent sensing element


Bhaskar Choudhury, Ruth Shinar, Joseph Shinar

Abstract

A platform for photoluminescence (PL) based biosensing is demonstrated for glucose. The sensor is structurally integrated, i.e., individually addressable organic light-emitting device (OLED) pixels (serving as the light source) and the sensing element are fabricated on glass or plastic substrates attached back-to-back. This results in a very compact, potentially miniaturizable sensor, which should strongly impact PL-based biosensor technology. The sensing element is an oxygen-sensitive dye co-embedded with glucose oxidase in a thin film or dissolved in solution. The glucose biosensor is demonstrated for two OLED/dye pairs: [blue OLED]/[Ru dye] and [green OLED]/[Pt dye]. Both PL-intensity and PL-lifetime modes are demonstrated for each pair; the lifetime mode eliminates the need for frequent sensor calibration. The sensor performance is evaluated in terms of design, dynamic range, limit of detection, and stability. The use of the glucose biosensor in conjunction with an oxygen sensor is also discussed.
1. INTRODUCTION

The next frontier in sensor technology is the development of structurally integrated, miniaturized chemical and biological sensor (micro)arrays for high throughput multi-analyte environmental and medical applications. Structural integration of a photoluminescence (PL) based sensing element with current light sources such as lasers and lamps is not possible, and integration with inorganic light-emitting diodes involves intricate design and procedures [1]. In contrast, a sensing element can be integrated with an organic light emitting device (OLED) light source in a straightforward, flexible, and uniquely simple design [2]. Such integration was demonstrated recently for a gas-phase oxygen sensor [3]. OLEDs have dramatically improved over the past decade [4, 5], and products incorporating them have begun to emerge. They are inherently advantageous as low-voltage, miniaturizable (see http://www.emagin.com), and flexible light sources; green and blue OLEDs with external quantum efficiencies of 18% (Refs. 6 and 7) and 5.7% [8], respectively, have been reported.

Glucose sensors are of major importance in clinical monitoring, biochemical research, and the food industry [9, 10]. Recent commercial developments include the “Glucowatch” sensor, which monitors subcutaneous glucose level by impedance spectroscopy. However, the device is largely limited to monitoring patterns and trends in blood sugar, and it requires daily calibration by a standard glucose meter. Its response is also affected significantly by motion, perspiration, and temperature (see www.diabetesnet.com). Glucose sensing methods often rely on the enzymatic oxidation of glucose in the presence of glucose oxidase (GOx). The glucose concentration $c_G$ can be determined by analyzing the reaction products [11], or by measuring the PL intensity $I$ or PL lifetime $\tau$ of an oxygen-sensitive dye, coembedded with GOx in a thin film or dissolved in solution. In the presence of glucose, the PL quenching of
the dye molecules is reduced (i.e., their PL increases) due to the enzymatic glucose-
oxidation-induced reduction in the local O$_2$ level [11–15]. Issues associated with this PL-
based detection of glucose utilizing an oxygen-sensitive dye include fluctuations in the light
intensity of the excitation source, instability of the oxygen sensitive dye, variations in the
local oxygen level in the samples, and leaching of the dye and/or GOx from the films.
Several approaches have been used to address these issues. For example, to address problems
due to changes in the excitation source intensity, two fluorescent dyes, an indicator oxygen-
sensitive dye, and a reference oxygen-insensitive dye, were incorporated together with GOx
in a ratiometric nanosensor [14]. To account for possible variations in the oxygen
concentration, $c_O$, which can compromise accurate glucose monitoring, two sensors, i.e., an
oxygen sensor and a glucose biosensor, were used simultaneously [11, 15]. The excitation
sources for investigating PL-based glucose biosensors have included Ar+ lasers operated at
20–40 mW [14, 15], Hg lamps [14], or a fluorometer equipped with a 150 W Xe lamp [13], $c_GI$
was usually monitored via changes in the PL intensity $I$.

This paper demonstrates a uniquely simple, structurally integrated platform for PL-based
biosensing using a glucose biosensor as an example. $c_GI$ is determined from either $I$ or $\tau$.
Individually addressable OLED pixels, operable as the light source, are integrated with the
sensing element. The OLEDs and the sensing element are fabricated on glass or plastic
substrates, which are attached back-to-back, resulting in an extremely simple and compact
device, which has the potential to advance the field of glucose sensing in various applications
as well as PL-based biosensing technology for other analytes.
2. EXPERIMENTAL PROCEDURE

