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Organic-film photovoltaic cell with electroluminescence

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An organic-film photovoltaic (PV) cell, in which N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and tris(acetylacetonato)-(monophenothroline) yttrium [Y(ACA)₃phen] were used as electron-acceptor and donor, respectively, has been fabricated. Under UV light (4 mW/cm²), the short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and the overall power conversion efficiency of the optimum PV cell were 46 μ A/cm², 2.15 V, 0.30%, and 0.7%, respectively. The photocurrent response region of the cell parallels the adsorption of NPB. The PV effect is attributed to exciplex formation at the interface between the two organic films. The PV cell described displays electroluminescence (EL) emission of blue light upon application of a dc voltage. The maximum luminance was 750 cd/m² at 15 V driving voltage.

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In the field of organic electronics considerable interest has been focused on the details of the processes in organic electroluminescence (EL) diodes. Similarly organic photovoltaic (PV) cells have obtained rapidly growing attention since the letter by Tang in 1986¹ because organic PV cells compared to inorganic PV ones have the potential advantages that they can be made lightweight, use economical material, and can be deposited on low-cost substrates. Most studies on PV effects were focused on conjugated polymers, such as poly(phenylene vinylene) and its derivatives.²⁻⁶ Attention was also paid to several small molecules recently,^{7,8} but an organic PV cell fabricated with rare earth (RE) complexes has not been reported before.

Our group has studied the EL properties⁹ and the IR emission¹⁰ of the devices containing the Eu and Yb complexes, respectively. We have fabricated ITO/NPB/RE(ACA)₃phen/Mg:Ag, EL diodes (1: RE-La, 2: RE-Y, 3: RE=Gd) and studied blue emission of them; RE(ACA)₃phen stands for tris(acetylacetonato)-(monophenothroline) RE as electron-transporting layer which is nonfluorescing.^{11,12} When these diodes were illuminated by UV light, we accidentally observed an obvious photocurrent and photovoltage, which prompted us to investigate their PV effects. Device 2 had a stronger PV effect than that of device 3, whereas device 1 was so unstable that measurements were very difficult to carry out. Therefore, only PV effects and EL performances of device 2 has been investigated in detail.

Figure 1 shows the molecular structures of the organic materials used and the configuration of the PV cell. In the PV cell, ITO/NPB(30 nm)/Y(ACA)₃phen(30 nm)/Mg:Ag(100 nm), Y(ACA)₃phen and NPB have been used as electron acceptor and donor, respectively. ITO and a Mg:Ag alloy were used as anode (hole-collecting electrode) and as

cathode (electron-collecting electrode), respectively. The absorption spectra were measured with a Shimadzu UV-3000 Spectrophotometer. The EL spectra, CIE color coordinates of the diodes and the fluorescence excitation and emission spectra of the NPB film and NPB/Y(ACA)₃phen two-layer film were measured with a Hitachi MPF-4 Fluorescence Spectrophotometer. The current was measured by a C63 type current meter. The spectral response curve of the photocurrent of a PV cell was determined by illumination with UV light with 3 nm bandwidth generated from a Xe lamp (40 μ W/cm²). The other experiment conditions have been described in the literature.¹⁰ All measurements were conducted in ambient atmosphere with the incident light admitted through the glass/ITO slide.

Figure 2 shows the excitation spectra of a NPB film and of a NPB/Y(ACA)₃phen two-layer film. The two excitation peaks at 350 nm originate from the NPB layer (monitored by 465 nm emission of NPB). Under these conditions only NPB is excited. Figure 2 also displays fluorescence emission spectra of a NPB film and of a NPB/Y(ACA)₃phen two-layer film. The main emission peak at 465 nm with a shoulder at 486 nm originates from NPB (the two films were excited by 350 nm). Figure 3 indicates the absorption spectra of NPB, Y(ACA)₃phen, and NPB/Y(ACA)₃phen films together with the spectral response curve of the photocurrent of the PV cell. It is obvious that the total absorption of NPB/Y(ACA)₃phen films comes about by the overlap of two single-film absorptions. By comparing Fig. 2 with Fig. 3, we find that the photoluminescence (PL) peaks originate from NPB excited by 350 nm ultraviolet radiation because Y(ACA)₃phen is not excited under these conditions. The spectral response curve of the photocurrent of PV cells upon illumination in the region between 300 and 420 nm is matched to that of the absorption of NPB, although the two-layer film absorption spectrum also contains the contribution of the absorption of Y(ACA)₃phen. It is remarkable that the photocurrent is only based on the absorption of NPB, which is different from the results reported by Tang.¹ The typical

