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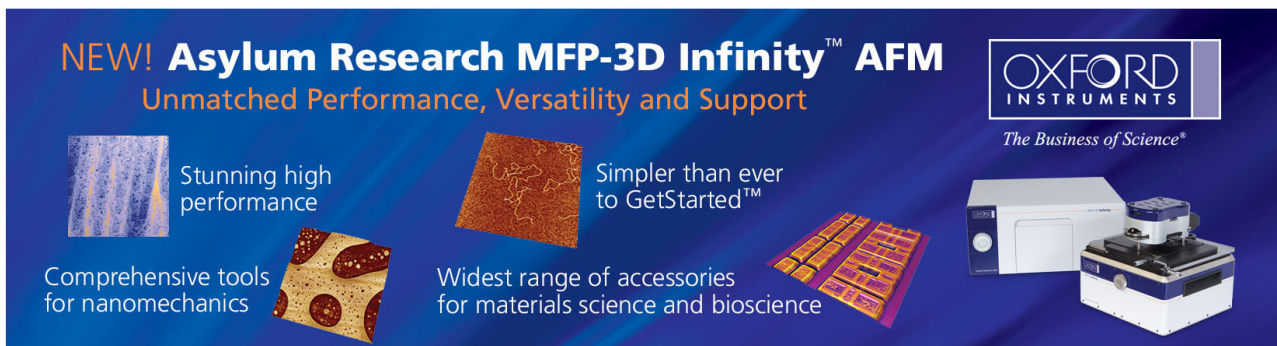
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Polymer infrared proximity sensor

En-Chen Chen,¹ Shin-Rong Tseng,² Jia-Hong Ju,¹ Chia-Ming Yang,¹ Hsin-Fei Meng,^{2,a)} Sheng-Fu Horng,¹ and Ching-Fong Shu³

¹Department of Electrical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

²Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan

³Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan

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A proximity sensor that combines a polymer light-emitting diode and a polymer photodiode is presented. The operation wavelength is in the near infrared from 700 to 850 nm. The infrared emission is obtained by adding a color conversion film of polyvinylpyrrolidone polymer matrix blended with infrared dye 1,1-diethyl-2,2-dicarbocyanine iodide to a red polymer light-emitting diode. The photodetector relies on the direct charge-transfer exciton generation in a donor-acceptor polymer blend of poly(3-hexylthiophene) and (6,6)-phenyl-C₆₁-butyric acid methyl ester. The detection distance is up to 19 cm for objects with various colors and roughness under ambient indoor lighting. © 2008 American Institute of Physics. [DOI: 10.1063/1.2949069]

Organic optoelectronic devices based on conjugated polymers attract a lot of interests in the past decade due to the possibilities of low cost large-area solution process on flexible surfaces. Such unique properties are highly desirable for the development of sensitive skin for a moving machine such as robot or car. If the skin of the machine can be covered by a high density array of proximity sensors it will be able to move in unstructured and unpredictable environments such as homes, crowded streets, or hospitals without collisions.¹ The conventional proximity sensor based on inorganic near infrared (NIR) light-emitting diodes and photodetectors cannot be integrated by monolithic fabrication as an array on flexible substrate, which is essential for robots and other machine surfaces. Contrarily it is rather easy to fabricate polymer light-emitting diodes (PLEDs) and polymer photodetectors on plastic substrates with a high pixel density. Recently, a polymer proximity sensor operating in the visible spectral range was reported² with a detection distance of only 10 mm, which is far below the requirement for robot applications. In order to enhance the detection sensitivity, PLED and photodetector operated in the infrared range are often necessary because the background noise is significantly lower than the visible range. The light scattering is also reduced at longer wavelength. It is, however, difficult to develop polymer semiconductor devices in the infrared because the bandgap of most organic semiconductors is higher than 2 eV corresponding to the photons in visible range. Nevertheless a few low bandgap organic semiconductors are synthesized for applications in NIR range.^{3,4} In this work we use a polymer donor-acceptor blend to detect the NIR photon in the proximity sensor. Even though both the donor and the acceptor absorb only a photon in the visible range, a charge-transfer exciton can be directly generated by a photon in the NIR range as an electron from the valence band of the donor is excited to the conduction band of the acceptor. Infrared PLEDs are made by adding a color conversion film composed of a polymer host blended with an infrared dye to the red PLED. The operation wavelength is between 700 and 850 nm. The polymer proximity sensor works for a wide

range of objects including paper with various colors, skins, and clothes under background indoor lighting.