2.1 OLED fabrication

Blue OLED arrays were fabricated by vacuum evaporation of organic layers on 150–200 nm thick indium tin oxide (ITO) (the anode) coated glass as described previously [3, 16–18]. The organic layers consisted of a 3.5 nm thick copper phthalocyanine (CuPc) hole injecting layer, a 40 nm thick N₁,N₁'-diphenyl-N,N₁'-bis(1-naphthyl phenyl)-1, 1'-biphenyl-4, 4'-diamine (α-NPD) hole transport layer, a 40 nm blue-emitting 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi) layer [3, 5, 16–18], and a 4 nm thick tris (8-hydroxy quinoline) Al (Alq₃) electron transport layer (see Fig. 1 for the molecular structures). A 0.8 nm CsF buffer layer was deposited on the organic layers [5, 16–20], followed by the, 150 nm Al cathode. The OLEDs were prepared as an encapsulated matrix array of ~4 mm² square pixels resulting from mutually perpendicular stripes of etched ITO and evaporated Al for “back-detection” (see below). Green Alq₃ OLEDs (Refs. 4, 5, and 20) were prepared by an identical procedure, in which the DPVBi was replaced by Alq₃. The total thickness of the OLED, excluding the glass or plastic substrate, was ~0.5 mm. For I measurements, the OLEDs were operated in a pulsed mode with a forward bias of 8–15 V. For τ measurements, they were operated in a pulsed mode with a bias of 10–15 V, a pulse width of 1–100 μs, and a repetition rate of 20–25 Hz. We note that the pulse width, amplitude, or repetition rate had no effect on the measured τ.
Fig. 5.1. The structures of copper phthalocyanine (CuPc), \( N,N' \)-diphenyl- \( N,N' \)-bis(1-naphthyl phenyl)-1 \( ,1' \)-biphenyl-4 \( ,4' \)-diamine (\( \alpha \)-NPD), 4,4\' -bis(2,2\' -diphenylvinyl)-1 \( ,1' \)-biphenyl (DPVBi), tris(8-hydroxy quinoline) Al (Alq3), tris(4,7-diphenyl-1,10-phenanthroline) Ru chloride [Ru(dpp)], and Pt octaethylporphyrin (PtOEP).

### 2.2. Sensing elements

The glucose sensing elements were based on the following.
(i) Coembedding GOx [EC 1.1.3.4, 162 units/mg type VII from *Aspergillus niger* (Sigma)] and the blue-absorbing-red-emitting dye tris(4,7-diphenyl-1,10-phenanthroline) Ru chloride (Ru(dpp)) in a sol-gel matrix (see Fig. 5.1). (ii) Depositing first a thin layer of the green-absorbing-red-emitting Pt octaethylporphyrin (PtOEP) (see Fig. 5.1) embedded in polystyrene, and then covering it with a thin layer of GOx in sol-gel. Ru(dpp) and GOx in aqueous solution also served as a sensing element. The sol-gel was prepared from 1 ml methyltriethoxysilane (MTEOS) precursor mixed with 0.18 ml water and 1 ml ethanol [3, 21]. The mixture was sonicated for 1 h and then kept at 4 °C in the dark for 24 h. 10–30 mg Ru(dpp) was mixed with the sol-gel, while 5–50 mg GOx was dissolved in 1 ml water. A film was prepared by blending 0.5 ml of the Ru(dpp)-containing sol-gel with 0.5 ml of the GOx solution. The GOx and dye-doped sol-gel was either spin coated at 2000–4000 rpm or dropcast and spread evenly onto cleaned glass slides. The films were allowed to dry at 4 °C in the dark. We note that the effect of the spin coating rate in this range was very small, resulting in slightly increased *I* for a given *c*_{GOx} with decreasing spin rate, probably due to an increased film thickness. As expected, the spin-coated films were visibly more homogeneous than the drop-cast films. Oxygen sensing elements were prepared similarly but without the GOx. The resulting films were aged at 70 °C for 5–6 h or air dried for 2–3 days for Ru(dpp) (Refs. 3 and 21) or a few hours for PtOEP. PtOEP-based sensing elements were prepared by dissolving PtOEP in toluene (3.5 mg/ml) together with polystyrene (10 mg/ml). Thirty microliters of the mixture were evenly drop-cast on a glass slide and allowed to dry for 1 h. Next, 100 ml of a solution containing 7.5 mg/ml Gox were drop-cast on top of the PtOEP film and allowed to dry in the dark for three days. Solution-based sensing elements were
contained in wells generated in poly(dimethyl siloxane) (PDMS) slabs. The solution contained 7.5 mg/ml each of the dye and Gox.

Fig. 5.2. (Color) (a) Schematic of the “back-detection” mode of operation; the drawing is not to scale. (b) Demonstration of the sensor back-detection design and operation. The green Alq3 OLED array is behind the PtOEP-based sensor film, which is largely confined to a region in front of the middle two OLED pixels. The green emission from these pixels combines with the red PL of the PtOEP dye to produce the observed yellowish spots. The PD is located behind the OLED array.

2.3 Detection system

The sensor PL was monitored with a Hamamatsu 3456 photomultiplier (PMT) tube operated at 1000 V. The sensor was operated in a “back-detection” geometry (see
below), which is shown schematically in Fig. 5.2(a); typically, two pixels were used for excitation [see Fig. 5.2(b)]. The PL lifetimes were obtained by monitoring the sensor response following the application of the OLED pulse; the electroluminescence (EL) decay times for the DPVBi and Alq3 OLEDs used in this study were dominated by the $RC$ time constants of the OLED circuits, which were $\sim 30$ ns [22]. The PL lifetimes of Ru(dpp) were calculated from the exponential decay from 0.5 to 13.2 ms. Similar values of the PL lifetimes were obtained when the lifetimes were calculated for other time ranges, starting at longer times. For the PL lifetimes of PtOEP, the range was 0.7–40 ms for 0 glucose to 0.7–150 ms for 5 mg/ml glucose. The experimental error in $I$ and $\tau$ was $\pm 5\%$.

