



# High speed responsive near infrared photodetector focusing on 808 nm radiation using hexadecafluoro-copper-phthalocyanine as the acceptor

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## ABSTRACT

We have demonstrated an organic photodetector (PD) which can detect 808 nm radiation in near infrared (NIR) region. The photodiode has a hybrid planar-mixed heterojunction structure: ITO/CuPc (10 nm)/CuPc:F16CuPc (1:2, 30 nm)/F16CuPc (20 nm)/LiF (1 nm)/Al. Here, CuPc and F16CuPc denote copper-phthalocyanine and hexadecafluoro-copper-phthalocyanine complexes, respectively. The photodiode behaves a response time of 80 ns and a bandwidth of 14 MHz, which are higher than those of recent reports. At the same time, the response waveband of the photodiode covers longer wavelength in NIR comparing to the PD reported. It is conjectured that the high detection performance is due to high electron-mobility of F16CuPc, the large band edge offset between D/A molecules as well reasonable design of the diode structure. The detail working mechanism is also augured.

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## 1. Introduction

Organic photodetectors (PDs) have been the subject of extensive research in the past decade due to several inherent advantages such as large-area detection, wide selection of materials and low-cost fabrication on flexible substrates [1–4]. Except for ultraviolet and visible PDs, organic near-infrared (NIR) PDs also have tremendous potential in industrial and scientific applications, especially commercial and military field including night vision, tomography and so on. Communication applications also need to extend organic PD sensitivity to the NIR waveband [5–8]. It is considered that the more the NIR absorption of an organic compound is, the stronger the PD response is in NIR spectral region. However, the photo-response spectrum of the reported NIR PDs were almost apart from NIR waveband [5–7], even a photo-response spectrum covered some red light radiation

[6,7]. Campbell et al. have reported a photoconductive type NIR PD, but its response bandwidth was too low (only 3 kHz) [8]. Image generation demands periodic read-out of a detector signal, hence the frame rate for image generation is dependent on the response speed of a PD [9]. It has been recognized that upon optical excitation of an organic material, localized Frenkel or charge-transfer excitons are generated, then energy level offsets at heterojunctions are essential to separate excitons because of the fundamental nature of the photogeneration process in organic materials [10].

We note that a CuPc derivative, hexadecafluoro-copper-phthalocyanine (F16CuPc) complex, presents two absorption peaks, 725 and 808 nm in the NIR spectral region, and is used as an electron acceptor in solar PV cells [11]. In addition, the complex behaves the highest occupied molecular orbital (HOMO) of –6.3 eV and lowest unoccupied molecular orbital (LUMO) of –4.9 eV [12]. In light of above spectral and electrical behaviors of F16CuPc and well-known hole transporting property of CuPc, in this letter CuPc and F16CuPc will be used as the electron donor and acceptor of the PD, respectively. The photocurrent response peak of

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the fabricated photodiode lies at 808 nm in the NIR waveband and it behaves fast response speed which could satisfy some special applications, such as medical back-check [13], etching technique [14].

