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Organic near-infrared upconversion devices: Design principles and operation mechanisms

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ABSTRACT

Optical upconversion devices up-converting near-infrared (NIR) light to visible light have attracted a great deal of research interest in the past decades. Among these devices, organic upconversion devices have been presented as an alternative strategy for simplifying the fabrication process and reducing the cost. In recent years, along with the development of organic electronics, several types of organic NIR upconversion devices have been reported. However, there have been very few systematic studies of the design principles and operation mechanisms of organic NIR upconversion devices. In order to illustrate the structural design principles and operation mechanisms, organic upconversion devices based on donor/acceptor planar heterojunction (PHJ) as NIR sensitizer and inverted OLED structure as emitter are fabricated and studied. Significantly, two types of photo-generated electron and hole based organic upconversion devices are realized by ingeniously exchanging the position of the PHJ and the inverted OLED in the devices, respectively. The light emission in the former results from the recombination of photo-generated electrons with the injected holes from the anode, while that of the later from the recombination of photo-generated holes with the injected electrons from the cathode. Both types of the upconversion devices demonstrated great potentials for future pixel-less NIR imaging applications.

1. Introduction

Near-infrared (NIR) imaging devices have attracted a great deal of research interest because of their potential applications in night vision, security, semiconductor wafer inspections as well as medical imaging [1–4]. An important alternative approach for NIR imaging is to up-convert NIR light to visible light that can be effectively detected by naked eyes or commercially available digital cameras. In the last two decades, various device architectures for NIR upconversion devices based on inorganic, hybrid organic/inorganic and organic materials have been reported [5–21]. Among these upconversion devices, organic optical upconversion have been presented as an alternative strategy for simplifying the fabrication process and reducing the cost due to the various advantages of organic semiconductors.

Early organic upconversion devices were investigated as photoresponsive organic light emitting diodes (OLEDs), in which the organic NIR-sensitive materials, such as titanyl phthalocyanine, were inserted into OLEDs as a photo-carrier generation layer and/or a buffer layer [17,18]. In recent years, along with the development of organic electronics, such as OLEDs, NIR organic photodetectors (OPDs) and organic photovoltaic (OPV) devices, several novel organic NIR upconversion devices realized by integrating NIR-sensitive bulk heterojunction (BHJ) into phosphorescent OLEDs have been reported [19–21]. D. Y. Kim and co-workers first reported this typical structure of organic NIR upconversion devices via integrating tin phthalocyanine (SnPc): C_{60} BHJ into phosphorescent OLEDs [19,20]. In their upconversion devices, the BHJ was designed as a poor-hole-transport NIR-sensitizing layer to keep the OLEDs in the off state in the absence of NIR illumination. And under NIR illumination, the holes generated from the BHJ are injected into

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the emitting layer and recombine with the electrons injected from the cathode to give off visible light. Much recently, S.-W. Liu and coworkers reported an organic NIR upconversion device for 3D imaging with a similar structure using chloroaluminum phthalocyanine: C_{70} BHJ as NIR sensitizer [21]. However, concluding the summary of the recent publications, there have been very few systematic studies of the design principles and operation mechanisms of organic NIR upconversion devices.

Organic NIR upconversion devices can be easily realized by integrating a NIR-OPD (or NIR OPV) and an OLED into one device. Light absorption in the active layers of an OPD or OPV leads to the generation of excitons, then excitons can be dissociated into free charge carriers, i.e., photo-generated electrons and holes. Therefore, organic upconversion devices can also be designed to achieve with photo-generated electrons or holes. However, only photo-generated hole based organic upconversion devices were reported up to now [17–21]. In addition, OLEDs can be classified by the position of their electrodes relative to the substrate, namely conventional OLEDs and inverted OLEDs. An inverted OLED consists of a bottom cathode (in contrast to a bottom anode in conventional OLEDs) followed by the formation of an electron transport layer, a light emission layer, a hole transport layer and an anode, and has been widely studied to match the existing n-type amorphous silicon thin film transistor technology [27–33]. By introducing the inverted OLEDs structure, top-emitting or transparent organic upconversion devices can be easily realized utilizing transparent conductive metal oxides as top anodes, such as indium tin oxide (ITO) and aluminum zinc oxide. So far, the reported organic upconversion devices as well as hybrid organic/inorganic upconversion devices are always fabricated utilizing the conventional OLEDs structure [13–21]. Herein, it is believed that the upconversion device based on inverted OLEDs structure will be a development tendency in future applications.