2.4. Reagents

$\alpha$-NPD, DPVBi, Alq3, and PtOEP were obtained from H.W Sands, Ru(dpp) from GFS Chemicals, GOx from Sigma, and MTEOS from Aldrich. The glucose (Sigma) solutions were prepared in a pH 7.00 phosphate buffer. All chemicals were used as received.

3. RESULTS AND DISCUSSION

The results described in this paper build on the successful integration strategy for a Ru(dpp)-based oxygen sensor [2, 3, 21], where the sensing element consists of Ru(dpp) immobilized in a sol-gel matrix, which is spin coated on a glass slide. A blue DPVBi OLED [16–19], is fabricated on a separate glass substrate and the sensing element and OLED are attached back-to-back. In this previously described oxygen sensor, the sensor geometry was
“front detection” geometry, i.e., a single OLED pixel was used and the photodetector (PD) was positioned in front of the analyte, which was positioned in front of the OLED/sensing element. The OLED was operated in a pulsed mode and $I$ and $\tau$ were monitored in Ar and oxygen atmospheres of various ratios [21]. Importantly, such operation results in negligible, otherwise often damaging, sensor or analyte heating [3,21]. In this work, the biosensor geometry is “back-detection” geometry, i.e., the sensing element is in front of the OLED array while the PD is behind it [see Fig. 5.2(a)]. This geometry is extremely compact and can lead to a complete structural integration of the OLEDs, the sensing element, and the PD. The thickness of the OLEDs is ~0.5 mm and that of the spin-coated sensing elements is also ~0.5 mm; the thickness of the drop-cast films is a few microns. Thus, the device thickness is determined by the thickness of the glass or plastic substrates. Typically, at least two OLED pixels are lit simultaneously [see Fig. 5.2(b)]; the PD monitors the PL passing through the gaps between the OLED pixels. For demonstration purposes, Fig. 5.2(b) shows the device with six ~ 4mm$^2$ green Alq3 OLED pixels lit simultaneously. As seen in the figure, the EL of the OLED pixels is very bright. Consequently, they appear white in the image; however, the green emission is evident in the green shades of the background. The analyte sample is placed in a region above the two middle pixels; the combined green emission of the OLED pixels and the red PL from the dye result in the yellow appearance of the middle pixels. The use of individually addressable array pixels, any number of which can be lit simultaneously, is unique for OLEDs in its simplicity. Moreover, OLEDs (and sensing elements) can be fabricated on transparent plastic substrates, providing additional device flexibility. The glucose sensing element includes a luminescent dye, whose PL intensity and PL lifetime are quenched by collisions with O$_2$ molecules, and GOx, which catalyzes the reaction between
Fig. 5.3. Normalized PL intensity $I$ of a DPVBi/Ru(dpp) sensor as a function of glucose concentration $c_{GL}$: (a) Sol-gel-based sensing elements. The films were fabricated by spin coating at 2000 rpm with a sol containing 7.5 mg/ml Ru(dpp) and 2.5 mg/ml GOx ($\circ$) or 7.5 mg/ml GOx ($\Delta$). (b) 20 µl solution-based sensing element in PDMS wells, containing 7.5 mg/ml each of Ru(dpp) and GOx ($\square$), and a drop-cast sol-gel film ($\bigcirc$) prepared from 30 µl solution containing 7.5 mg/ml Ru(dpp) and 7.5 mg/ml Gox. Excitation was obtained using a blue DPVBi OLED. In the solution based sensing element, $c_{GL}$ is the concentration in the 40 µl sample; combined with the 20 µl sensing element, the total solvent amount is 60 µl.
O2 and glucose. The dye and GOx are coembedded in a transparent (e.g., a sol-gel) film, or dissolved in solution. Glucose is monitored by analyzing its effect on I or t, which is due to its effect on the O2 level at the location of the dye. The oxygen-sensitive dyes are Ru(dpp) and PtOEP [11, 13, 14, 23-26]. The excitation source is an array of blue DPVBi or green Alq3 OLED4 [5, 16-20], pixels, respectively. The behavior of I and τ vs glucose concentration is shown for various sensing elements. For comparison, results for a solution-based sensing element are also shown (see Fig. 5.3). Most reports on PL-based glucose biosensors are based on monitoring the effect of c_gl on I [1, 11, 14, 15, 23]. Though not often used, PL-lifetime measurements are expected to provide similar information [27] with the advantage of being independent of changes in the intensity of the light source or moderate dye degradation (e.g., leaching or photodegradation [28]). This advantage eliminates the need for frequent sensor calibration, which remains an issue in real world applications. In the case of Ru(dpp), the reported PL lifetimes of the molecules in oxygen sensors range from 0.3 to 8 ms, depending on the matrix and cO2 [15, 29-32]. The far longer phosphorescence lifetime of PtOEP, ~100 μs in the absence of oxygen [33], renders this dye ideal for monitoring glucose using the lifetime mode, especially in conjunction with the stable green Alq3 OLED. The fast decay of the EL pulse, which has a decay constant of ~30 ns [22], enables monitoring the significantly longer PL lifetimes of the dyes used. The glucose sensor performance, including the dynamic range and limit of detection (LOD), is affected by the nature and configuration of the sensing element, the amounts of the indicator dye and GOx, and the oxygen level in the analyte sample [12-15]. A dynamic range 0.1 ≤ cGl ≤ 15 mM (mg/dl) was reported for a PL-based sensor in which GOx was sandwiched between two sol-gel layers, one of which contained Ru(dpp) [13]. It was possible to extend the dynamic range to 20 mM (360 mg/dl).
by increasing the oxygen partial pressure or decreasing the level of the immobilized Gox, though the latter situation resulted in decreased sensitivity! The data detailed below include results for sensing films that show additional extension of the dynamic range for PL-based sensors.

