Polymer Infrared Proximity Sensor Array

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***Abstract*—A near-infrared proximity sensor array is achieved by integrating a polymer light-emitting diode and a polymer photodetector (PD). A green emission is converted into deep red peaked at 670 nm by the inorganic phosphor Intematix R670 with quantum efficiency of over 20%. A bandpass filter is used to select a spectral tail of phosphor luminescence with a wavelength above 700 nm. The emissive polymer is green polyfluorene. The infrared PD contains a thick film of a blend of poly(3-hexylthiophene) and (6,6)-phenyl-C61-butyric acid methyl ester up to a thickness of 8 μm. Position of a moving object at a distance of 10 cm is detected in real time by the array with dynamic images displayed on the computer screen.**

***Index Terms*—Array, photodetector (PD), polymer, proximity sensor.**

I. Introduction

In THE last decade, there has been tremendous interest in developing robots that are able to closely interact with humans and move in unpredictable and unstructured environments around us, such that the robots can work safely in homes, offices, or hospitals to provide substantial help. One major obstacle for such robots is inevitable collisions in complex and changing environments. In order to realize this imagination, a robot skin needs to be covered with a sensor array to detect proximity of an object, i.e., an artificial skin. Inorganic semiconductor light-emitting diodes (LEDs) and photodetectors (PDs) have been used widely for proximity sensing by detecting reflected light. They are, however, impractical for a robot artificial skin, which needs to be thin, flexible, and in a large area. In contrary, organic semiconductor devices, particularly the ones processed in a solution, naturally satisfy the requirement for a robot skin. Infrared is preferred to visible light in proximity sensing because the former is invisible and has lower background noise from indoor lighting or outdoor sunlight. Furthermore, a light scattering is proportional to the inverse of the fourth power of a wavelength; therefore, reflected light is much stronger for infrared than visible for the same incident intensity. Near-infrared (NIR) polymer PDs has been realized by low-band-gap polymers [1] or by blending a wide-gap electron donor and an acceptor, taking advantage of weak infrared aggregate absorption of a fullerene acceptor [2], [3]. External conversion of a visible emission from a polymer LED (PLED) by a laser dye into infrared has been used for a proximity sensor with a detection distance up to 20 cm [4]. The photocurrent signal is, however, low because PL efficiency of the laser dye in a solid-state matrix is below 2%. In fact, all organic materials with a low band gap either has severe concentration quenching as laser dyes or has intrinsic poor PL as in the case of donor–acceptor type polymers studied for a solar cell. Weak infrared emission and low photocurrent make it difficult for dynamic signal processing for a robot skin involving many pixels. A thin film with high-conversion efficiency from visible to infrared is highly desired.

Instead of organic dyes, in this paper, we employ an inorganic phosphor as a conversion layer. While phosphors with an infrared emission usually have poor quantum efficiency, some deep red phosphor with emission extending into near infrared has high quantum efficiency. Using a color filter to remove mostly visible emissions, we realize a proximity sensor using solution-processed polymer devices operated in a desired NIR region with a photocurrent above 100 nA. Such a high signal makes the subsequent signal process easy; therefore, a 3×3 array polymer proximity sensor array is demonstrated to detect the motion of an object in real time, and such information can be feed to the processing unit of a robot for responses.

II. Fabrication

A PLED and a PD are fabricated on glass substrates with a poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) layer on a patterned indium–tin–oxide layer. A PEDOT:PSS film is baked at 200 °C for 15 min in an ambient environment. On the top of the PEDOT:PSS surface, the PLED structure is cross-linkable poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4″-{N-[4-secybutylphenyl]}diphenylamine)] (cross-linkable TFB) (23 nm)/green B (70 nm)/Ca (35 nm)/Al

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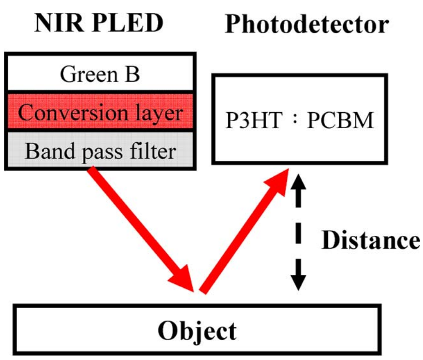


Fig. 1. Schematic working principle of the NIR proximity sensor.

