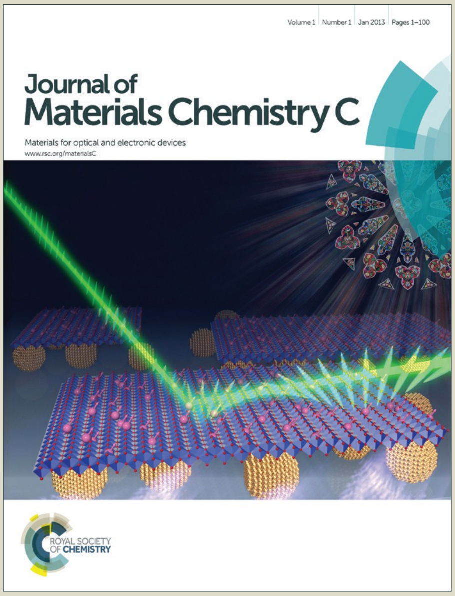
Journal of Materials Chemistry C

Accepted Manuscript



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Dual-function optoelectronic polymer device for photoelectric conversion and electroluminescence

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Abstract: A novel polymer-based optoelectronic device is created to independently realize either photoelectric conversion or light emission. It is produced by coating photoactive materials on one side of an aligned carbon nanotube sheet electrode and polymer light-emitting materials on the other side of the carbon nanotube sheet electrode through an all-solution process. The power conversion efficiency exceeds 2% and the brightness reaches 1040 cd/m^2 for photoelectric conversion and light emission parts, respectively. This work indicates a promising potential for a wide variety of applications including micro-electronic, smart and multi-function devices through all-solution-based processes.

Multi-function devices have been recognized as a mainstream direction in the development of the next-generation electronics and may be extensively used in biomedical, military and aerospace fields.[1-6] They can remarkably reduce the number of electronic devices while perceive required functions to commendably meet the requirements in many new emerging fields, for example, portable electronic devices. Currently, a lot of interests are attracted to develop polymer-based electronic devices,[7-13] e.g., polymer-based energy storage devices, polymer solar cells, polymer light-emitting diodes and polymer light-emitting electrochemical cells (PLECs), owing to their many advantages including the diversity of polymer materials and possibility for an all-solution-based process and large-scale production. More importantly, they can be made into flexible and thin films, which satisfy the widely explored portable electronic devices.[14-16] A variety of polymer-based electronic devices are stacked to realize multiple functions with a tedious fabrication, a complex structure and a low performance.[1,3] It is far away from the really integrated single device that has been desired to display two or more functions in a concise and elegant design for many years.

In this Communication, we have developed a novel polymer-based optoelectronic device that can independently realize either photoelectric conversion (PC) or light emission (LE). It is produced by coating photoactive materials on one side of an aligned carbon nanotube (CNT) sheet electrode and polymer light-emitting materials on the other side of the CNT sheet electrode through an all-solution process. The power conversion efficiency exceeds 2% and the brightness reaches 1040 cd/m^2 for the PC and LE parts, respectively.

The structure of the dual-function device is schematically shown in **Fig. 1**. For the PC part, the ZnO nanoparticles had been used as the electron-transporting layer.[12] The crystalline nanoparticles with diameters of appropriately 6 nm (**Fig. S1**) were spin-coated onto the indium tin oxide (ITO) substrate to produce a uniform and compact layer (**Fig. 2a**). The thickness of the ZnO nanoparticle layer was increased and controlled by repeating the coating process. The selective nature of the ZnO nanoparticle layer is necessary and important to achieve a high performance in the PC part.[12] The photoactive layer of poly (3-hexyl thiophene): phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) had been then spin-coated onto the ZnO layer that was also uniform (**Fig. 2b**).[17] Aligned carbon nanotube (CNT) sheet was further paved onto the P3HT/PCBM surface to serve as a hole-transporting layer and electrode to obtain the PC part. The aligned CNT sheet was prepared from a spinnable CNT array and described in the Supporting Information.[18,19] It was flexible and could be easily bent or twisted into various shapes without obvious damages in structure. In addition, it was also transparent and electrically conductive.[18,19] Therefore, the CNT sheet may serve as a high-performance flexible electrode in the electronic device.