## 2. Experimental

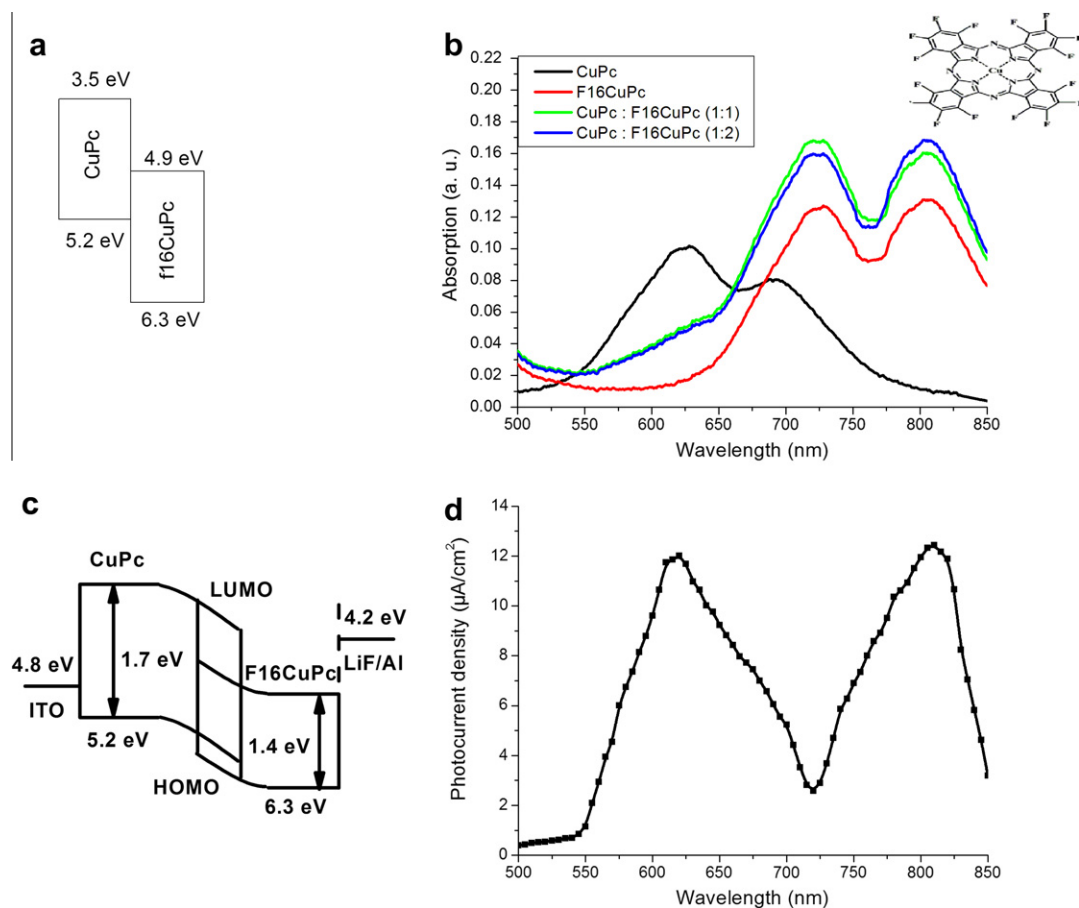
The NIR PD has the three-layer structure, ITO/CuPc (10 nm)/CuPc:16FCuPc (1:2, 30 nm)/F16CuPc (20 nm)/LiF (1 nm)/Al (200 nm), which is called as an organic hybrid planar-mixed heterojunction (H-PMHJ), that is, the blend of CuPc and 16FCuPc is sandwiched in between two layers. The advantage of this PD structure is that two diodes with planar heterojunction and mixed heterojunction, respectively, can be combined into a single device by stacking their high-efficiency regions in the H-PMHJ diode.

F16CuPc is purchased from Suzhou-Nakai Sunatech Inc., and other materials were commercial materials which were not further purified before use. The photodiodes were fabricated on cleaned indium tin oxide (ITO) coated glass substrates with a sheet resistance of  $25 \Omega/\text{sq}$  in vacuum chamber and the device active area is  $2 \times 2 \text{ mm}^2$ . The organic layers were deposited at a rate of  $2 \text{ \AA/s}$ , and the evaporating rate of LiF and Al cathode were controlled to

be 0.5 and  $10 \text{ \AA/s}$  with the thickness of 1 and 200 nm, respectively. All the vacuum chambers were also controlled at a pressure of  $5 \times 10^{-4} \text{ Pa}$  and deposition rates and thickness of the layers were monitored using oscillating quartz monitors. Absorptions of films and photocurrent spectral responses of the PDs were measured with a Shimadzu UV-3101 PC spectrophotometer and a Hitachi F-4500, respectively. Current–voltage ( $I$ – $V$ ) characteristics of the PD devices were recorded in dark and under illumination of 808 nm NIR light with different intensities and through the ITO side. NIR light source was provided by an LD-009 infrared laser diode with 808 nm radiation which was powered by a Keithley 2400 SMU. Transient response was measured and the output signal was displayed on a 500 MHz digital oscilloscope (TDS 3052, Tektronix). The LUMO and HOMO levels of CuPc were cited from Ref. [15]. All the measurements were carried out at room temperature under an ambient condition.