The PLED and photodetectors are fabricated on glass substrates with a poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer on a patterned indium-tin-oxide layer. The PEDOT:PSS film is baked at 200 °C for 15 min in an ambient environment. In PLED the emissive layer is formed by spin coating LUMATION RP158 red polyfluorene derivative (from the Dow Chemical Company, now Sumitomo) and then baking at 130 °C in nitrogen atmosphere for 20 min. The NIR dye 1,1-diethyl-2,2-dicarbocyanine iodide⁵ purchased from Sigma-Aldrich is blended with a polymer matrix of polyvinylpyrrolidone (PVP) also from Sigma-Aldrich. The concentration of the dye is kept low to avoid self-quenching.⁶ The convertor is made of the blend film with thickness of 10 μm deposited on a plastic substrate by drop casting from dimethyl sulfoxide solution. The convertor is placed in front of the PLED such that the red emission from the PLED pumps the dye and becomes converted into the NIR photoluminescence (PL). The PLED device structure is shown in Fig. 1(a) together with the chemical structures of the dye and polymer host PVP. The active material for the NIR photodetector is the donor-acceptor blend of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM) developed for solar cell application where P3HT is the donor and PCBM the acceptor.⁷ We observe the NIR absorption of the P3HT:PCBM blend with thickness up to several microns due to charge-transfer excitons which peak at 750 nm and extends up to 950 nm. P3HT:PCBM (1:1 wt %) solution in 1,2-dichlorobenzene is drop cast in PEDOT:PSS to form a 14 μm thick film and slowly dried at room temperature in nitrogen atmosphere. The device is coated with Ca/Al cathode and then packaged in the glovebox. The whole process is completed in nitrogen atmosphere. The structure of the photodetector and the chemical structure of donors and acceptors are shown in Fig. 1(b). Note that the infrared photon is detected by the excitation of a charge-transfer exciton existing at the interface between the donor and acceptor, which is schematically shown in Fig. 1(c). Without such a charge-transfer exciton the donor-acceptor blend would be transparent in the infrared.

^{a)} Author to whom correspondence should be addressed. Electronic mail: meng@mail.nctu.edu.tw.

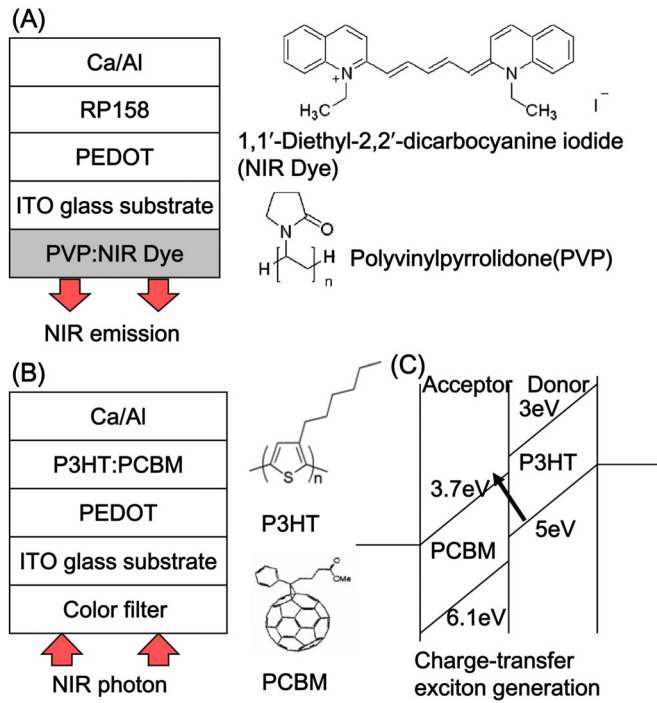


FIG. 1. (Color online) Device structures of (a) the NIR PLED, (b) the NIR photodiode, and the chemical structure of NIR dye, PVP, P3HT, and PCBM. (c) Illustration of the charge-transfer exciton generation at the interface between the donor and acceptor.