Note that the PC part was fabricated without using the hole-transporting layer, e.g., poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), as the existence of water and acid in the PEDOT:PSS solution was harmful to the polymer active layer.[20] Meanwhile, the fabrication of the PC part was remarkably simplified to be beneficial for large-scale applications. The PC part had been fabricated with an inverted structure. The inverted structure was beneficial for the vertical phase separation in the photoactive layer and avoided the use of low-work-function electrodes that were sensitive to air and needed a complex preparation with high cost.[21,22] As a result, the PC part shared the high-work-function CNT electrode with the LE part. Meanwhile, the CNT electrode had been also used as an air-stable layer for the device.

PLECs are explored as a new family of effective electroluminescent devices.[23,24] The PLEC accepted as the simplest light-emitting device is usually composed of an organic semiconductor sandwiched between two electrodes that inspired us to design the LE part at this work. First, the emissive polymer layer was spin-coated at the top of the aligned CNT sheet (**Fig. 2c**). Here the used emissive polymer layer was composed of an emissive conjugated polymer (PF-B) (**Fig. S2**), lithium trifluoromethanesulphonate (LiTf) and ethoxylated trimethylopropane triacrylate (ETT-15).[9,15] ETT-15 and LiTf served as an ionically conductive component and ionic dopant for the formation of a light-emitting PIN junction, respectively. Finally, another aligned CNT sheet electrode (**Fig. 2d**) was paved onto the emissive polymer layer to complete the LE part. The electroluminescent polymer layer of the LE part can form a light-emitting PIN junction *in situ*.[13] The PIN junction can be operated at rough surfaces, which is beneficial for many practical applications with low cost and high efficiency.

The PC and LE functions can be independently operated by connecting the middle CNT sheet electrode with the other electrode in the two parts. When the middle CNT sheet electrode was connected to the ITO electrode, the device converted solar energy to electric energy; when an external bias voltage was applied between the two CNT sheet electrodes, it emitted light. The working mechanism of the dual-function device is summarized below.[22] In the light of the schematic energy level diagram demonstrated in **Fig. 3a**, the photoactive layer produces excitons that are separated into electrons and holes upon connecting the middle CNT sheet and ITO under the light irradiation. The electrons are transported to the ITO electrode through the ZnO nanoparticle layer while the holes are transported to the middle CNT sheet electrode.

To fabricate the PC part, the CNT sheet played a crucial role in achieving high power conversion efficiency due to both high electrical conductivity and hole collection capability. The electrical resistances of the CNT layers (5 mm in width) were gradually reduced from 2.5 to 0.17 kΩ/cm with the increasing thickness from 18 to 360 nm (**Fig. S3**). A series of PC parts had been studied for photovoltaic performances with increasing CNT layer thicknesses. **Fig. 3b** compares the current density versus voltage characteristics under standard air mass 1.5 illumination (100 mW/cm^2). The power conversion efficiencies were increased from 0.78%, 1.02%, 1.28% and 1.87% to 2.07% with the increasing thickness of the CNT layer from 18, 36, 90 and 180 to 360 nm, respectively (**Fig. S4**). The best performance with the efficiency of 2.07% corresponding to an open-circuit voltage of 0.57 V, short-circuit current density of 9.31 mA/cm^2, and fill factor of 39.2%. With the further increase in the CNT layer thickness, the power conversion efficiency remained almost unchanged. Therefore, a thickness of 360 nm for the CNT layer is studied below unless specified otherwise. The aligned CNT sheet was also explored for remarkable thermal and mechanical properties, and the resulting PC part without encapsulation exhibited a relatively high stability that was verified by tracing the efficiency with the time. It could be maintained by over 80% in ten days in dried air (**Fig. S5**). Note that the efficiency of PC part is a little lower than the conventional polymer solar cells with the structure of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al,[25] which is mainly attributed to the inexistence of hole-transporting layer of PEDOT:PSS and Ca/Al cathode that can remarkably improve the performance.

The LE part started to work when the two CNT sheet electrodes were connected.[9,13] It emitted light when an external bias voltage exceeded its turn-on voltage (**Fig. 4a**). The light-emitting PIN junction can be formed *in situ* in the emissive polymer layer without using the low-work-function cathode. Hence, electrons and holes were injected into the emissive polymer layer from the two CNT sheet electrodes. Finally, the electrons and holes re-combined in the emissive polymer layer and subsequently emitted light.