## 3. Results and discussion

Fig. 1a depicts schematic energy level diagram at the interface of CuPc/F16CuPc and the LUMO level difference between CuPc and F16CuPc is 1.4 eV. This indicates that



**Fig. 1.** (a) Schematic energy level diagram at the interface of CuPc/F16CuPc. (b) The solid state absorption spectra of neat films of CuPc and F16CuPc as well as blend films of CuPc:F16CuPc with 1:1 and 1:2 ratios by weight, respectively, inset: chemical structure F16CuPc. (c) The schematic level diagram corresponding to the H-PMHJ structure PD. (d) The photocurrent response as a spectrum at zero bias.

at such a DA interface the charge separation of the photo-generated excitons easily occurs because 1.4 eV is markedly larger than the coulombic force of the binding electron and hole pair (exciton) [16]. Fig. 1b illuminates the solid state absorption spectra of the neat films of CuPc and F16CuPc as well the blend films of CuPc:F16CuPc with 1:1 and 1:2 by weight ratio, respectively. From Fig. 1b it can be seen that the neat F16CuPc film shows the two absorption bands which locate at 725 and 808 nm, respectively, in NIR range and the longer waveband can be extended out to 1000 nm. We also note that both the two blend films have higher absorption intensity over the neat F16CuPc film at the NIR spectral region and the 808 nm absorption intensity of the 1:2 blend film is considerably higher than that of the 725 nm peak.

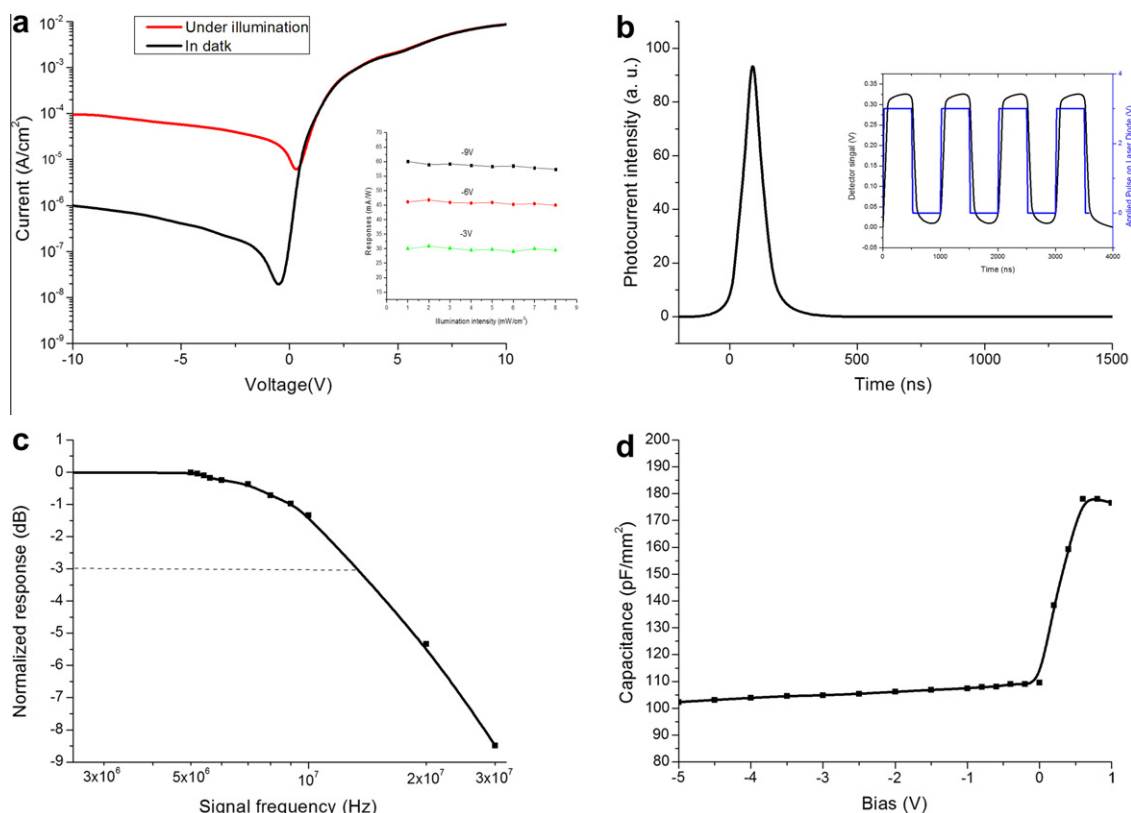
In terms of above the absorption properties of the blend films and energy level alignment between CuPc and F16CuPc, the 1:2 blend film was used to construct a PD which has H-PMHJ structure with ITO/CuPc (10 nm)/CuPc:F16CuPc (1:2, 30 nm)/F16CuPc (20 nm)/LiF (1 nm)/Al. The schematic level diagram of the photodiode is described in Fig. 1c can offer a maximum photocurrent response of about  $12.5 \mu\text{A}/\text{cm}^2$  at 808 nm peak, while 725 nm absorption peak (see Fig. 1b) does not almost con-

