Published in final edited form as:

Anal Chem. 2010 April 1; 82(7): 2734–2742. doi:10.1021/ac9026109.

A Planar, Chip-Based, Dual-Beam Refractometer Using an Integrated Organic Light Emitting Diode (OLED) Light Source and Organic Photovoltaic (OPV) Detectors

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Abstract

We present a simple chip-based refractometer with a central organic light emitting diode (OLED) light source and two opposed organic photovoltaic (OPV) detectors on an internal reflection element (IRE) substrate, creating a true dual-beam sensor platform. For first-generation platforms, we demonstrate the use of a single heterojunction OLED based on electroluminescence emission from an Alq₃/TPD heterojunction (tris-(8-hydroxyquinoline)aluminum/*N,N'*-Bis(3-methylphenyl)-*N,N'*-diphenylbenzidine) and light detection with planar heterojunction pentacene/C₆₀ OPVs. The sensor utilizes the considerable fraction of emitted light from conventional thin film OLEDs that is coupled into guided modes in the IRE instead of into the forward (display) direction. A ray-optics description is used to describe light throughput and efficiency-limiting factors for light coupling from the OLED into the substrate modes, light traversing through the IRE substrate, and light coupling into the OPV detectors. The arrangement of the OLED at the center of the chip provides for two sensing regions, a “sample” and “reference” channel, with detection of light by independent OPV detectors. This configuration allows for normalization of the sensor response against fluctuations in OLED light output, stability, and local fluctuations (temperature) which might influence sensor response. The dual beam configuration permits significantly enhanced sensitivity to refractive index changes relative to single-beam protocols, and is easily integrated into a field-portable instrumentation package. Changes in refractive index ($\Delta R.I.$) between 10^{-2} and 10^{-3} R.I. units could be detected for single channel operation, with sensitivity increased to $\Delta R.I. \approx 10^{-4}$ units when the dual beam configuration is employed.

Keywords

organic light emitting diode; organic photovoltaic; refractive index; lab-on-chip

Introduction

Chip-like, field-portable sensing platforms are of increasing interest, especially if the platforms can be economically produced while retaining high sensitivity and selectivity comparable to achievable limits with less portable sensing platforms.^{1–21} Optically based sensors with detection schemes involved in monitoring changes in absorbance, luminescence, reflectance,

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Supporting Information Available. A list of chemicals, fabrication and cleaning procedures, and device testing techniques. This material is available free of charge via the Internet at <http://pubs.acs.org>.

refractive index or other related optical properties are normally used in both thin film and bulk solution formats and are particularly promising if they can be created on a waveguide platform without the need for free-space optics in excitation or detection of the optical response.^{1,2,9,11,22–25}

Organic light emitting diodes (OLEDs) are an attractive thin film light source for chemical sensor platforms which operate either in transmission modes of absorbance and luminescence detection or in modes which make use of internally reflected light in waveguide-like platforms.^{4,5,16–18,26} In OLED displays, a sizeable fraction of the emitted light is lost in guided modes in the organic layers and the bottom transparent conducting oxide (TCO) layer, and/or in modes internally reflected within the substrate. Here the substrate functions as an internal reflection element (IRE).^{27–38} These light-loss pathways, while problematic for display applications, provide an opportunity to utilize internally reflected modes from OLEDs in waveguide-based sensor applications.^{5,12,18,39}

The device-integrated counterpart to the OLED light source is the thin film organic solar cell (OPV) photodetector.^{13,17,19,20,40–46} Most OPVs are based either on vacuum deposited donor and acceptor small molecules in “planar heterojunction” (PHJ) formats^{20,24,45,47–51} or “blended heterojunctions” (BHJ) based on combinations of donor polymers and electron acceptor small molecules.^{13,17,39,41,44,46} Organic photodetectors can be easily placed on sensor platforms by vacuum deposition or solution processing protocols and show the kind of rectification, low dark currents, and photocurrent efficiencies necessary for a variety of sensor technologies. The ease of integration of both the OLED and OPV “in-plane” on waveguide platforms is extremely appealing and relieves the need for free-space optics for excitation and detection of the optical signal. The combination of OLED and OPV provides for an inexpensive, easily produced and disseminated sensor platform. This report focuses on the most straightforward application of OLED/OPV sensors, i.e. detection of refractive index changes down to sensitivities of ca. 10^{-4} R.I. units.