The thickness of the CNT layer at the top was critical to achieve a high brightness, and it was important to balance the optical transmittance and electrical resistance. The optical transmittances of CNT layers had been decreased from over 91% to 77% (at a wavelength of 550 nm) with increasing thicknesses from 18 to 54 nm (**Fig. S6**). In contrast, the resistances of CNT layers were decreased with the increasing thickness. The highest brightness occurred at 1040 cd/m^2 with the CNT layer thickness of 36 nm (**Fig. S7**). To obtain high performances, the CNT layer with the thickness of 36 nm was used below.

Fig. 4b demonstrates the current density-luminance-driving voltage characteristic curves of the LE part. It started to emit light when the voltage was higher than 5.5 V, and the brightness was increased with the increasing applied voltage. The peak brightness of 1040 cd/m^2 was achieved at 27 V. The current efficiency–luminance characteristic curve of the LE part was further shown in **Fig. 4c**. The highest current efficiency was 1.09 cd/A at a brightness of 1040 cd/m^2. The corresponding external quantum efficiency was 0.4%. Note that here the LE part emitted the light with blue-green color. According to the CIE 1931 standard color-matching functions, this can be expressed as (0.22, 0.36) regarding the x,y chromaticity coordinates (**Fig. S8**). Compared with the photoluminescence spectrum of the light-emitting polymer layer (**Fig. S9**), the electroluminescent spectrum of LE part witnessed some changes which were probably attributed to the formation of keto-defects during work.[26] The turn-on response of light emission from the PIN junction in the emissive polymer layer of the LE part was investigated by a pulse voltage operation (**Fig. S10**). As expected, the pre-charged LE part indicated a rapid turn-on response.

In conclusion, we have successfully developed a dual-function optoelectronic device to convert solar energy to electric energy and emit light by designing a three-electrode configuration. This dual-function optoelectronic device exhibits a reasonable power conversion efficiency of 2.07% from the PC part and a high luminance of 1040 cd/m^2 from the LE part. As it can be independently operated to generate electric energy for power and emit light for display, they are promising for a broad spectrum of applications such as micro-electronic and smart devices.[27,28] This work also represents a new and general strategy in developing multi-function devices through a solution process.

Experimental section

Synthesis of ZnO nanoparticles. The synthesis of ZnO nanoparticles had been previously reported.[12] Briefly, zinc acetate dihydrate (0.59 g) was first dissolved in methanol (25 mL) in a 100 mL flask and then heated to 65 ^oC under magnetic stirring. Subsequently, potassium hydroxide (0.30 g) was dissolved in methanol (13 mL) and slowly dropped into the flask within 15 min, followed by reaction for 2.5 h at 65 ^oC. The resulting solution was cooled down to room temperature and stayed overnight. The supernatant was removed and the precipitant was washed with methanol for several times. Finally, methanol (1 mL), chloroform (1 mL) and n-butanol (14 mL) were added to disperse the ZnO nanoparticles with a concentration of 6 mg/mL. The ZnO nanoparticle solution was filtered by a poly (vinylidene fluoride) membrane (0.45 μm in diameter) prior to the use.

Fabrication of the PC part. ITO-coated glass substrates were successively pre-cleaned with the deionized water, acetone and 2-propanol in ultrasonic baths each for 20 min.[9,12] The ZnO nanoparticle layer was spin-coated onto the ITO substrate at 3000 revolutions per minute for 30 s and annealed at 120 ^oC for 5 min. The above process was repeated for three times. The P3HT:PCBM layer was spin-coated onto the ZnO layer at 1000 revolutions per minute for 60 s. The concentration of the mixture solution of P3HT and PCBM in chlorobenzene (weight ratio of 5/4) was 30 mg/mL. The resulting material was annealed at 150 ^oC for 10 min at an argon atmosphere in the glovebox. Finally, the aligned CNT sheet was paved onto the P3HT:PCBM layer with a thickness of approximately 360 nm to complete the fabrication of the PC part.