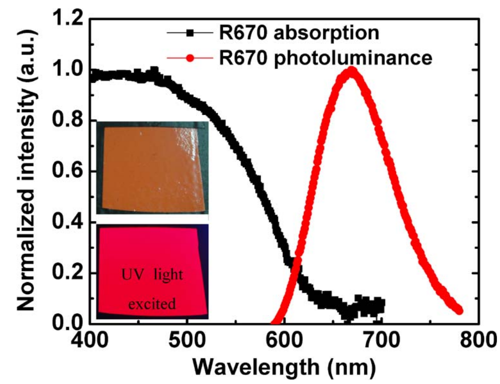


Fig. 2. Absorption (solid square) and PL spectra(solid circle) of the phospor R670.

(100 nm). A hole transport layer of cross-linkable TFB (0.5 wt% in toluene) is formed by spin coating and then baked at 180 °C for 60 min. An emitting layer is also formed by spin coating the polyfluorene derivative LUMATION Green B by Dow Chemical (1.2 wt% in toluene) and then baking at 130 °C for 30 min. A deep red R670 phosphor purchased from Intematix is blended with a binder 6450 from Silmore with a weight ratio of 1 : 1.5 to form a visible-to-infrared conversion layer. The conversion layer made of the aforementioned blend film with a thickness of 50 μm is deposited on a glass substrate by screen printing. The conversion layer is placed in front of the PLED such that the green emission from the PLED pumps the phosphor. Photons are therefore down-converted into deep red phosphor photoluminescence (PL). Finally, we get a NIR emission with a wavelength between 700 and 800 nm by a bandpass filter. The active layer of the NIR PD is the blend of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) where P3HT is the electron donor and PCBM is the acceptor. We observe NIR absorption and photoresponse from 650 to 950 nm due to a PCBM aggregate [5], [6] in the P3HT:PCBM blend with a thickness up to several micrometers. A P3HT:PCBM (1 : 1 wt%) solution in 1,2-dichlorobenzene is drop cast and slowly dried at room temperature upon PEDOT:PSS to form a 8.3-μm thick film. The PD is completed by coating a Ca/Al cathode. All devices are processed and packaged in a glove box.

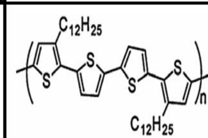
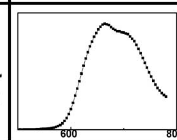
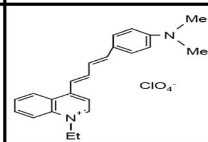
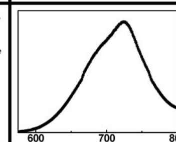
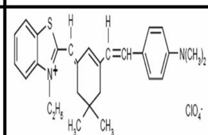
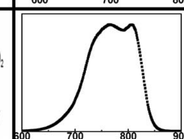
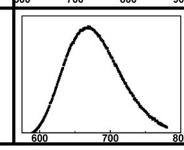
III. Results and Discussions

The schematic working principle of a NIR proximity sensor is shown in Fig. 1. The PLED with a NIR conversion layer and the polymer PD are placed side by side in the same plane to form a proximity sensor. In principle, they can be integrated on the same flexible substrate not only as a single pixel but also as an array. For simplicity, they are made on separate glass substrates in this paper. An object is placed in a normal direction with changing distances. Fig. 2 shows the absorption and PL spectra of the powder of the R670 phosphor. The emission of R670 peaks at 670 nm and extends up to 800 nm with a wide excitation range from 200 to 640 nm. In Table I, the R670 phosphor is compared with other organic conversion materials including the typical red polymer poly(3,3-didodecylquaterthiophene) and the laser dyes 798 and 821. PL quantum efficiency of R670 is by far the highest. With this efficient conversion layer, a clear reflected signal under low PLED bias becomes possible. Current density and luminance of the green PLED are shown in Fig. 3. The PL and absorption spectra of the R670 conversion layer as well as the electroluminescence (EL) spectrum of the green PLED are shown in Fig. 4. There is a major overlap between the EL of the green polymer and the absorption of the phosphor, resulting in an efficient NIR emission. By utilizing a bandpass filter, the operation wavelength is located between 700 to 800 nm with a peak at 716 nm. External quantum efficiency (EQE), defined as the number of electron per photon, of the PD made of a blend with a thickness of 8.3 μm under a reverse bias of 20 V is shown in Fig. 5. Despite of the wide band gaps of both P3HT and PCBM, the PD has an EQE value of around 20% at a wavelength of 750 nm. A reverse bias of 20 V is used in the measurement below.