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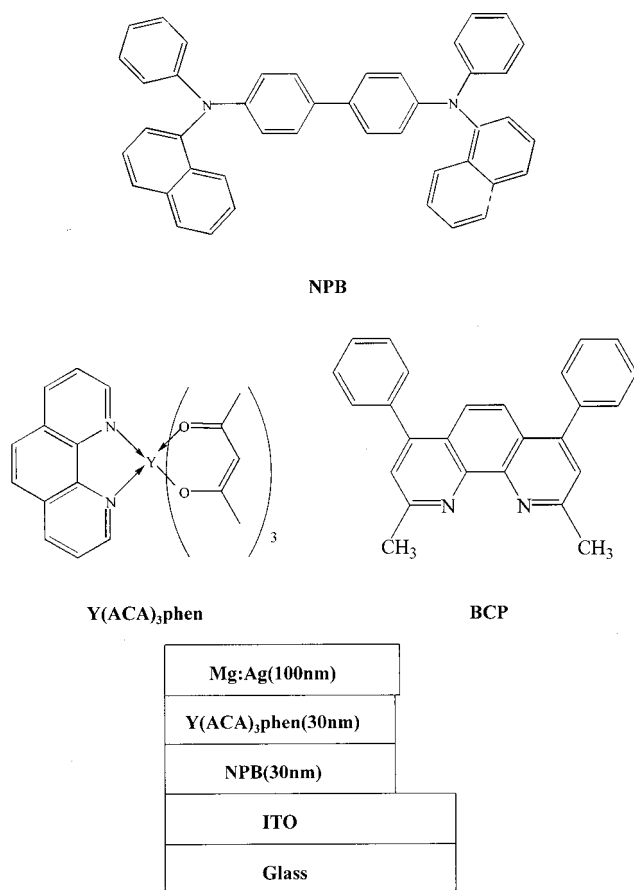


FIG. 1. Configuration of the PV cell and the molecular structure of the materials used.

parameters, open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), and fill factor (FF), of the optimum PV cell reached about 2.15 V, 46 and 0.30 $\mu\text{A}/\text{cm}^2$, respectively, and the overall power conversion efficiency was about 0.7% under illumination with 365 nm UV light at 4 mW/cm^2 .

It was proved that Y(ACA)₃phen has good electron-transporting ability,¹² and NPB is a good hole-transporting material.¹³ According to the photocurrent response curve and the excitation spectrum of the NPB/Y(ACA)₃phen film, it is concluded that the photovoltaic process in the cell [ITO/NPB/Y(ACA)₃phen/Mg:Ag] is as follows. First, excitons are photogenerated in NPB in a region near to the interface between NPB and Y(ACA)₃phen films because efficient photoabsorption only takes place in the NPB layer; second,

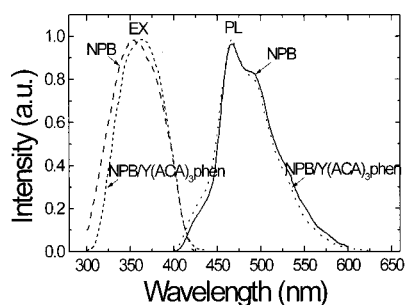


FIG. 2. Excitation and emission spectra of a NPB film and a NPB/Y(ACA)₃phen film (NPB: excitation (dashed line) and emission (dotted line); NPB/Y(ACA)₃phen: excitation short dashed line) and emission (solid line).