Fabrication of the LE part. The light-emitting polymer layer was spin-coated onto the aligned CNT sheet at 3000 revolutions per minute for 60 s, followed by drying in vacuum for 1 h. The emissive polymers were dissolved in anhydrous tetrahydrofuran, followed by addition of ETT-15 and LiTf. The weight ratios for the polymer/ETT-15/LiTf were 20/10/1, and the final concentration of conjugated polymer was 40 mg/mL. Finally, another aligned CNT sheet was attached onto the emissive polymer layer with a thickness of approximately 36 nm.

Keywords: carbon nanotube, polymer, photoelectric, light-emitting, integrated device

Acknowledgements

This work was supported by NSFC (21225417, 51573027), STCSM (12nm0503200, 15JC1490200) and the Program for Outstanding Young Scholars from Organization Department of the CPC Central Committee.

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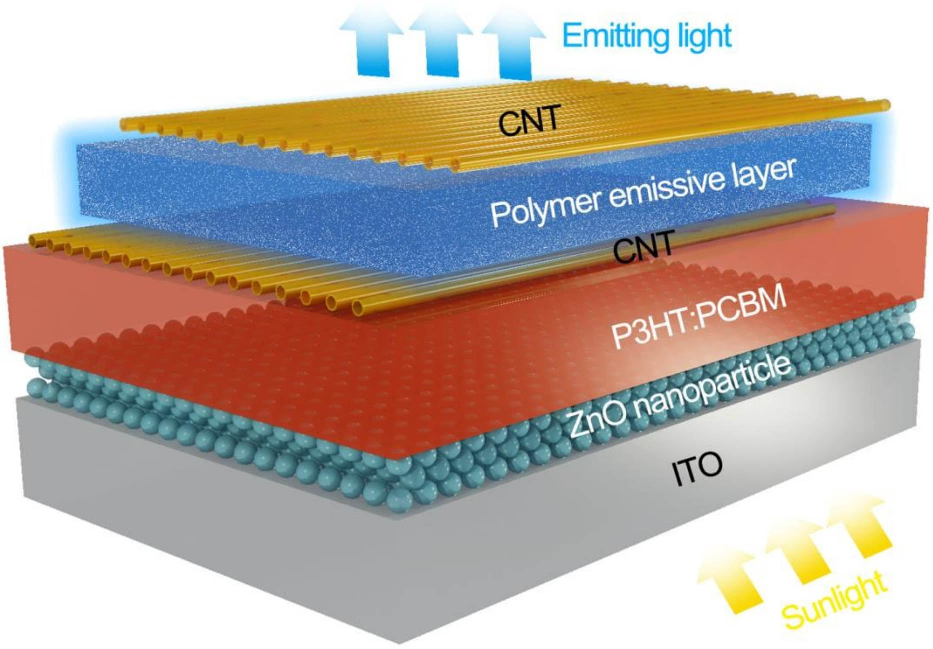

Figure 1. Schematic of the structure of the dual-function optoelectronic device.