For an organic NIR upconversion device, the NIR sensitizer functions as NIR light-sensitive switch, the properties of the sensitizer are critical, which is commonly realized by BHJs. The most reported organic NIR upconversion devices are realized via integrating BHJ as NIR sensitizer with conventional OLED structure. We propose that one can also design upconversion device via integrating BHJ with the inverted OLED structure. According to our unpublished research work, the upconversion device realized via integrating lead phthalocyanine (PbPc):C_{60} BHJ with the inverted OLED structure exhibited very poor performance because of the relatively large dark current density resulted from the poor electron blocking efficiency of the BHJ layer. Planar heterojunctions (PHJs) are generally used in OPDs and OPVs, which can also exhibits high external quantum efficiency (*EQE*) in NIR region by using the certain NIR-absorbing materials, such as PbPc [22–26]. Besides, BHJ mixed films often showed reduced absorption coefficient than PHJ films. For example, the absorption coefficient of the mixed film of SnPc:C_{60} in NIR region is much lower than that of SnPc/C_{60} PHJ due to the suppression of the dimer absorption [19]. Therefore, one can design organic upconversion devices by introducing PHJs as NIR sensitizer. Thus, it is proposed that organic NIR upconversion devices can be realized via integrating donor/acceptor (D/A) PHJs and inverted OLEDs, or integrating A/D PHJs and conventional OLEDs. Moreover, upconversion devices were always realized by integrating OLEDs onto NIR-sensitive layers. Considering charge carriers transport properties in the active layers of PHJ and OLED, one can fabricate both types of photo-generated electron and hole based upconversion devices by reasonably exchanging the position of the PHJ and the OLED in the devices. That is, for the configurations of D/A PHJs and the inverted OLEDs, photo-generated electron based upconversion devices can be realized via integrating inverted OLEDs onto the D/A PHJs (Fig. 1a, Upconversion Device A). While, photo-generated hole based upconversion devices can be realized via integrating D/A PHJs onto the inverted OLEDs (Fig. 1a, Upconversion Device B). In order to verify the design principles and illustrate the operation mechanisms of the proposed organic NIR upconversion devices, we fabricated and studied two types of organic upconversion devices utilizing D/A PHJs as NIR sensitizer and inverted OLEDs as emitter.

In our upconversion devices, PbPc/C_{60} PHJ with a copper phthalocyanine (CuPc) template layer was used as NIR sensitizer, and a simple inverted fluorescent OLED structure with active layers of "2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP)/tris-(8-hydroxyquinoline) aluminum (Alq_3)/1, 4-bis(1-naphthylphenylamino) biphenyl (NPB)" was chosen as emitter, in which BCP is used as electron transport layer (ETL) and hole blocking layer (HBL), Alq_3 as emitting layer (EML) and NPB as hole transport layer (HTL). Both types of the photo-generated electron and hole based upconversion devices were realized by exchanging the position of the NIR sensitizer and the emitter in the devices, as shown in Fig. 1a. The light emission in the former results from the recombination of photo-generated electrons with the injected holes from the anode, while that of the later from the recombination of photo-generated holes with the injected electrons from the cathode.

2. Experimental section

All the organic materials were commercially obtained and used as received. CuPc was purchased from J&K Chemical Ltd., PbPc from Sigma–Aldrich Ltd., and C_{60} from Luminescence Technology Co., Ltd., BCP, NPB and Alq_3 from Jilin OLED Co. Ltd. China, respectively. Devices were fabricated on 30 Ω/square patterned ITO coated glass substrates, which were ultrasonically cleaned by acetone, ethanol and de-ionized water, and were dried with N_2 gas blowing and baked in an oven with a temperature of 60 °C for 20 min. The substrates were UV ozone treated before loaded into a vacuum evaporation system with six organic material thermal evaporation sources. All organic films were successively deposited on the substrate with a vacuum level below 1.0×10^{-4} Pa without breaking vacuum, and the deposition rates were kept at the range of 0.75–1 nm/min (monitored by a quartz crystal oscillator). After organic films were deposited, the samples were transferred into another vacuum chamber with a vacuum level of 8×10^{-4} Pa to evaporate the top electrodes. Top electrodes with 100-nm-thick Al or 70-nm-thick Au were vacuum deposited through a shadow mask which defined an active area of ~16 mm^2. In this paper, two upconversion devices and a typical D/A PHJ NIR-OPD (schematic device architectures as shown in Fig. 1) were fabricated and characterized.

In the measurement, devices were bottom-up loaded in a vacuum chamber (vacuum level ~10 Pa) with a top glass window for viewing and light incoming, and images were captured using a digital single-lens reflex camera. Current–voltage (*I–V*) characteristics of devices were measured using an organic semiconductor characterization system, coupled with a picoammeter connected to a calibrated Si photodiode (HAMAMATSU S1223) for photocurrent measurements. A commercially available NIR laser with a power density of 200 mW/cm^2 and emission centered at 850 nm was used as the light source. And the variation in light intensity was achieved by neutral density filters with various transmittances. For NIR optical absorption measurements, PbPc or CuPc (50 nm)/PbPc films with different PbPc layer thickness of 10, 20, 30 and 40 nm were deposited on cleaned quartz substrates, respectively. And a TU-1901 spectrometer was used for the measurements of absorption spectra.