3.1. Blue DPVBi OLED/Ru(dpp)-based sensor

As mentioned above, glucose biosensors with the dye and GOx embedded in a sol-gel film exhibit responses ($I$ and $\tau$) that depend on the levels of GOx and local O$_2$ level, which were related to the preparation method of the sensing element. Figure 5.3(a) shows $I$ vs $c_{Gi}$ of typical glucose biosensors with sol-gel films differing in the levels of embedded GOx. The films were prepared by spin coating at 2000 rpm. The Ru(dpp) concentration in the solution used for preparation of the films was 7.5 mg/ml; that of GOx was 2.5 mg/ml in one and 7.5 mg/ml in the other. As seen in Fig. 5.3(a), by increasing $c_{Gi}$ from 0 to 5 mg/ml, $I$ increased linearly by a factor of $\sim$1.8 and $\sim$2.7, respectively. However, further increase in the level of the GOx to 25 mg/ml, while maintaining the Ru(dpp) level, deteriorated the sensor performance, significantly decreasing the dynamic range. Figure 5.3(b) shows similar plots for a drop-cast sol-gel film prepared from 30 µl containing 7.5 mg/ml Ru(dpp) and 7.5 mg/ml GOx, and a 20 µl solution-based sensing element containing 7.5 mg/ml Ru(dpp) and 7.5 mg/ml GOx, to which a 40 µl buffered solution of glucose was added. The drop-cast film was significantly thicker than the spin-coated films with larger amounts of embedded Ru(dpp) and Gox. As seen, the dynamic range for the drop-cast film is limited to $c_{Gi} \sim$2 mg/ml, with $I$ (and $\tau$, see below) values saturating at higher $c_{Gi}$. The response is highest for the spin-coated
sol-gel film prepared from 7.5 mg/ml GOx and the solution based sensing element; their LOD is estimated to be ~0.2 mg/ml. Figure 4 shows the effect of $c_{Gi}$ on $\tau$ for different sensing elements. In the films prepared from solutions containing 2.5 mg/ml or 7.5 mg/ml GOx, increasing $c_{Gi}$ from 0 to 5 mg/ml resulted in a linear increase in $\tau$ from 1.8 $\mu$s to 3 and 4.4 $\mu$s, respectively. The increased $\tau$ (and $I$ for a given $c_{Gi}$ in the presence of a larger amount of GOx is consistent with a stronger reduction in the local oxygen level. A similar increase in $I$ was previously observed for a fiber-optic glucose sensor.\textsuperscript{11} However, increasing the GOx level

![Graph showing the PL lifetime of DPVBi/Ru(dpp) sensors with different sensing elements.](image)

**Fig. 5.4.** PL lifetime of DPVBi/Ru(dpp) sensors with different sensing elements. (O) spin-coated sol-gel prepared from a sol containing 2.5 mg/ml GOx, (n) spin-coated sol-gel prepared from a sol containing 7.5 mg/ml GOx, (h) solution-based sensing element, and (L) drop-cast film prepared from 30 ml containing 7.5 mg/ml Rusdppd and 7.5 mg/ml GOx. Excitation was obtained using a blue DPVBi OLED.
further, to 25 mg/ml in the solution used for film preparation, resulted in an increased $\tau \sim 6 \mu s$ in the absence of glucose, and a limited dynamic range. This situation is suspected to result from a reduced local oxygen level, possibly due to reduced film porosity, a consequence of incorporation of higher Gox levels. Figure 4 also shows that the PL lifetimes for a given $c_{\text{Gox}}$ for the solution-based sensing element are longer, ranging from 2.4 to 3.7 $\mu s$ for a $c_{\text{Gox}}$ range of 0 to 2 mg/ml, in comparison to those of the spin-coated films, where they vary from 1.8 to 2.25 $\mu s$ in the same concentration range. The $\tau$'s for the drop-cast film are the longest, ranging from 4 $\mu s$ for a buffer solution without glucose to 5.5 $\mu s$ for a solution containing 2 mg/ml glucose. We speculate that the shorter lifetimes in the spin-coated films are due to small air bubbles trapped within the porous matrix, resulting in a higher local level of oxygen in comparison to the oxygen dissolved in solution or trapped in the drop-cast film. The scanning electron microscopy (SEM) images shown in Fig. 5.5 are consistent with this assumption. They show that the drop-cast film is less porous in comparison to the spin-coated film. The denser drop cast film is believed to have a lower level of trapped oxygen. Additionally, its denser texture inhibits glucose from penetrating the film. This situation, together with the larger amount of GOx that can further result in depletion in the oxygen level, is believed to contribute to the measured longer lifetimes and the reduced dynamic range. In summary, the dynamic range of up to ~1.5–2.0 mg/ml glucose obtained using the OLED-based glucose sensor with the drop-cast film is comparable to or larger than those reported using other excitation sources and device configurations [11, 13–15]. It was possible, however, to extend the dynamic range of the PL-based sensor to 5 mg/ml glucose, which is comparable to the dynamic range in commercial electrochemical-based sensors.
Fig. 5.5. SEM images of sol-gel sensing elements with a 5003 magnification: (a) drop-cast film and (b) spin-coated film.
The extension of the dynamic range was achieved, without reducing the response magnitude of the OLED-based sensors, by spin coating the sensing films. An additional increase in the detection sensitivity, without limiting the dynamic range, was obtained by using a second OLED/dye pair, as detailed below.