Characteristics of a single proximity sensor under a static condition is shown in Fig. 6. The pixel contains one PD surrounded by four PLEDs on its four sides. The active areas of the five devices are all 1 × 1 cm, and they are on the same plane. A white paper as the object is placed in parallel to the plane. OFF current is defined as the PD current when the PLED is off; it is the summation of PD dark current and photocurrent due to background indoor lighting. The OFF current (empty square) is shown in Fig. 6 as a function of the white paper normal distance. It decreases as the distance is reduced because more indoor light is blocked. Net photocurrent is the difference between PD currents at a PLED ON-state and a PLED OFF-state. The only origin of the net photocurrent is the light emitted by the PLED and reflected by the white paper. For a fixed PLED voltage at 6 V, the net photocurrent, directly determined by the object distance, is plotted against the distance in Fig. 6. It increases as distance decreases because there is more reflected light from the PLED. Detection up to 20 cm is realized with a R670 conversion layer and a 700–800-nm bandpass filter. Net photocurrent as a function of PLED voltage at a fixed paper distance of 10 cm is also shown. The PLED is stable below a bias of 10 V.

In order to detect the real-time motion of an object, an electronic system for dynamic measurement is developed for the same pixel. The PLED is driven in a pulsed mode with a

TABLE I
COMPARISON BETWEEN R670 AND THE ORGANIC CONVERSION MATERIALS

Material (Solid Film)	Chemical structures	Emission wavelength (nm)	Photo luminance Conversion Efficiency (%)
PQT-12			1%
Laser dye 798 (blended with polymer matrix)			1.2 %
Laser dye 821 (blended with polymer matrix)			1.4 %
R670 phosphor (blended with binder)			23.3%

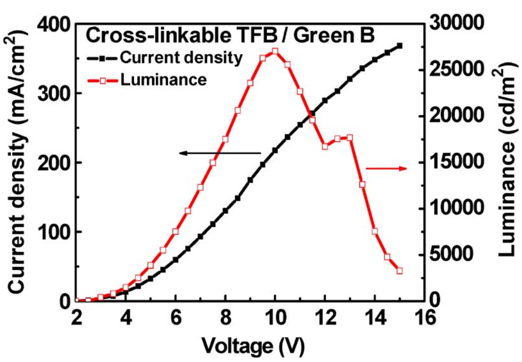


Fig. 3. Current density and luminance of the green PLED.

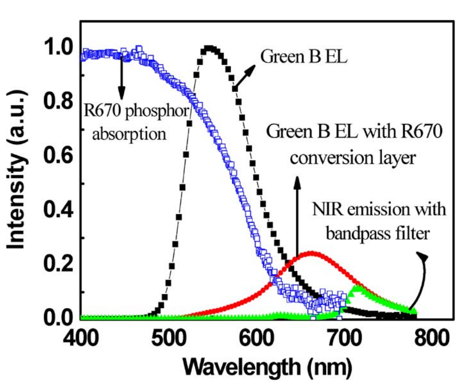


Fig. 4. EL spectrum of Green B (solid square) converted to an NIR emission (solid triangle) by the R670 conversion layer and the bandpass filter.

150-ms period, as shown in Fig. 7. In the first half period, the PLED is on at 6 V, whereas it is off in the second half period. The PD photocurrent is converted into voltage and amplified,

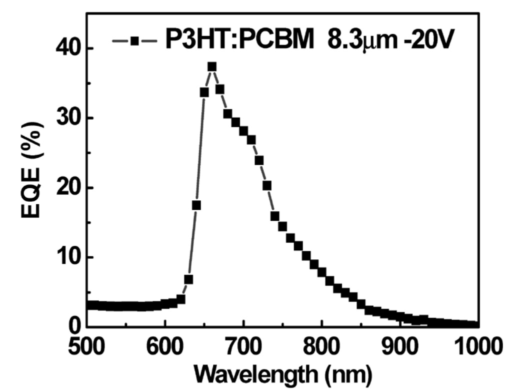


Fig. 5. EQE of the NIR PD with a thickness of 8.3 μm under a reverse bias of 20 V.