Numerous label-free, *in-situ* refractive index-based sensor platforms and protocols are now known, including those based on surface plasmon resonance (SPR), ellipsometry, optical waveguide lightmode spectroscopy (OWLS), reflectometry, resonant mirror refractometry and backscattering interferometry.^{21,52–59} In general it has been seen that sensitivity to refractive index (R.I.) changes of ca. 10^{-4} to 10^{-7} can be achieved in most of these sensing platforms. Sensing platforms with good sensitivity, versatility, and high throughput are becoming more widespread in applications requiring dissemination of large numbers of sensors, such as in drug development, pathogen detection in food processing, and toxin detection in air, water and soils. A number of these R.I. sensors, however, are constrained to large optical benches requiring mechanical and optical alignment, resulting in non-portable sensors.

Here we show the development of a unique chip-like refractometer, using a true dual-beam platform, where the emission of a pulsed central OLED light source is coupled into IRE substrate modes in opposing directions toward two well matched OPVs, forming a “sample” and “reference” channel. OPV transient photocurrents, after current-to-voltage conversion and signal processing, are either divided and/or subtracted to compensate for small drifts in OLED output and OPV response, which is significant in single-beam OLED/OPV sensor applications. The combined use of: *i*) a dual-beam configuration, *ii*) drive-current modulation of the OLED, and *iii*) on-board filtering and lock-in-amplifier-based signal processing provide enhanced sensitivity to refractive index changes, versus single-beam platforms operated without modulation of the OLED.

We first describe the coupling of OLED emission into the IRE, focusing on those factors which limit the optical sensitivity of these platforms, and sources of stray light, followed by a

description of an OLED/OPV dual beam sensing platform based on aluminum quinolate (Alq₃) OLEDs,^{60,61} and pentacene/C₆₀ heterojunction OPV detectors.^{20,49,62,63} We show the use of this first-generation sensing platform for the detection of refractive index changes in bulk solutions, down to levels of ca. 10⁻⁴ R.I. units, and discuss their possible utilization in new refractometer-based sensing configurations.

Theory

The net light propagation efficiency of the sensor platform, η_{sensor} , is evaluated as the product of the individual efficiencies for each light generation and throughput event, from OLED light generation to OPV detection, as outlined in Figure 1 and Equation 1, with each efficiency term defined below:

$$\eta_{\text{sensor}} = \eta_{\text{OLED}} \cdot \eta_{\text{OLED-sub}} \cdot \eta_{\text{IRE}} \cdot \eta_{\text{sub-OPV}} \cdot \eta_{\text{OPV}} \quad (1)$$

The light is generated in the emission zone of the OLED, at an efficiency described by the ratio of the number of photons generated to the number of electrons injected, η_{OLED} .^{27,30,64} Emitted photons are coupled from the OLED into the substrate modes of the platform with a coupling efficiency $\eta_{\text{OLED-sub}}$ determined by the refractive indices of the substrate, superstrate, and organic components of the OLED, the angular distribution of emitted light, and the individual layer thicknesses; $\eta_{\text{OLED-sub}}$ is described below. Light within the substrate (IRE modes) interacts with the sensing region, and the throughput efficiency of the IRE, η_{IRE} , is limited by optical propagation loss due to absorbance and scattering events in the IRE and adjacent media.^{1,9,11,23,65} This is the basis for the sensor response.