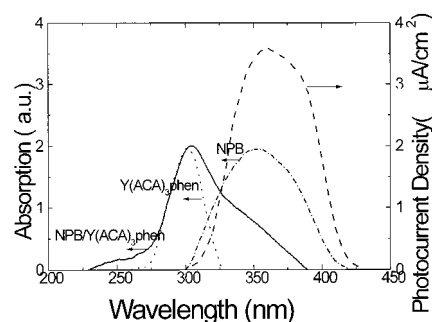


FIG. 3. Absorption spectrum of a NPB film (short dashed line), a Y(ACA)₃phen film (dotted line), and a NPB/Y(ACA)₃phen film (solid line) and the spectral response curve of the photocurrent of the PV cell (dashed line).

the excitons generated diffuse towards the interface because exciton dissociation is known to be efficient at interfaces between materials with different electron affinities and ionization potentials where the electron is accepted by the material with the larger electron affinity and the hole by the material with the lower ionization potential,^{3,14-16} last, electrons and holes originating from the exciton dissociation are transported through the Y(ACA)₃phen layer and the NPB layer into cathode and anode, respectively.

For an ITO/NPB/Mg:Ag and an ITO/Y(ACA)₃phen/Mg:Ag single organic layer PV diodes, PV effects were hardly observed under our measurement condition. Thus, we thought that the interface between the NPB and the Y(ACA)₃phen layers as the active site should play an important role in PV effects. Usually, bathocuproine (BCP) is an effective hole-blocking layer between organic layer and cathode.¹⁷ Therefore we inserted BCP layers with different thickness to separate the Y(ACA)₃phen film from the NPB film in order to understand the dependence of PV performance on the interface. We fabricated the following devices: ITO/NPB(30 nm)/BCP(x nm)/Y(ACA)₃phen(30 nm)/Mg:Ag(100 nm) (a : $x=0$, b : $x=1$, c : $x=3$, d : $x=5$). Upon illumination with 365 nm UV light at 4 mW/cm^2 , the values of I_{sc} of these devices were 40.3, 27.5, 22.9, and 14.8 $\mu\text{A}/\text{cm}^2$ for the devices a , b , c , d , respectively. With increasing the thickness of BCP film the values of I_{sc} were reduced from 40.3 to 14.8 $\mu\text{A}/\text{cm}^2$. We conclude that the dissociation efficiency of the excitons was reduced at the interface due to the insertion of the BCP layer between the two organic layers.

In a previous article,¹¹ we reported that the EL emission peak intensities of devices 1 and 2 at about 560 nm originating from exciplexes¹⁸ were larger than that of device 3; device 1 had the strongest exciplex emission. When these devices were illuminated by 365 nm UV light at 40 $\mu\text{W}/\text{cm}^2$, the I_{sc} values of devices 1, 2, and 3 were 2.8, 1.4, and 0.4 $\mu\text{A}/\text{cm}^2$, respectively. We found that the stronger the exciplex emission from the interface, the better the performance of the PV cell was. The exciplex emissions formed by the interaction between the excited singlet-state hole-transport material (NPB) and the ground-state electron-transport materials [RE(ACA)₃phen], which reflects improved interfacial properties.^{19,20} When a suitable light illuminates the cell through the glass/ITO side, we expect the excited NPB molecule (NPB*) to be a good electron donor to the acceptor [RE(ACA)₃phen] in its ground state, leading to the

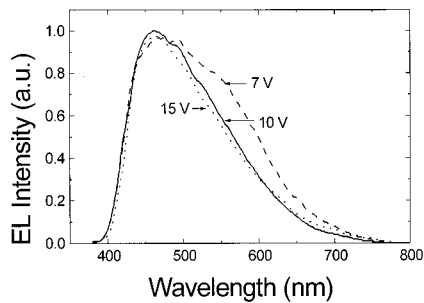


FIG. 4. EL spectra of the diode driven by different voltages (7 V: dashed line, 10 V: solid line, 15 V: dotted line).