3.2. Green Alq3 OLED/PtOEP-based sensor

Figure 5.6 shows the effect of \(c_{Gi}\) on the PL intensity (a) and lifetime (b) of a typical Alq3/PtOEP sensor. The best results were obtained from a mixture containing 3.5 mg/ml PtOEP and 10 mg/ml polystyrene in toluene. As described in the Experimental Procedure, the solution was drop-cast on a glass substrate and allowed to dry for 1 h. Next, a sol-gel containing 7.5 mg/ml Gox was drop-cast over the polystyrene film and allowed to dry in the dark at 4°C for 3–4 days. As seen in the figure, the PL lifetime increased linearly from 28 to 100 μs when \(c_{Gi}\) increased from 0 to 5 mg/ml; the normalized intensity increased by a factor of 3.5. The sensitivity of the Alq3/PtOEP-based sensor is higher (LOD ~0.1 mg/ml) than that of the DPVBi/Ru(dupp)-based sensors over a similar dynamic range. The large dynamic range and long PL lifetimes, together with the stability of the Alq3 OLED, which is superior to that of the oxygen-sensitive dyes, render this type of sensor very attractive. The detection sensitivity of PL-based sensors excited by OLEDs may be further increased by increasing the porosity of the sensing element and using brighter OLEDs. Recently developed phosphorescent OLEDs with a higher external quantum efficiency of ~18% are attractive for sensor applications, however, when using the lifetime mode of operation, usable dyes are only those with significantly longer PL lifetimes in comparison to the OLED EL decay time.
The response of the aforementioned glucose sensors depends on the level of the oxygen in the analyte sample in contact with the sensing element. To determine this level, a second sensor, similarly prepared without GOx and in close proximity to the glucose sensor, can be used simultaneously with the glucose detection. We note that the Alq3 /PtOEP oxygen sensor, like other PtOEP-based sensors [24], is suitable for detection of trace O2 levels.

An additional reference dye that is insensitive to oxygen can also be used to compensate for variations in light intensity when glucose or oxygen are monitored by measuring changes in \( I \). However, the need for the reference dye is eliminated when operating the sensor in the lifetime mode. We note that due to the individually addressable pixel design of the OLED, the two sensors, i.e., for oxygen and glucose, can be fabricated next to each other on the same substrate, enabling simultaneous monitoring of different analytes in the same sample. Finally, we emphasize that the long-term stability of the integrated [DPVBi OLED]/Ru(dpp) and [Alq3 OLED] / PtOEP glucose biosensors is determined not by the stability of the OLEDs, but rather by that of the dyes, as the dyes degrade more rapidly than the OLEDs. We have recently shown that this is the case for [DPVBi OLED]/Ru(dpp) oxygen sensors under normal operating conditions [21], and Alq3 OLEDs are much more stable than DPVBi-based devices. Indeed, we have shown that even Alq3 OLEDs encapsulated crudely by epoxy bonding of a glass cover operate continuously for over 2 months under conditions suitable for excitation of the PtOEP-based biosensor.
Fig. 5.6. Effect of glucose concentration on the PL normalized intensity (a) and lifetime (b) for an Alq3/PtOEP-based sensor.
4. SUMMARY AND CONCLUDING REMARKS

An OLED-based structurally integrated platform for biosensors has been demonstrated by fabricating and studying DPVBi/Ru(dpp)- and Alq3/PtOEP-based glucose sensors. The integrated, compact size of the sensors, the individually addressable OLED pixels, and their extremely simple and flexible design, enable fabrication of sensor arrays for multitasking, multianalyte detection. Detection is possible through monitoring both the PL intensity and lifetime. A more compact sensor is obtained with “back-detection” geometry. With further size reduction and optimization, such device structures will be potentially suitable for *in vivo* and high throughput analysis.

ACKNOWLEDGMENTS

This work was supported by the National Aeronautics and Space Administration sNASAd. Ames Laboratory is operated by Iowa State University sISUd for the United States Department of Energy sUSDOEd under Contract No.W-7405-Eng-82.

REFERENCES


Chapter 6. Detection of Bacillus Anthracis (Anthrax) Lethal Factor (LF) using Organic Light Emitting Devices

1. Introduction

Current sensors and detectors for anthrax, a disease caused by Bacillus anthracis, a bacterial pathogen acutely relevant for bioterrorism issues, are bulky to the point of being immobile, require skilled operators, and yield a result only following an elaborate procedure. Clearly, a compact, autonomous, and inexpensive sensor, which would detect anthrax real time, is sorely needed. The objective of this work is to conduct the first steps towards the development of such a compact, autonomous, fast, battery-operated luminescence-based sensor. Beyond the applications for combating bioterrorism, the sensor will be attractive for widespread medical, environmental, biological, food, and health/safety applications.