Light is then out-coupled from the substrate into the OPV, with an efficiency $\eta_{\text{sub-OPV}}$ determined by the refractive index of the substrate ITO layer and the organic layers of the OPV, as well as the angular distribution of light and layer thicknesses. Finally, the light is detected by the OPV, with an efficiency η_{OPV} , defined as the number of electrons generated relative to the number of photons absorbed in the OPV platform.⁴⁵

For thick IREs $\eta_{\text{OLED-sub}}$ and $\eta_{\text{sub-OPV}}$ are described using simple ray optics models. OLEDs (both small molecule and polymer-based) are treated as Lambertian light sources, producing nearly isotropic emission profiles over large viewing angles.^{27,30} The emission of an OLED is dependent on the refractive index of the substrate, organic layers and refractive index of the emission zone (usually air),^{27,30,66,67} however, only ~20% of this emission is detected in the display direction. Previous modeling studies have shown that the refractive index mismatch between the organic emitting layers and the substrate and air results in the majority of light trapped in guided modes in the substrate, organic layers, or ITO layers.^{3,12,18,28,30,33,34,37,38} Improving the out-coupling of OLED emission has been achieved using diffraction gratings, or roughened substrates,⁶⁷ or through the use of high refractive index substrates.³⁸ A simple approach was first used by Friend and coworkers to describe the fraction of light coupled in each direction from the thin film light source, assuming that: *i*) the top metal cathode acts as a pure reflector (Figure 1); *ii*) there is no diffuse scattering occurring at the interfaces within the OLED; and *iii*) the organic layer is an isotropic emitter.²⁷ This treatment was subsequently extended to small molecule OLEDs;³⁰ the most complete models consider micro-cavity effects for a more accurate simulation of OLED output.^{30,66,68}

Treating the OLED as a single monochromatic point source is sufficient to evaluate $\eta_{\text{OLED-sub}}$ assuming no diffuse scattering at the interfaces. The OLED is a multilayer structure consisting of a planar glass substrate ($t_{\text{glass}} \sim 1$ mm, $n_{\text{glass}} \sim 1.51$), an ITO layer ($t_{\text{ITO}} \sim 100$ nm, $n_{\text{ITO}} \sim 1.8$), and multiple organic layers ($t_{\text{organic}} \sim 20$ – 100 nm, $n_{\text{organic}} = 1.6$ – 1.8), where t refers to layer thickness and n is the index of refraction at $\lambda \sim 540$ nm.⁶⁹ We use an effective

refractive index for the combination of the thin ITO and organic layers, $n_{\text{organic}} \approx 1.75$, as a further simplification. The angular distribution of photon emission from the OLED (θ_{em}) is modeled with respect to the various internal angles within the emission layer, bound on one side by the metal cathode and the other with the glass substrate, interfaced to the superstrate (analyte solution).

The emission of an OLED arises from three zones, *i*) the superstrate zone (or forward display), *ii*) the substrate zone (IRE), and *iii*) the patterned organic/ITO zone, as illustrated in Figure 2A. The fraction of light coupling into each zone is governed by the refractive indices of adjacent layers and the corresponding critical angles set by Snell's Law. Photons escape into the superstrate zone at angles of emission below the critical angle defined by the refractive indices of the organic components of the OLED and the superstrate ($\theta_{\text{cri,organic,super}}$) in Equation 2 ($0 \leq \theta_{\text{em}} < \theta_{\text{cri,organic,super}}$).

$$\theta_{\text{cri,organic,super}} = \sin^{-1} \frac{n_{\text{super}}}{n_{\text{organic}}} \quad (2)$$

Photons emitted at angles between $\theta_{\text{cri,organic,super}}$ and the critical angle between the glass substrate and the organic layer, $\theta_{\text{cri,organic,glass}}$, defined in Equation 3 ($\theta_{\text{cri,organic,super}} \leq \theta_{\text{em}} < \theta_{\text{cri,organic,glass}}$), are trapped within the substrate zone and propagate through the IRE to the OPV detectors.

$$\theta_{\text{cri,organic,glass}} = \sin^{-1} \frac{n_{\text{glass}}}{n_{\text{organic}}} \quad (3)$$

Finally, photons emitted by the OLED at angles greater than $\theta_{\text{cri,organic,glass}}$ ($\theta_{\text{cri,organic,glass}} \leq \theta_{\text{em}} < \pi/2$) are trapped and/or scattered and will be the predominant source of stray light to reach the OPV detectors, if not absorbed by the cathode.