The PL and absorption spectra of the NIR dye in a solution and in a film as well as the electroluminescence (EL) spectrum of the red PLED are shown in Fig. 2(a). There is a major overlap between the EL of the red polymer and the absorption of the NIR dye, resulting in an efficient NIR emission. The peak of the NIR emission is of 750 nm. The concentration of the NIR dye is 0.4 wt% in PVP. The luminescence-voltage characteristics of the red PLED with and without the color converter are shown in Fig. 2(b) together with their emission spectra. Even though the color conversion film is as thick as 10 μm the red emission is about the same as the NIR emission due to the small absorption cross section of the conversion film with low concentration of the dye. Nevertheless due to the high luminescence of the red PLED the NIR emission is strong enough for the proximity sensor when the PLED is biased at only 9 V.

Compared to NIR emission the detection of the photons in NIR range is more challenging. The detail of NIR detection is reported elsewhere.⁸ The incident photon to current conversion efficiency (IPCE), defined as number of electron per photon, of a photodetector made of a blend with thickness of 200 nm under reverse bias of 5 V is shown in Fig. 3. The photocurrent spectrum basically follows the absorption spectrum of P3HT and the device responds only to the visible photons with the residual response at the NIR barely seen. As the blend film thickness is increased to 14 μm the NIR photocurrent response due to the charge-transfer excitation dominates the IPCE spectrum. The reverse bias of 10 V is used in the proximity sensor measurement below.

The PLED with NIR color converter and the polymer photodetector are placed side by side in the same plane to form the proximity sensor. The active area is 0.25 cm^2 for both PLED and photodetector. In principle they can be integrated on the same substrate not only as a single pixel but also as an array. For simplicity they are made on separate

