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Photovoltaic effects of diodes containing lanthanide complexes

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Abstract

We present a systematic study of organic photovoltaic (PV) diodes containing a series of lanthanide (Ln) complexes, tris(dibenzoylmethanato)(monobathophenanthroline) (Ln)(III) [Ln(DBM)$_3$ bath] used as an electron acceptor. For making a convenient comparison among all diodes, they were fabricated by adopting the same structure, ITO/*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-l,l′-diphenyl-4,4′-diamine (TPD) (30 nm)/Ln(DBM)$_3$ bath (60 nm)/Mg:Ag (200 nm), which was not optimized. Although these diodes under bias voltage almost show an exciplex emission relating to PV effects, they indicate distinct performances due to their different 4f electrons and f^n configurations. Especially, the PV effects of the diodes containing La^{3+} (4f^0), Y^{3+} (4f^0), Gd^{3+} (4f^7), and Lu^{3+} (4f^{14})-complexes having the relative stable electron configurations in the 4f orbital are best under illumination with 365 nm UV light. And the diodes containing Pr^{3+}-, Yb^{3+}-, and Sm^{3+}-complexes have better PV effects, the other diodes containing Ln(DBM)$_3$ bath (Ln: Nd, Eu, Tb, Dy, Ho, Er and Tm) only show poor PV effects.

Keywords: Organic photovoltaic diodes; Lanthanide complexes; Exciplex

1. Introduction

Diodes based on the effects of light on organic molecular materials, complexes, and polymers have been seriously exploited commercially. In an electroluminescent (EL) process, an electron and a hole recombine to form an exciton described as an electron–hole pair loosely bound to each other by their Coulomb attraction, they must release their excess energy in the form of visible light, or luminescence when they meet and then radiate. Another possible application in organic electronic field is based on the photovoltaic (PV) effect. In a PV process, excitons are formed under a suitable illumination and dissociated by an inner electric field or by charge transfer to a nearby donor or acceptor at the interface between two organic layers. The field pushes the holes toward anode, and the electrons toward cathode, respectively. Those carriers reaching the electrodes provide a voltage that could be used in photo-electric conversion applications ranging from photodetectors to solar cells. Either EL or PV diodes with organic materials have some advantages, such as light weight, low cost and easy fabrication, over their inorganic diodes [1,2]. In the past decade, important steps have been achieved in applying organic materials for solar cell and photodetector production [3]. Most studies on organic PV effects are focused on conjugated polymers, such as poly(phenylene vinylene) and its derivatives [4,5], and attention is also paid to several small molecules, recently [6,7]. We have reported that PV diodes containing rare earth (RE) complexes as an electron-acceptor and an electron-transport layer simultaneously showed not only excellent PV effects but also EL performances [8].

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When a hole-transporting material (donor) and an electron-transporting material (acceptor) are in intimate contact, either in a blend/mixture or at the interface between the two molecular solid films, exciplex (excited state complex) can be formed through charge transfer between an excited state molecule and a ground state molecule [9–12]. Some of exciplex emissions could be used to obtain white light emission or to tune EL emission color from multiplayer LEDs [13,14], however, an exciplex emission must be generally suppressed in order not to bother color purity in EL devices [15].

It has been reported by our group that diodes using tris(dibenzoylmethanato)(monobathophenanthroline)lanthanide-(III) [Ln(DBM)$_3$ bath] (Ln: Pr, Eu, Gd, and Yb) as an electron-acceptor often show exciplex emissions [16–19], the other Ln(DBM)$_3$ bath series (Ln: Y, La, Nd, Sm, Tb, Dy, Ho, Er, Tm, and Lu) should be also expected to form exciplexes with *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-l,l′-diphenyl-4,4′-diamine (TPD) as an electron-donor material. According to our previous results that PV effects of RE-diodes are attributed to exciplex-formation at the interface between the donor and the acceptor molecules [8], and a series of Ln(DBM)$_3$ bath complexes might be ideal electron acceptors for organic PV diodes. In this article, we systematically study the performances of PV diodes containing a series of Ln(DBM)$_3$ bath and discuss relationships between PV performances and Ln^{3+} ions in the diodes in order to develop more excellent organic PV diodes.

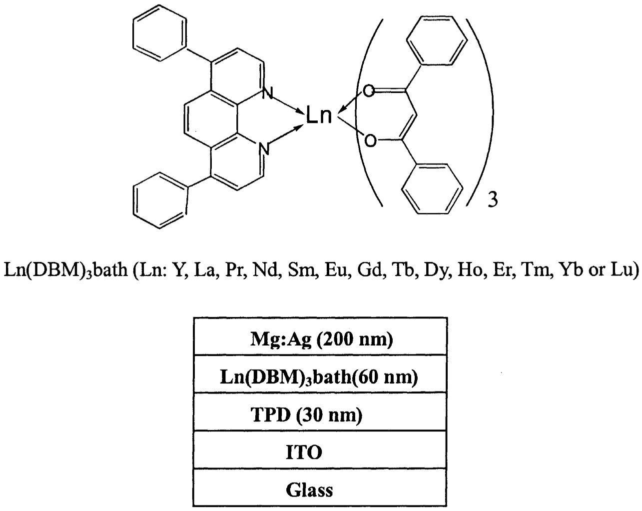

Fig. 1. The molecular structures of Ln(DBM)$_3$ bath complexes used and the configuration of a general PV diode.