Ignoring the dependence of transmitted intensity on incident angle and polarization, the fraction of total light emitted which escapes from the OLED into the display mode χ_{ext} is:

$$\chi_{\text{ext}} = \int_0^{\theta_{\text{cri,organic,super}}} \sin \theta d\theta = 1 - \cos \theta_{\text{cri,organic,super}} \quad (4)$$

and the fraction of light trapped within the substrate (χ_{subs}) and ITO/organic zones ($\chi_{\text{ITO/org}}$):

$$\chi_{\text{subs}} = \int_{\theta_{\text{cri,organic,super}}}^{\theta_{\text{cri,organic,glass}}} \sin \theta d\theta = \cos \theta_{\text{cri,organic,super}} - \cos \theta_{\text{cri,organic,glass}} \quad (5)$$

$$\chi_{\text{ITO/org}} = \int_{\theta_{\text{cri,organic,glass}}}^{\pi/2} \sin \theta d\theta = \cos \theta_{\text{cri,organic,glass}} \quad (6)$$

Where χ_{subs} is proportional to $\eta_{\text{OLED-sub}}$.

Figure 2A demonstrates light coupling into the three zones. Figure 2B shows the change in the critical angle $\theta_{\text{cri,organic,super}}$ with respect to R.I. of the superstrate and Figure 2C shows the

change in the light fraction (χ) coupled into each of the three emission regions with respect to the R.I. of the superstrate. The coupling efficiency of the OLED emission into the substrate ($\eta_{\text{OLED-sub}}$) is governed by the fraction of light within the substrate modes, with respect to light out-coupled to the superstrate. By increasing the refractive index of the superstrate (analyte solution or an analyte layer adsorbed to the IRE surface), the critical angle defined by the organic components of the OLED and the superstrate increases, increasing light out-coupled into the superstrate region and decreasing light coupled into substrate modes, yielding a net decrease in $\eta_{\text{OLED-sub}}$. Such changes become the basis for the response of this sensor platform.

A similar model is employed to estimate out-coupling efficiency from the substrate zone into OPV detectors (ie, $\eta_{\text{sub-OPV}}$). Light propagating through the glass substrate ($t_{\text{glass}} \sim 1$ mm, $n_{\text{glass}} \sim 1.51$) from the OLED is coupled into the organic layers ($t_{\text{organic}} \sim 20$ – 100 nm, $n_{\text{organic}} = 1.6$ – 1.8) of the OPV through the ITO ($t_{\text{ITO}} \sim 100$ nm, $n_{\text{ITO}} \sim 1.8$), modeled as an effective index of $n_{\text{organic}} = 1.75$. As light passes through the ITO and the organic layers of the OPV, some loss due to absorbance by these layers, and light scattering at the interfaces, is expected yielding a $\eta_{\text{sub-OPV}} < 1$.

This ray optics model works well to describe the coupling of OLED emission to OPVs and conversion to photocurrent, owing to our use of relatively thick IRE substrates for these first generation devices. This provides for a large range of propagation angles in the IRE, which is not the case if one attempts to couple OLED emission into thin IRE elements and single-mode waveguides, where significantly less light is destined to arrive at the OPV detector, and geometric constraints on coupling are more restrictive.¹⁸