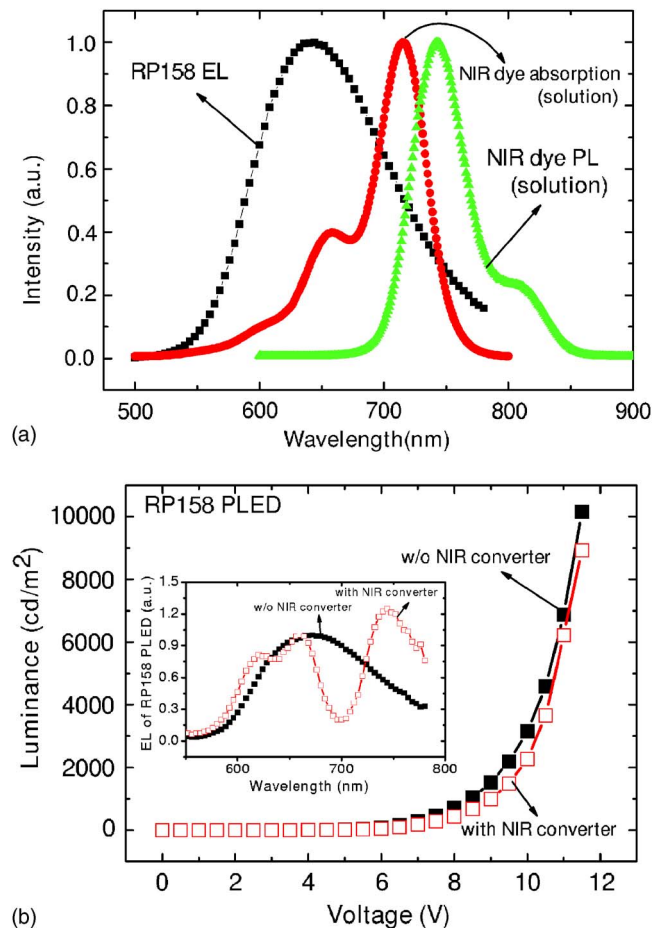


FIG. 2. (Color online) The panel shows (a) the EL spectrum of RP158 (solid square) and the absorption (solid circle) as well as PL (solid triangle) spectra of the NIR dye in methanol, and (b) the luminescence-voltage characteristics of the red PLED with (empty square) and without (solid square) the NIR color converter. Inset is the EL spectra.

glass substrates in this work. An object is placed in the normal direction with changing distances. We measure the NIR proximity sensor in two different modes, dc mode and ac mode. In the dc mode the photocurrent is obtained by subtracting the off current from the on current when the NIR PLED is turned on. The dark current is independent of the object while the ambient infrared current depends on the distance of the object since it either blocks or reflects the ambient lights. The total off current as a function of the distance is shown in Fig. 4(a) as the object is a white paper. The dark current contributes about 50 nA. The proximity of the white paper can be detected up to a distance of 15 cm when the PLED bias is 9 V. Objects with surface not normal to the sensor will give lower signals. However for a high density sensor array the area of the object closest to the array is always locally normal.

Objects with different colors and roughness are compared. Five colors of paper are measured, including white, black, red, blue, and green. White styrofoam with rough surface and aluminum foil with glossy surface are also compared. The maximum detection distances are 15 cm for white and red papers, 12 cm for green and blue, and 9 cm for black. The detection sensitivity depends on the NIR absorption of the surfaces. Therefore the detection distances of red and white are the largest due to the lowest absorption of NIR. On the contrary the detection distance of black materials is shortest due to the largest absorption of NIR. The detection

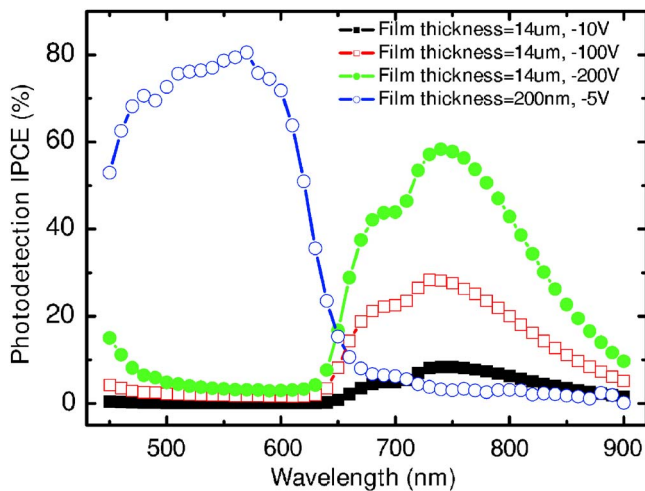


FIG. 3. (Color online) The IPCE of the photodiodes with different film thicknesses under reverse bias are shown. Devices with a 14 μm thick film under the reverse bias of 10 V (solid square), 100 V (empty square), and 200 V (solid circle) respond to photons in the NIR range. The device with the film thickness of 200 nm (empty circle) only responds to the photons in the visible range.

distances are 15 cm for styrofoam and 15 cm for aluminum foil. The sensitivity for the detection of skin and clothes is about the same as white paper.