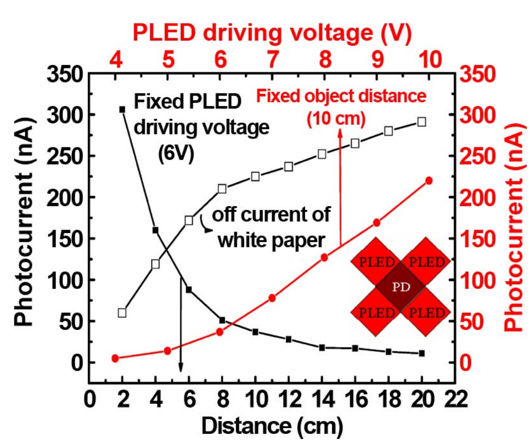


Fig. 6. Characteristics of the single proximity sensor in two different ways: fixed distance (10 cm) versus PLED driving voltage and fixed PLED driving voltage (6 V) versus distance under a static condition.

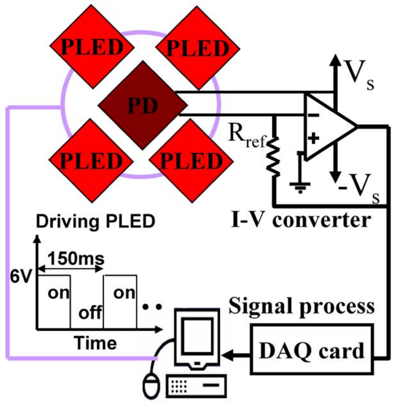


Fig. 7. Electronics system for dynamic measurement to detect the real-time motion of an object.

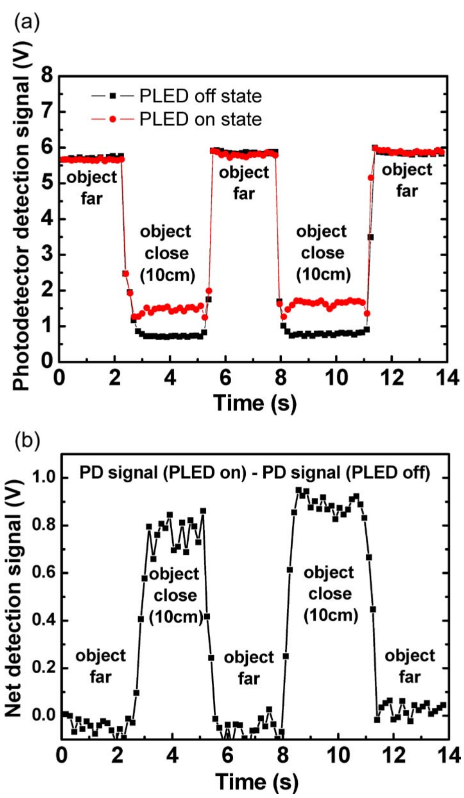


Fig. 8. (a) PD detection signal when the PLED is at the ON-state and when the PLED is at the OFF-state in the single promixity sensor. (b) Net signal after subtraction.

and the amplified signal is then registered by a computer through a data acquisition card, as shown in Fig. 7. The net detection signal in volts is the difference between the PLED ON-state and the PLED OFF-state, both shown in Fig. 8(a). When the object is far, there is no difference between these two because of absence of reflection. When the object is close at 10 cm, the signal is higher as the PLED is on due to reflection. The object moves from far to close several times in Fig. 8(a). The net signal after subtraction is shown in Fig. 8(b). The net signal is zero when the object is far and is around 0.8 V when the object is at 10 cm Proximity of an object is therefore dynamically captured by the pixel.