Sensor Platform Design and Operation

A chip-based sensor platform was constructed using vacuum deposition of organic layers and aluminum cathodes through a series of masks onto pre-patterned ITO substrates. * Emission from a segmented OLED is derived from a N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-1,1'-biphenyl-4,4'-diamine (TPD)/aluminum quinolate (Alq₃) heterojunction,⁶⁰ and the OPV detectors are planar pentacene/C₆₀ heterojunctions.⁶² The width of the OPV detectors was designed to match the radial emission width (in the plane of the IRE substrate) of the segmented OLED light source in order to reduce noise due to stray light. Each chip contains two sets of sensors, or channels, parallel to each other, as shown in Figure 3A, with only one channel operated at a time. In order to minimize device degradation due to atmospheric exposure and to reduce light scattering, the sensor platform was placed within a pressure fit cell constructed from black Delrin (acetal homopolymer and polyoxymethylene, McMaster-Carr) with fitted O-rings cut from 1 mm thick Kalrez Perfluoroelastomer (McMaster-Carr). To minimize ambient conditions within the cell, the platform and casing were assembled inside a glove box prior to use. The pressure cell has two solution chambers per sensor (four total, see figure 1, SI section); one used for a reference solution over one sensing region between the OLED and one of the OPV detectors, and the other chamber for a sample solution over the other sensing region of a single sensor. Solution chambers were open to air for ease of sample injection and removal of solutions. Electrical contact was made to the respective anodes and cathodes of the OLED and OPVs with stainless steel foils (5/1000, McMaster-Carr), sandwiched between the electrode and the o-ring within the pressure cell. The configuration of these cells is such that only light emitted line-of-sight from the OLED to the OPV detectors is relevant; all additional emission which might be scattered from the sides of the glass chip are absorbed by the black plastic cell.

*The specifics of the platform construction may be found in the full experimental section within the Supporting Information section.

Control of OLED drive current (modulated) and signal processing of the OPV photocurrent(s) were accomplished with battery-powered instrumentation shown schematically in Figure 3B. OLED emission is controlled with constant drive current (ca. 12 – 60 mA), modulated (on/off) at 256 Hz. The OPVs are operated in short-circuit mode (0 V applied bias) and their respective currents (at short circuit, J_{SC}) are coupled into separate current-to-voltage (J - V) converters. The OLEDs and the OPVs must be electrically isolated from one another on the sensor platform; leakage pathways are sometimes introduced during fabrication of either the OLED or OPV systems, and need to be removed prior to operation. The voltages from the J - V converters are filtered (4th order bandpass filters, $Q = 7.2$) and fed into independent on-board lock-in amplifier circuits, along with a reference signal from the power supply used to control OLED emission.

Results and Discussion

In these first-generation devices, pentacene/ C_{60} planar heterojunction OPV detectors were used for the good spectral overlap with Alq₃/TPD OLED emission^{70–72} (peak emission near 540 nm, Figure 4) and high incident light current efficiencies (IPCE).⁴⁹ The noise floor for these OPV detectors is set by the reverse saturation current (J_0) (dark current), as defined by the Shockley Equation,

$$J = J_0 \left[e^{\frac{qV}{nk_B T}} - 1 \right] \quad (7)$$

where J is the current density in the OPV (photodiode), J_0 is the reverse saturation (dark) current, q is the charge on an electron, V is the voltage across the diode, n is the ideality factor, T is the temperature and k_B is the Boltzmann constant. J_0 represents the minimum current output of the detector and can be estimated from the current output of the OPV when the OLED is off. An estimation of the dark current response (J_0) for an average OPV (area of this detector is 0.25 cm²) is 4 nA, which is acceptably low so as to allow relatively low light intensities to be measured above the background; however, as the maximum output of the OPV detectors in these experiments is within 100× of the dark current response, it is necessary to correct for the dark current offset of the OPV current output (see below).