tribute to the response, as showed in Fig. 1d. It is surprised that there is a wave-trough at 720 nm which response is around 5.7 times lower than response for 808 nm. Thus, an organic PD with pure 808 nm NIR photo-response could be realized by using a cut-off filter (see the latter of the text).

In order to understand the photo-response feature, we used the 808 nm NIR laser diode with continuous work mode and the monochromatic light source to determine the photo-response. Fig. 2a illuminates the current–voltage ( $I$ – $V$ ) characteristics of the photodiode. From Fig. 2a we can speculate a rectification ratio of  $10^4$  at  $\pm 10$  V biases. Power conversion efficiency (PCE) of 0.2% was obtained under 808 nm laser illumination. The device showed an external quantum efficiency (EQE) of 9.22% at  $-9$  V under illumination with 808 nm radiation. The photodiode figure of merit is the noise equivalent power (NEP), i.e., the minimum impinging optical power that a detector can distinguish from the noise can be shown by the formula (1)

$$\text{NEP} = (A\Delta f)^{1/2} / D^* \quad (1)$$

where  $A$  is the effective area of the photodiode in  $\text{cm}^2$ ,  $\Delta f$  is the electrical bandwidth in Hz, and  $D^*$  is the detectivity measured in units of Jones. The detectivity can be



**Fig. 2.** (a)  $I$ – $V$  characteristics of the photodiode in the dark and under 808 nm laser radiation with an intensity of  $3 \text{ mW}/\text{cm}^2$ . Inset: the photocurrent response of the NIR PD at different biases. (b) Photocurrent response of the photodiode based on the structure of ITO/CuPc/CuPc:F16CuPc/F16CuPc/LiF/Al under 808 nm stimulation with 100 ns pulse-width, inset: time response of the same detector to a train of light pulses at a wavelength of 808 nm and with a 1 MHz repetition frequency. (c) Frequency response of the photodiodes with a device area of  $2 \times 2 \text{ mm}^2$ . (d) Capacitance–voltage measurements at frequency of 10 kHz.

expressed as reported by Refs. [17,18],  $D^*$  is shown by the formula (2)

$$D^* = R/(2qJ_d)^{1/2} \quad (2)$$

where  $R$  is the response (as shown in Fig. 2a inset),  $q$  is the absolute value of electron charge ( $1.6 \times 10^{-19}$  C) and  $J_d$  is the dark current. At zero bias the calculated detectivity using Eq. (2) is, respectively,  $D^* = 4.6 \times 10^{10}$  Jones at  $-9$  V and  $5.2 \times 10^{10}$  Jones at  $-6$  V for our NIR photodiode under illumination of 808 nm NIR laser with an intensity of  $3 \text{ mW/cm}^2$ . Fig. 2b displays the photocurrent response of the photodiode under 808 nm NIR stimulation with 100 ns pulse-width, and inset is the time response of the same detector to a train of light pulses at a wavelength of 808 nm and with a 1 MHz repetition frequency. From Fig. 2b both the rise and fall times of 80 ns were obtained. Fig. 2c indicates the frequency response of the photodiode with an area of  $2 \times 2 \text{ mm}^2$ , it has been attained that at this area a bandwidth is about 14 MHz at  $-9$  V bias. According to Fig. 2a and c using Eq. (1), a NEP of  $1.7 \times 10^{-12} \text{ W}$  was calculated. Capacitance of the PD was almost independent of reverse bias by capacitance–voltage measurements in Fig. 2d, which was in contrast to the p-i-n or Schottky-barrier PDs made of inorganic semiconductors. Thus, fast response could be achieved even at zero or low biasing voltage.