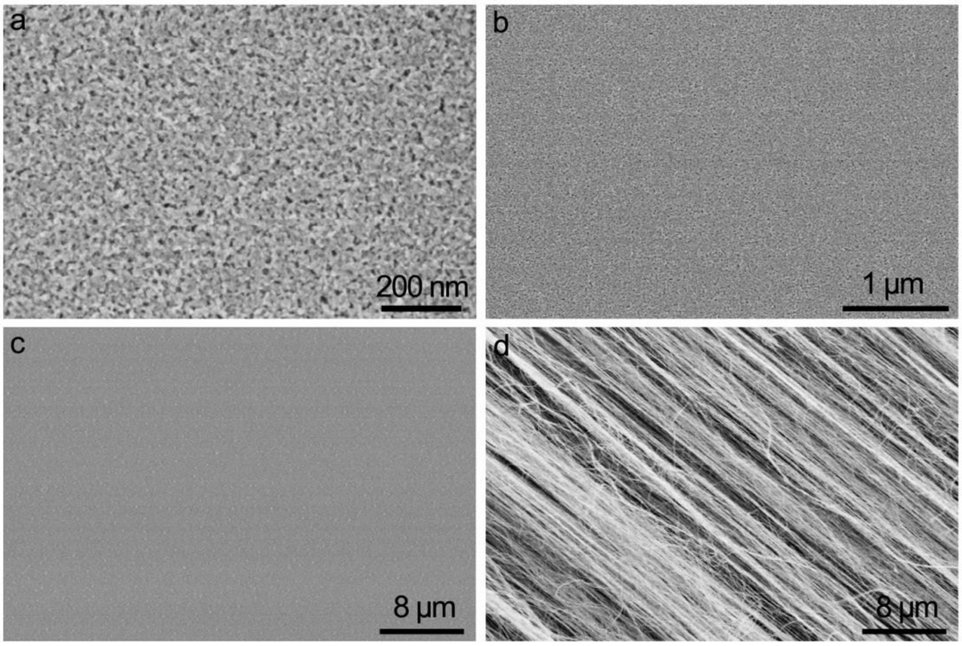

Figure 2. SEM images of the dual-function optoelectronic device. **a.** ZnO nanoparticle layer. **b.** P3HT:PCBM layer. **c.** Emissive polymer layer. **d.** Aligned CNT sheet.

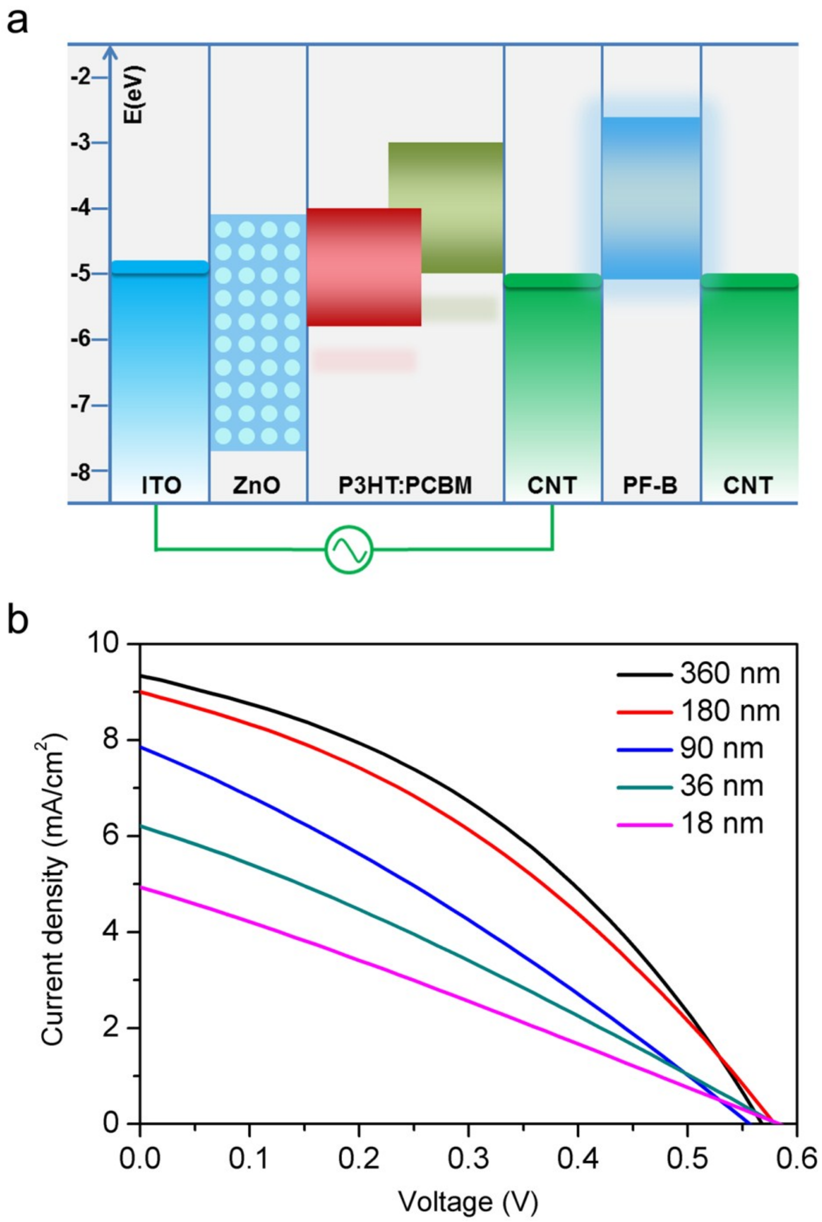

Figure 3. a. Schematic of the PC part consisted of the P3HT:PCBM bulk-junction layer generating electrical energy under light irradiation. **b.** Current density versus voltage characteristic curves of the PC parts with increasing aligned CNT layer thicknesses from 18 to 36, 90, 180 and 360 nm.