For various OPV platforms J_0 is related to both the energy barrier for dark injection of charge carriers at the donor/acceptor interface(s) within the OPV,⁴⁷ and the degree of intermolecular interactions, aggregation, and polycrystallinity of the donor materials.⁷³ Lower J_0 values and lower dark current responses are therefore expected in future sensor platforms, with spectral match to the OLED; minimization of the dark current in the OPV will further improve the limit of detection.^{46,48}

Figure 5 shows how the short-circuit current J_{SC} of the OPV changes with increasing OLED drive current. OLED drive currents from 0 to 120 mA produce J_{SC} values in the OPV from 10⁻² to 3 μA/cm². Luminance versus OLED drive current data is provided in the SI section; for low drive currents the luminance of the OLED is approximately linear versus the drive current of the device. Figure 5A and B show the change in the respective linear and logarithmic current-voltage response of the OPV versus applied bias for multiple OLED drive currents. Figure 5C shows the linear change in J_{SC} and an increase in the open circuit voltage, V_{OC} , of the OPV with response to increasing OLED drive current. In accordance with Equation 7, V_{OC} should scale logarithmically with light intensity (OLED drive current), but over these small light intensity ranges, the relationship appears linear. At a typical 12.5 mA drive current for the OLED, the OPV produced 0.38 μA/cm², representing an overall throughput efficiency $\eta_{sensor} = J_{SC(OPV)}/J_{OLED} = 7 \times 10^{-4} \%$ for the sensor platform in contact with air.

Figure 5D shows the phase coupled response of the two channels as the OLED is turned on and off at approximately 10 second intervals with respect to different OLED drive currents. At low frequencies, where the sensor platform is currently operated (up to 256 Hz), the two OPVs are operating in phase with one another in a true sample and reference channel configuration. Over periods of ten seconds a small drift in OLED emission is evident, particularly at the highest drive currents (53 mA). A second reference channel is beneficial to account for light source drift through the duration of the refractive index sensing experiments described below. OLED drift is attributed in part to thermal instabilities arising from local heating during OLED operation. This problem is minimized in part by segmentation of the OLED light source (see Supporting Information), and will be further reduced in platforms using smaller (pixilated) and more efficient OLEDs.

The influence of OLED drift on the sensitivity of the sensor platform to changes in the superstrate refractive index is most evident over long time periods (> 100 seconds). Incremental additions of ethanol in water were used to measure refractive index using the sensor platform. A known mass of water was placed in both the reference and the sample chambers of the platform and incremental additions of ethanol were added to the sample channel only, while measuring the OPV response from the sample and the reference channels with respect to time. Figure 6A gives the response of both the reference and sample channel (operated as single beams) with respect to time. All data presented were first corrected for dark current, followed by normalization to the initial analyte solution (water) signal, as given in Equation 8,

$$Signal = \frac{S_{EtOH} - D^{Sample}}{S_{H_2O} - D^{Sample}} \quad (8)$$

where S_{EtOH} is the output of the lock-in amplifier from the OPV with respect to time and additions of ethanol, D^{Sample} is the dark response of the OPV, collected before and after the experiment, and S_{H_2O} is the output of the lock-in amplifier when only water is in the sample well. The reference channel contained only water for the duration of the experiment. The drift and fluctuations in the OLED signal with respect to time are clear, and are the limiting sources of noise in the single beam configuration. The response of the single beam sample channel has a staircase-like appearance with fluctuations in signal upon the introduction of additional ethanol increments approximately every 20–30 seconds. There is a steady decrease in OPV current with the addition of each increment of ethanol; as the refractive index of the superstrate is incrementally increased with each incremental addition of ethanol, there is a decrease in light coupled into the substrate modes, as predicted by the model presented in Figure 2.

The changes in refractive index ($\Delta R.I.$ units) were calibrated with respect to refractive index values of standard ethanol/water solutions at 25°C.⁷⁴ Figure 6B shows the measured calibration curve for refractive index with respect to normalized OPV response for the single beam sample channel, calculated from averaging over each “stair” step in Figure 6A. Average data variance for each stair step is approximately 10^{-7} (R.I.),² and is presented as error bars in Figure 6B. A linear fit was assumed for $\Delta R.I.$, as indicated by the dashed line, with a deviation of 1×10^{-4} R.I. units from the expected values using a mass ratio of water and ethanol. Variance from the linear fit (1×10^{-5}) yielded a detection limit of approximately 3×10^{-3} R.I. units, assuming a minimum signal-to-noise threshold (S/N) of 3. However, due to a general decrease in OLED luminance with respect to time which is embedded in the calibration step curve, it is suspected that this is an upper limit to detection capabilities and that actual sensitivity is on the order of 10^{-2} to 10^{-3} R.I. units for single beam operation.