In light of the data shown in Fig. 2, we concluded that our 808 nm NIR PD behaved more fast response speed and wider response bandwidth than those of reported NIR PDs [5–9]. At the same time, the spectral peak of our NIR detector focuses on 808 nm which was also much longer than those of reported NIR PDs [5–8], though the EQE at 808 nm needs to be improved further.

The achievement of so good NIR detection performance can be understood as bellow. One of main reasons is the higher hole mobility of  $7 \times 10^{-4} \text{ cm}^2/\text{V s}$  for CuPc [15] and electron mobility of  $4.2 \times 10^{-4} \text{ cm}^2/\text{V s}$  for 16FCuPc which were measured in our lab; another is that the larger band edge offsets between DA molecules [11] is beneficial

to exciton dissociation. The response time of planar heterojunction device was 80 ns, which also thanked to adoption of H-PMHJ structure which favoured the efficient exciton dissociation and charge-carrier generation throughout the blend layer as well at the interfaces between the mixed and two adjacent homogeneous layers in the NIR PD. So, excitons had higher probability to reach at DA interfaces prior to recombination. By adding the charge transport layers at two sides of the blend layer, a higher efficiency for extraction of photogenerated charges from and through the blend layer was obtained because the intermolecular distances in D:A blend extent were significantly shorter than that of corresponding charge collection length at either built in field or in addition of the reverse bias. The higher hole and electron mobilities would be in favor of balancing the charge carrier transports in order to collect charge carriers generated.

In addition, we noted that the photocurrent response spectrum of our NIR photodiode also covered visible region from 400 to 700 nm. If the PD is required to detect the NIR waveband, we could use a filter – IPG-700T2 filter to block visible light so that only the NIR radiation can enter into the PD. The photocurrent response of the diodes with the filter is shown in Fig. 3. It is seen that the NIR waveband response is unchanged.

#### 4. Conclusion

In conclusion, CuPc and 16FCuPc with high carrier mobilities act as the D and A species were used in the NIR photodiode and its photocurrent response spectral peak focused on 808 nm. The photodiode having H-PMHJ structure offered a response time of 80 ns and a response bandwidth of 14 MHz, respectively, which were higher than the recent reported results, though the EQE needed to be further improved. The high performance of a PD would be ascribed to larger energy edge offsets of CuPc and 16FCuPc, balance of free carrier transport forwards to the two electrodes and stronger absorption at the NIR waveband of the 16FCuPc,

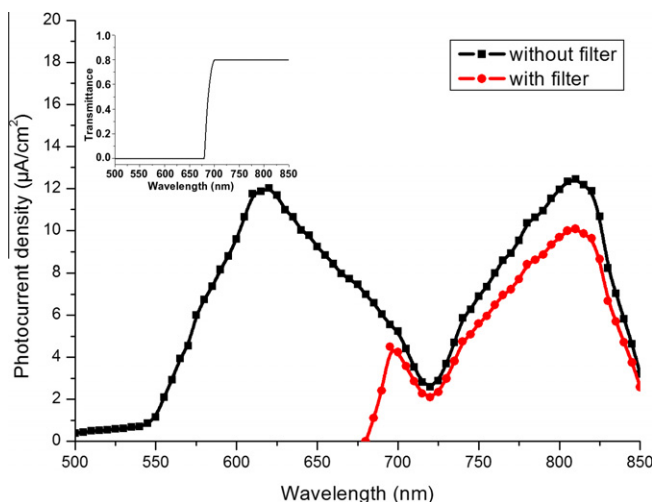


Fig. 3. The photo-response spectra of the H-PMHJ structure photodiode with the NIR through filter. Inset: transparency of IPG-700T2 type filter.

as well skillfully diode design. If the PD is asked to only detect NIR waveband, the photo-response at the visible spectral region must be reduced by selecting such DA materials having no visible absorption.

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