The sensor is based on the novel structural integration of the sensing component (e.g., a porous film with an embedded dye, surface immobilized species whose luminescence changes upon interaction with agent, or microfluidic channels with recognition elements in solution) and its excitation source, which is an OLED. The OLED-based integration has some important advantages. One of the important advantages of this platform is in its pulsed operation (see chapter 3, 4, 5) mode, which generates negligible heat and is thus particularly suitable for heat sensitive recognition elements and agents. It also enhances the stability of both the OLED and the sensing element.
2. Structure of Bacillus anthracis

Bacillus anthracis is a bacterium of the genus Bacillus, which causes the disease known as anthrax. B. anthracis was the first bacterium ever shown to cause disease, by Robert Koch in 1877. The specific name anthracis comes from the Greek word anthrax, meaning coal and referring to the most common form of the disease, cutaneous anthrax, in which large black skin lesions are formed.

Like other Bacillus species, B. anthracis is rod-shaped with a Gram positive stain. Each cell is about 1 by 6 micrometres in size. The bacteria produce endospores which rest in the soil, and can survive for decades in this state. When ingested by a herbivore, they start multiplying inside the animal and eventually kill it, then continue to reproduce in its carcass. Once the nutrients are exhausted, new endospores are produced. (see Fig. 6.1)

B. anthracis comes in 89 known strains, ranging from virulent Ames and Vollum strains with biological warfare and bioterrorism applications to benign Sterne strain used for inoculations. The strains differ in presence and activity of various genes, determining their virulence and production of antigens and toxins.

The anthrax toxin consists of three proteins, a receptorbinding component designated protective antigen, and two enzymatic components termed edema factor and lethal factor (LF) [2]. Edema factor is a calmodulin-dependent adenylate cyclase, whereas LF is a zinc-dependent metalloprotease that has been shown to cleave near the N termini of several MAP
kinase kinases (M KKs). Although the complete mechanism of pathogenesis is unclear, the
disruption of key signaling pathways mediated by M KKs seems to lead first to the lysis of
macrophages and later to the death of the host. The pivotal role of LF in the virulence of the
toxin suggests that inhibitors of the enzyme may provide protection against cytotoxicity.

The three separate proteins that make up anthrax toxin PA, EF and LF act in binary
combinations to produce two distinct reactions in experimental animals: edema (PA+EF) and
death (PA+LF).

PA and LF acting together to produce death in animals are often referred to as lethal toxin.
It has been shown that lethal toxin suppresses proinflammatory cytokine production in
macrophages by inhibiting transcription of cytokine messenger RNA, even at extremely low
levels of lethal toxin. Thus, one way lethal toxin causes the disease anthrax is by suppressing
the inflammatory response.
Another action of lethal toxin is to lyse macrophages, which are one of the body's important defense mechanisms against invading organisms. Lethal factor is a zinc-binding protein with metalloproteinase activity. The MAP kinase kinases Mek1 and Mek2 are macrophage proteins that interact with it. Lethal factor cleaves Mek1 and Mek2 and an additional related factor MKK3.

3. Principle of sensor operation

The anthrax LF sensor is based on a fluorescence resonance energy transfer (FRET) assay [31]. LF is known to cleave certain peptides at specific sites. A suitable donor-acceptor pair can be attached to the peptide, with the donor on one side of the cleaving site and the acceptor on the other site. In the absence of LF, the PL of the donor is quenched by the acceptor. Upon exposure to LF, the peptide is cleaved, and when the cleaved parts are separated, the PL of the donor can be detected by the photo detector.

The basic principle of FRET is discussed briefly below.

3.1 Fluorescence Resonance Energy Transfer (FRET) [41]

Fluorescence resonance energy transfer (FRET) is a distance-dependent interaction between the electronic excited states of two dye molecules in which excitation is transferred from a donor molecule to an acceptor molecule without emission of a photon. The efficiency of FRET is dependent on the inverse sixth power of the intermolecular separation, making it useful over distances comparable with the dimensions of biological macromolecules. Thus,
FRET is an important technique for investigating a variety of biological phenomena that produce changes in molecular proximity. When FRET is used as a contrast mechanism, colocalization of proteins and other molecules can be imaged with spatial resolution beyond the limits of conventional optical microscopy.

**Primary Conditions for FRET**

- Donor and acceptor molecules must be in close proximity (typically 10–100 Å).
- The absorption spectrum of the acceptor must overlap the fluorescence emission spectrum of the donor (see Fig. 6.2).
- Donor and acceptor transition dipole orientations must be approximately parallel.