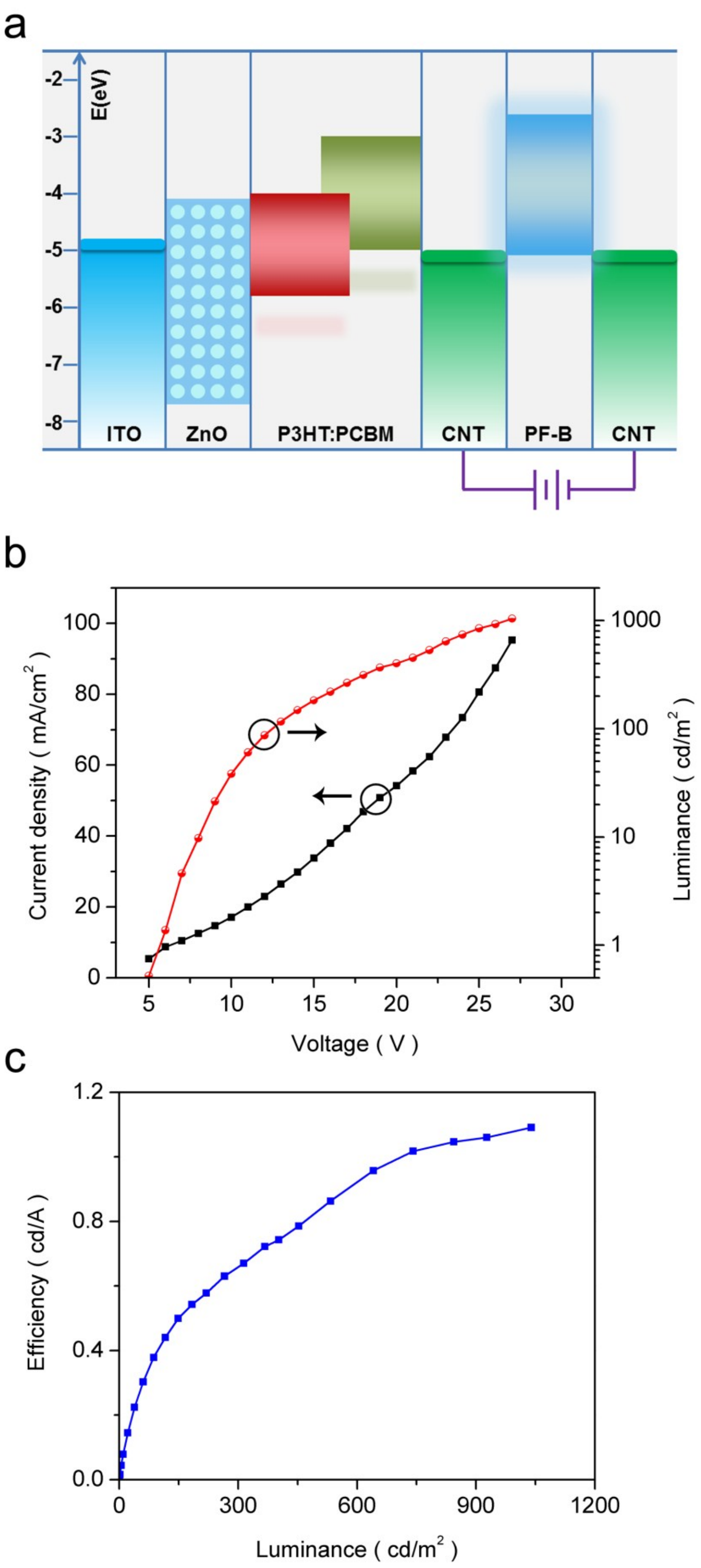

Figure 4. a. Schematic of the LE part consisted of the emissive polymer layer producing light under bias voltage. **b.** Current density-luminance-voltage characteristics of the LE part. **c.** Current efficiency-luminance characteristics of the LE part.

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A dual-function optoelectronic device is created to realize both photoelectric conversion and electroluminescence through an all-solution process.