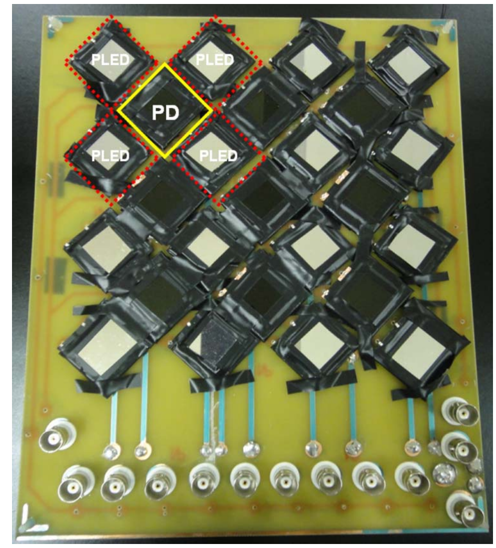


Fig. 9. Nine PD and 16 PLED are integrated into a 3 × 3 array with positions on the circuit board. The amplifiers are on the back side. The terminals for nine output signals are shown on the lower part.

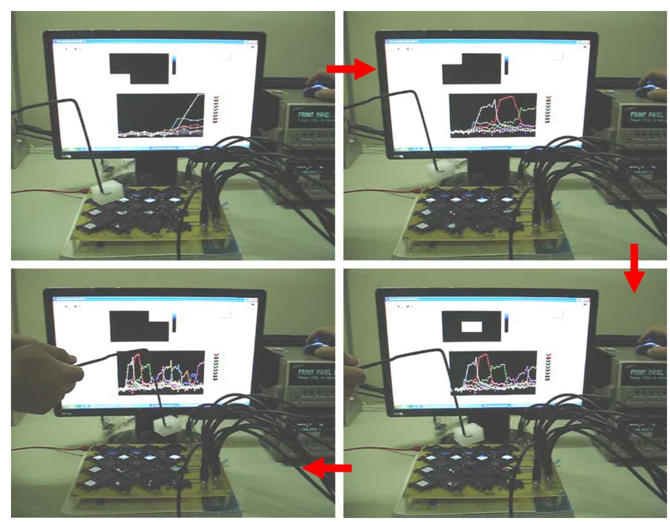


Fig. 10. As the object moves above the array, its position is instantly detected and displayed on the computer screen as a white block. Each block corresponds to one PD in the array.

Finally, nine PD and 16 PLED are integrated into a 3 × 3 array with positions shown in Fig. 9. All devices are driven simultaneously with a 150-ms period as in the one-pixel case. Nine net signals from the nine PD are registered together by the computer once per 150 ms, corresponding roughly to a 7-Hz frame rate. All of devices including the amplifiers are integrated on a printed circuit board, as shown in Fig. 9. In order to demonstrate the location of an object in the computer instantly, in the software, we designate nine blocks on the screen standing for the nine PDs on the circuit board. The block is white as the object is close and black if otherwise. Whereas there is some slight variation in the sensitivity of nine PDs and the performance of sixteen PLEDs, we set up the specific threshold detection signal for each PDs. Finally, Fig. 10 shows the real-time detection of a 4 × 4-cm white paper moving from one side to another continuously, A white block standing for a particular PD will appear on the computer screen when the paper is above it. The real-time detection of other moving objects such as hands is also successful. The light on the PLED is the reflected indoor lighting by the bandpass filter. Note that the operation spectral range from 700 to 800 nm is still barely visible for human eyes. It is however not apparent particularly under a pulsed mode with a low duty cycle and under background lighting. Replacing the lower limit of the filter from 700 to 780 nm makes the emission entirely invisible, but the signal would become too weak. The real-time proximity sensor with an operation wavelength over 700 nm is impossible in the given scheme for other conversion materials listed in Table I due to poor PL quantum efficiency relative to R670.

IV. Conclusion

In conclusion, a near-infrared proximity sensor array is realized by the combination of a PLED, a polymer PD, and, most importantly, an inorganic phosphor to convert visible emission into NIR with high quantum efficiency. The motion of an object 10 cm away from the array is captured and displayed on the computer screen. Because the LED, the PD, and the conversion layer are all processed in a solution, the array can be fabricated in a large area on a flexible substrate to form an artificial skin for robots. Such a robot will be free from collision and can closely interact with humans as it works in complex environments like homes and offices.

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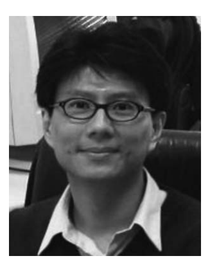

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