A dual beam approach to measure reflectivity accounts for the drift and fluctuations in the OLED over time. Figure 6 also shows the reflectance data corrected using the dual channel

configuration (Equation 9). The reflectivity signals from both the reference (R) and sample (S) channels were first corrected for dark current (D_{ref} and D_{sample}), followed by a baseline correction factor fitted to the reference channel OPV response with respect to time ($R_{baseline}$ and $S_{baseline}$), and these signals were finally normalized to the response for pure water, to provide a fully normalized reflectance sensor response:

$$\frac{S_{Sample} - S_{Reference}}{S_{Reference}} = \frac{\frac{S - D_{sample}}{S_{baseline} - D_{sample}} - \frac{R - D_{ref}}{R_{baseline} - D_{ref}}}{\frac{R - D_{ref}}{R_{baseline} - D_{ref}}} \quad (9)$$

The raw data in Figure 6A demonstrates a significant reduction in noise for each stair “step” for the dual beam response over the single beam, while still demonstrating response spikes for addition of each ethanol increment. Average variance for each stair “step” was found to be 10^{-9} (R.I. units)², a factor of 100 decrease from the single channel data. Figure 6B gives the results of the calibration curve as well as the estimated linear fit to refractive index changes, with a variance of 5×10^{-7} (Δ R.I.)². The detection limit for the dual channel configuration was estimated at 4×10^{-4} R.I. units, on the order of the limitation of the standard solution preparation and a factor of 10 to 100 increase in sensitivity over the single channel configuration. The apparent detection limit of 10^{-4} R.I. units is a limit imposed by our ability to change the R.I. of the standard solutions, and does not reflect the ultimate sensitivity of this platform. Figure 6B also shows the predicted response of the sensor platform based on the ray optics model, discussed above and in Figure 2. The slopes of the two fits are comparable, but there is a systematic offset, with a lower absolute response implied in the acquired data. This offset may be due to stray light in the OPV response as well as the assumptions made to simplify the ray optics model (described above).

Conclusions

We have demonstrated the implementation of a simple refractometer fabricated from an integrated OLED light source and dual OPV detectors operated in a dual beam configuration. The refractometer operates by monitoring the change in light flux from the OLED to the OPV in the sample channel, arising from changes in refractive index of the analyte solution, with respect to a reference solution. This permits significant enhancement in analytical performance over a single-beam configuration while still being capable of facile integration with field-portable instrumentation packages. The ability to detect refractive index changes on the order of 10^{-4} R.I. should enable detection of low concentrations of various adsorbed materials selectively captured on the sensing surface; for example, the adsorption of proteins results in a local refractive index change of 10^{-3} R.I. on many substrates.^{52,75} Protein adsorption to chemically modified silica or metal surfaces is often characterized with optical techniques such as optical waveguide lightmode spectroscopy (OWLS), which currently has R.I. sensitivity of ca. 10^{-3} R.I., i.e. a concentration sensitivity of ca. 1 ng/cm² for changes in adsorbed protein concentration.^{52,76}

The dual beam approach reduces the impact of OLED instability and is sufficient for certain sensing applications, but it should be noted that higher efficiency OLEDs with higher stabilities are likely to improve sensing capabilities significantly. Sensor platforms in development focus on enhanced OLED efficiencies and OPVs with lower reverse saturation currents and higher photo-sensitivities. The use of thinner IREs, or single-mode waveguide platforms, while more challenging for light coupling (particularly for OLEDs), will provide higher sensitivities for R.I. changes, for both solutions and adsorbed layers.^{1,25}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by grants from the National Institutes of Health R01-EB007047 (Saavedra and Armstrong), the National Science Foundation CHE-0517963 (Armstrong), and the NSF Science and Technology Center-Materials and Devices for Information Technology --DMR-0120967 (Armstrong).