formation of an exciplex at the interface by photoinduced electron transfer: $\text{NPB}^* + \text{Y}(\text{ACA})_3\text{phen} \rightarrow \{\text{NPB}^+ \cdots [\text{Y}(\text{ACA})_3\text{phen}]^-\}^*$, that is, donor-acceptor ($D-A$) pair. At the same time, photogeneration excitons are formed in NPB layer, and then migrate to $D-A$ interface where exciton dissociation is known to be efficient. An exciton is separated by exciplex, creating electron in the A layer and holes in the D layer at the interface, respectively. The charges should be removed by transfer toward the opposite collection electrode.^{7,21} From the above discussion, it is proposed that PV effects should here also be associated with exciplex formation, and this is another method to choose suitable materials to fabricate a PV cell.

The ITO/NPB/Y(ACA)₃phen/Mg:Ag diode can also be operated as an EL device. Figure 4 displays the EL emission spectra of the device, and Table I lists the CIE color coordinates of the device at different driving voltages. Blue light emission has been achieved, but the color purity is not fully satisfactory. There are two emission peaks at 466 and 550 nm in the spectrum of the diode when driven at 7 V; with increasing driving voltage, the former peak and the latter one increased and decreased, respectively. Upon comparing the EL to the PL spectrum (see Figs. 2 and 4), it was concluded that the 466 nm peak comes from the excitation of NPB, and the 550 nm band presumably originates from exciplex emission at the interface. The 550 nm emission disappears at higher voltage, which is thought to be caused by a shift of the recombination zone of the excitons from the interface to the NPB layer. Figure 5 indicates the current-voltage and luminance-voltage properties of the EL device. The device had a maximum luminance of 750 cd/m² at 15 V.

It is found that the ITO/NPB/Y(ACA)₃phen/Mg:Ag diode has both PV response performance and remarkable EL properties. We have also tested the stability of the diode: When a PV cell was continuously illuminated under UV light at 365 nm at an intensity of 2.8 mW/cm², I_{sc} decreased to 50% of the original value (46 $\mu\text{A}/\text{cm}^2$) after 18 h. Another cell was tested at a constant driving current (45 $\mu\text{A}/\text{cm}^2$),

TABLE I. CIE color coordinates of the diode with different driving voltage.

Driving voltage (V)	7	10	15
Color coordinate			
X	0.266	0.222	0.204
Y	0.323	0.229	0.216

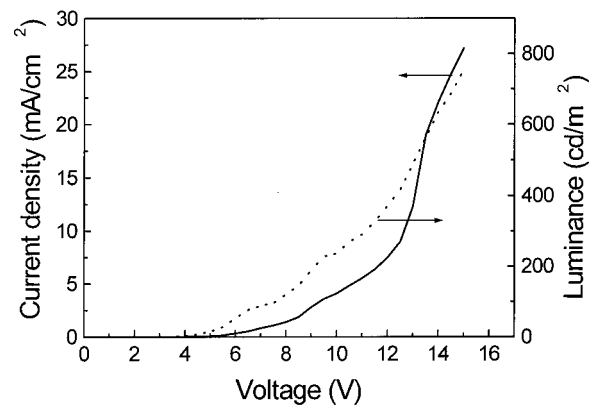


FIG. 5. Luminance-voltage and current-voltage characteristics of the ITO/NPB/Y(ACA)₃phen/Mg:Ag diode (current: solid line, luminance: dotted line)

and I_{sc} decreased to 40% of the original value (35 $\mu\text{A}/\text{cm}^2$) after 18 h.

In conclusion, Y(ACA)₃phen-containing organic bifunctional diodes with light to electricity and electricity to light conversions have been achieved. The PV effect is ascribed to exciplex formation at the interface between the two organic films; and the obtained EL emission originates from recombination of an electron and a hole coming from the electrodes. We anticipate that in the future a display which does not require an additional power supply could possibly be made if the energy taken up in the PV mode could be stored in such a way as to be used for the EL emission.

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