![Fig. 6.2. Schematic representation of the FRET spectral overlap integral](image-url)


**Fürster Radius**

The distance at which energy transfer is 50% efficient (i.e., 50% of excited donors are deactivated by FRET) is defined by the Fürster radius ($R_0$). The magnitude of $R_0$ is dependent on the spectral properties of the donor and acceptor dyes:

$$R_0 = [8.8 \times 10^{23} \cdot k^3 \cdot n^4 QY_D \cdot J(\lambda)]^{1/6} \text{ Å}$$

where $k^3$ = dipole orientation factor

$QY_D$ = fluorescence quantum yield of the donor in the absence of the acceptor

$n$ = refractive index

$J(\lambda)$ = spectral overlap integral (see Fig. 2)

$$= \int \varepsilon_A(\lambda) \cdot F_D(\lambda) \cdot \lambda^4 d\lambda cm^3 M^{-1}$$

where $\varepsilon_A$ = extinction coefficient

$F_D$ = fluorescence emission intensity of donor as a fraction of the total integrated intensity

**Donor/Acceptor Pairs**

In most applications, the donor and acceptor dyes are different, in which case FRET can be detected by the appearance of sensitized fluorescence of the acceptor or by quenching of donor fluorescence. When the donor and acceptor are the same, FRET can be detected by the resulting fluorescence depolarization. Typical values of $R_0$ for some dye pairs are listed in
the table 6.1. Note that because the component factors of $R_0$ are dependent on the environment, the actual value observed in a specific experimental situation is somewhat variable. Nonfluorescent acceptors such as dabcyl and our QSY dyes have the particular advantage of eliminating the potential problem of background fluorescence resulting from direct (i.e., nonsensitized) acceptor excitation. FRET efficiencies from several donor dyes to the QSY 7 quencher in molecular beacon hybridization probes have been calculated. Probes incorporating fluorescent donor–nonfluorescent acceptor combinations have been developed primarily for detecting proteolysis and nucleic acid hybridization.

Table 6.1. Typical Values of $R_0$

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>$R_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>Tetramethylrhodamine</td>
<td>55</td>
</tr>
<tr>
<td>IAEDANS</td>
<td>Fluorescein</td>
<td>46</td>
</tr>
<tr>
<td>EDANS</td>
<td>Dabcyl</td>
<td>33</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>Fluorescein</td>
<td>44</td>
</tr>
<tr>
<td>BODIPY FL</td>
<td>BODIPY FL</td>
<td>57</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>QSY 7 and QSY 9 dyes</td>
<td>61</td>
</tr>
</tbody>
</table>

Selected Applications of FRET

- Structure and conformation of proteins
- Spatial distribution and assembly of protein complexes
- Receptor/ligand interactions
- Immunoassays
- Probing interactions of single molecules
3.2 OLED based sensing principle

The working principle of OLED has been described in chapter 1 and 2. The FRET donor and acceptor pair used in this study are either Carboxytetramethylrhodamine as the donor and QSY-7 as the acceptor when a green Alq3 based OLED is used. The spectrum of the donor/acceptor pair is shown in Fig. 6.3.

Alternatively a Ruthenium based donor and QSY-21 have been used as donor and acceptor respectively when a blue DPVBi based OLED is used as the exciter light source. It is clear from the Fig. 6.3, that TAMRA and QSY-7 will work as an effective FRET as the overlap
between emission spectra of TAMRA and absorption spectra of QSY-7 is more than 40%. The detection scheme is shown pictorially in Fig. 6.4.

The method for fabrication of anthrax sensor is based on a very recent paper by Cummings et al [43] and an invention by Burroughs-Tencza [44]. Both describe a FRET assay for monitoring Bacillus anthracis lethal factor (LF). FRET can occur between a fluorescent donor fluorophore and an absorbing acceptor (which may also fluoresce, but at longer wavelengths), is the emission spectra of the donor overlaps the absorption spectrum of the acceptor, and if they are in close proximity. Thus, in the presence of FRET, the donor fluorescence will be quenched by the acceptor. The sensing method exploits the fact that LF, which is a zinc metalloprotease [45], cleaves substrates such as MEK1 and MEK2 (members of the group of mitogen-activated protein (MAP)-kinase-kinases (MKK) [46,47]). Thus, if
the donor and acceptor are attached to a synthetic peptide at amino acid residues that are on opposite sides of the cleavage site, fluorescence quenching due to FRET disappears when the LF cleaves the peptide and separates the donor and acceptor, and the increase in the fluorescence will be detected by the photodetector.

In a similar but distinct method, both the donor and the acceptor fluoresce, but with distinct emission spectra. The presence of LF then changes the ratio of the fluorescence of the donor and acceptor molecules. The fluorescence of the donor and/or the acceptor described by Burroughs-Tencza [44] consists of bands at 520nm and 570nm obtained by exciting at 493 nm. Hence, these bands would be easily excited by either violet or blue OLEDs [11,12,17,18,49].

The recognition site for LF each require the presence of a proline residue followed by a hydrophobic residue or a glycine residue, between which LF cleaves. The recognition sites further require an uncharged amino acid following the hydrophobic residue, and at least one
further require an uncharged amino acid following the hydrophobic residue, and at least one positively charged amino acid (and no negatively charged amino acid) within the 5 amino acids to the N-terminal side of the proline residue. Other residues in the sequence provide appropriate spacing between the critical residues or between the donor and acceptor, and thus their composition is not critical, and can include any natural or synthetic amino acid.