Even though the detection is achieved, the sensitivity of the dc mode of detection is limited by the large background off current, which exists before the PLED is turned on. In order to remove the background we perform on ac mode of detection where the PLED is modulated by a square wave of 10 Hz and a lock-in amplifier is used to read the modulated signal. The interferences from the ambient light and the dark current are removed. The results of ac mode measurement are shown in Fig. 4(b). Here we use a resistor to convert the photocurrent to voltage, which can be measured by the lock-in amplifier. As expected the background signal before the PLED is turned on is now much smaller than the desired signal with the PLED switched on. There is now no need to subtract a large background as in the dc mode. The maximum detection distances are 19 cm for white and red papers, 17 cm for green and blue, and 9 cm for black. In the comparison of different surfaces the maximum detection distances are 15 cm for styrofoam and 19 cm for aluminum foil. Although the detection distance is effected by the color and surface roughness of the object, the detection distances for all the materials are larger than 9 cm. We expect all other objects in common surroundings of the moving machine to have a higher reflection of NIR light than the black paper and can, hence, be detected beyond 10 cm distance. By the fabrication of arrays of such NIR PLED and photodetector in a flexible substrate as sensitive skin the moving machine will be able to avoid collisions with random objects as it navigates through unstructured environment.

In conclusion we have combined a PLED and a polymer photodiode to make an optical proximity sensor. The operation of the sensor is in NIR range to reduce the influence of the scattered light and the visible light noise. The detection distance depends on the color and roughness of the object surface. The maximum detection distance under normal incidence is almost 20 cm for white paper, styrofoam, and aluminum foil. For all the objects the detection distances are

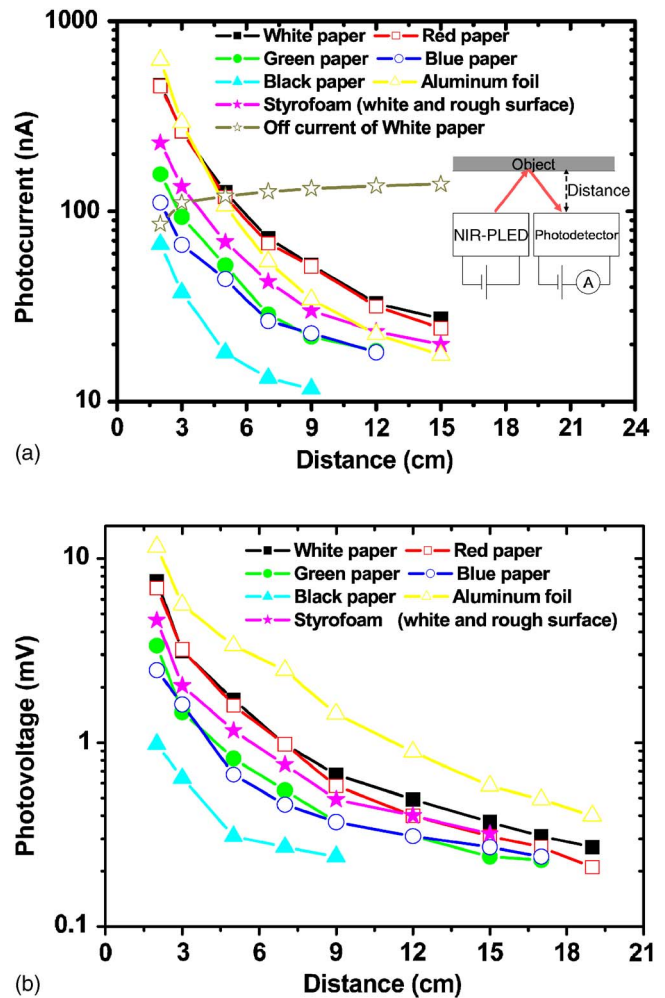


FIG. 4. (Color online) The response of the detection as function of the distance of white paper (solid square), red paper (empty square), green paper (solid circle), blue paper (empty circle), black paper (solid triangle), aluminum foil (empty triangle), and styrofoam (solid star) measured in (a) dc mode and in (b) ac mode. The total off current is composed of the device dark current and photocurrent induced from surrounding NIR is also shown on the panel (empty star). The inset shows the schematic working principle of the polymer proximity sensor.

larger than 9 cm, which is enough for the application in skins of robots or machines, which need to move in an unpredictable surrounding.

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