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Figure 1.

(A) Schematic (side) illustration of dual channel sensor platform. (B) Schematic of the ray optics description of internal reflection governing the response of a single channel device. The throughput efficiency of the sensor platform (η_{sensor}) can be estimated from the product of the individual event efficiencies, where η_{OLED} is the light generation efficiency of the OLED, $\eta_{OLED-sub}$ is the coupling efficiency between the OLED and the IRE element, η_{IRE} is the efficiency of the IRE, $\eta_{sub-OPV}$ is the coupling efficiency between the IRE element and the OPV, and η_{OPV} is the photon conversion efficiency of the OPV.

Figure 2.

Classic ray optics model of OLED/OPV sensor platform. (A) Illustration of reflection of light within respective layers of the sensor platform. Light emitted from the OLED can be traced to one of three zones, depending on the angle of emission and the refractive index of the respective layers, (i) superstrate zone (forward display mode), (ii) substrate zone (IRE modes), or (iii) organic/ITO zone. Light trapped within the substrate modes propagates through the substrate and can couple into the organic layers of the OPV. (B) Calculated critical angle between the organic layer and the superstrate with respect to superstrate refractive index. (C) Estimated fraction of light within each zone with respect to refractive index of the superstrate layer. The larger the refractive index of the superstrate, the lower the fraction of light coupled into the substrate (ii). Curve ii represents the total estimated fraction of light emitted by the OLED that actually reaches the OPV with respect to refractive index of the superstrate, ignoring light scattering and absorbance effects, incident angle, and polarization, and assuming that the OLED is a monochromatic light source.

Figure 3.

Schematic of sensor platform operation. (A) Schematic representation of the dual beam sensor platform chip with two complete sensors. One segmented OLED and a pair of OPVs are operated at one time. (B) Schematic of the signal processing electronics for the dual channel sensor platform (details given in Supporting Information). The OLED drive circuitry and signal processing systems are integrated onto a circuit board, with on-board battery power. The sensor can be operated in either single or dual beam mode.

Figure 4. Spectral overlap between the emission spectrum of the Alq₃/TPD OLED light source and the IPCE spectrum of a pentacene/C₆₀ OPV detector. Experimental details are given in the SI section.

Figure 5.

(A) Linear plots of OPV current density versus applied bias to the OPV, at different OLED drive currents, from 0 to 120 mA. (B) Log plots of the data in (A). (C) Measured short circuit current density (J_{SC} , when applied bias (V) to the OPV = 0), and open circuit voltage (V_{OC}) of an OPV detector with respect to OLED drive current. (D) The responses of the OPV detectors when the OLED is turned on and off in a dual beam configuration. The OLED couples into both OPVs, whose response are in phase with one another.

Figure 6.

Measurement of change in refractive index of the superstrate with time, demonstrating differences in sensitivity between single and dual beam configurations. In the dual beam configuration, one OPV is treated as a reference beam and the other is treated as the sample beam. Both the reference and the sample chambers contain water and increments of ethanol (increasing refractive index) are added to the sample chamber only. (A) Response of both the reference (—) and the sample (—) OPVs in a single beam configuration with respect to time and introduction of changing refractive index solutions. Calculated dual beam response (—) outlined by Equation 11 included for comparison. There is less variance in the dual beam than in the single beam configuration. (B) Sensitivity of the sensor platform with respect to refractive index in the single beam (○) and dual beam (□) configurations. Theoretical estimate (Δ) based upon the model presented in Figure 2 given for comparison. The sensitivity to changes in refractive index ($\Delta R.I.$) of the single beam is estimated to 10^{-2} to 10^{-3} $\Delta R.I.$ units while the dual beam has an increased sensitivity of 10^{-4} $\Delta R.I.$ units.