4. Materials

The labeled peptide was synthesized in Protein Facility of Iowa State University using an Advanced Chemtech Model 396 Multiple Peptide Synthesizer and an Applied Biosystems Model 432A Synthesizer. Following the methods described by Cummings [43], the peptide synthesized was:


where

Nle - - norleucine CH3-(CH2)3-CH(NH2)-COOH

(methionine, CH3-S-(CH2)2-CH(NH2)-COOH, isostere)

K - - lysine NH2-(CH2)4-CH(NH2)-COOH

V - - valine (CH3)2-CH-CH(NH2)-COOH

L - - leucine (CH3)2-CH2-CH(NH2)-COOH

P - - proline NH-(CH2)3-CH-COOH

I - - isoleucine CH3-CH2-CH(CH3)-CH(NH2)-COOH

Q - - glutamine NH2-CO-(CH2)2-CH(NH2)-COOH

N - - asparagine NH2-CO-CH2-CH(NH2)-COOH
A - alanine CH$_3$-CH(NH$_2$)-COOH
T - threonine (CH$_3$)$_2$-CH(OH)-CH(NH$_2$)-COOH
D - aspartic acid HOOC-CH$_2$-CH(NH$_2$)-COOH
G - glycine NH$_2$-CH$_2$-COOH

A donor, a rhodamine-based dye, was attached to the peptide on one side of the cleaving site, which is between the proline, P, and isoleucine, I, residues, and a dark quencher, Molecular Probes QSY7 [32], was attached to the other side.

We used certain buffer solution to make the final peptide solution once the solid peptide is synthesized in Protein Facility. We used the same buffer to make desired concentration of LF. The assay buffer was prepared mixing 50 mM HEPES (pH 7.0), 20 mM NaCl, 10 mM MgCl$_2$, 100 μM CaCl$_2$, 10 μM ZnCl$_2$, 0.1 mg/ml of bovine serum albumin (BSA) and 1 mM Dithiothreitol (DTT).

The FRET pairs were bought from Molecular probes.

5. Results and discussion

The change in PL was monitored as described in chapter 3,4 and 5. An green Alq$_3$ based OLED was driven with an AC pulse of width 100 μs was used to excite the donor molecule and the PL was measured using the PMT. Fig. 5 shows the response of the peptide in absence and in presence of LF when a single pulse is applied to the OLED. The donor molecule used for this study is fluorescein and the acceptor molecule is QSY-7.
A second set of experiment was done using a different pair of donor and acceptor pair. Fig. 6.6 shows the change in PL when a TAMRA molecule is used as the donor and the QSY-7 is used as the acceptor molecule.

It is clear from Fig. 6.6 that the change in PL is maximum for a peptide concentration of 76.5 μM. In this experiment the total volume of the peptide is 75 μl and to this peptide solution 25 μl of 100 nM LF was added to make a total volume of 100 μl. As the peptide concentration increases, the change in PL increases as the each LF molecule can now see more peptide to cleave in its vicinity. It is also clear that after certain amount of time (typically 20 minutes) all the available peptide molecules are cleaved and the PL reaches a steady state value.
Fig. 6.6. % PL change as a function of time for 3.2 to 76.5 μM peptide exposed to 25 nM LF.

Fig 6.7 shows the PL intensity as function of time when different LF concentration is used and Fig. 8 shows the percentage change in PL as function of LF concentration after 60 minutes incubation. With the same concentration of LF, the reaction takes about 35 minutes to reach the peak reactivity. It is also clear that as the LF concentration increases the percentage PL change increases as the number of LF molecules are more as the concentration increases and hence more cleavage of the peptide.
Fig. 6.7. PL intensity versus time for 63 to 74 nM of LF

Fig. 6.8. % PL change versus LF concentration after 60 minutes incubation
6. Conclusion

In this work we have clearly demonstrated the possibility of an OLED based anthrax sensor. The very basic goal of this project to make a portable anthrax sensor is so possible as the OLEDs can be fabricated on any substrates.

Acknowledgement

This work was supported by the National Aeronautics and Space Administration, the National Science Foundation, the National Institutes of Health, and the Institute for Physical Research and Technology of Iowa State University (ISU). Ames Laboratory is operated by ISU for the United States Department of Energy under Contract W-7405- Eng-82.

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[29]. Note that 5 mg/mL = 500 mg/dL, which is the conventional medical unit.


[32]. www.probes.com- Fluorophore supplier and active in FRET research
Chapter 7. Conclusions

This thesis describes multidisciplinary projects where studies of OLEDs and its use towards the development of miniature biosensor have been successfully done. The turn off dynamics of DPVBi based blue OLEDs has been studied as function of temperature and three different mechanisms of decay have been modeled successfully.

First completely integrated biosensor for gas and solution phase monitoring of oxygen has been developed. This sensor is very small and the exciting light source for the sensing element is integrated to the sensing element itself. This enables to develop the sensor virtually on any substrate and shows a path to develop portable, disposable and cheap sensors for industrial and household use.

Based on the oxygen sensor, a very sensitive glucose sensor has been developed which is very sensitive in the medical range of interest, e.g., for detecting 0-5mg/ml of glucose. Integration of the glucose sensing film to the OLEDs make it very simple and light weight and a test of the glucose content on any solution can be made anywhere anytime.

Using the FRET technology and using OLED as the exciting light source, a novel anthrax sensor has been developed. Successful realization of this sensor opens up possibility of a new handheld sensor to counter bioterrorism.