2. Experimental

Ln(DBM)$_3$ bath and TPD were chosen as an electron acceptor and a donor in organic PV diodes, respectively. Trivalent Ln ion represented Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}, and here Ce^{3+} ion was not included in the study due to its special electron structure. A series of Ln(DBM)$_3$ bath complexes was synthesized from LnCl$_3$ and the corresponding organic ligand materials (from Aldrich) following the reported method [20]. Fig. 1 shows the molecular structure of Ln(DBM)$_3$ bath complex used and the configuration of a general PV diode. For making a convenient comparison among of all diodes, the same structure, ITO/TPD (30 nm)/Ln(DBM)$_3$ bath (60 nm)/Mg:Ag (200 nm), which was not optimized, was adopted. ITO and a Mg:Ag alloy were used as anode (hole-collecting electrode) and as cathode (electron-collecting electrode), respectively. All thin films were deposited on an ITO glass substrate with resistance of $100\,\Omega/\square$ by conventional vapor vacuum evaporation at a pressure of 5×10^{-4} Pa and onto areas of 0.15 cm^2. The film thickness was controlled in vacuo with a quartz crystal monitor. The absorption and EL spectra were recorded with a Shimadzu UV-3000 Spectrophotometer and a Hitachi 4000 Fluorescence Spectrophotometer, respectively. The current was measured by a C63 type currentmeter. The spectral response curves of photocurrents of PV diodes were determined by illumination with UV light with 3 nm bandwidth generated from a Xe lamp (40 μW cm^{-2}). All measurements were conducted in ambient atmosphere with the incident light admitted through the glass/ITO side.

3. Results and discussion

Table 1 lists typical parameters, open voltage (V_{oc}), short current (I_{sc}), fill factor (FF) and external quantum efficiency (η_{ex}), of the series of PV diodes under illumination with 365 nm UV light at 4 mW cm^{-2}. It is found that all PV diodes show obvious PV effects. Because photocurrent response regions of these PV diodes all lie at 300–400 nm and the shapes of their curves are very similar each other, Fig. 2 only shows the photocurrent response curves of the PV diodes containing Ln(DBM)$_3$ bath (Ln: Pr, Sm, Gd, Tb and Er), and also only shows the absorption spectra of a TPD film, a Y(DBM)$_3$ bath

Table 1
Typical parameters of all PV diodes

Ln(DBM)$_3$ bath	$4f^n$	V_{oc} (V)	I_{sc} (μA cm^{-2})	FF	η_{ex} (%)
Y	$4f^0$	1.20	47.58	0.30	4.04
La	$4f^0$	1.21	48.62	0.30	4.14
Pr	4^2	0.99	21.20	0.25	1.80
Nd	$4f^3$	0.61	7.48	0.15	0.64
Sm	$4f^5$	0.99	20.90	0.25	1.78
Eu	$4f^6$	0.54	11.33	0.14	0.96
Gd	$4f^7$	1.10	43.58	0.27	3.71
Tb	$4f^8$	0.69	14.76	0.17	1.25
Dy	$4f^9$	0.35	6.46	0.09	0.55
Ho	$4f^{10}$	0.76	16.28	0.19	1.38
Er	$4f^{11}$	0.41	6.53	0.10	0.56
Tm	$4f^{12}$	0.30	5.95	0.08	0.51
Yb	$4f^{13}$	0.84	25.25	0.21	2.15
Lu	$4f^{14}$	1.12	43.78	0.28	3.73

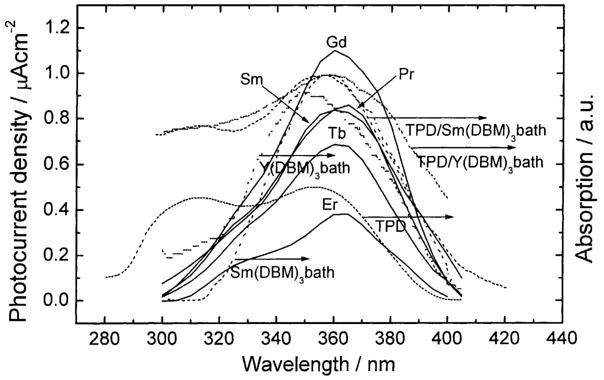

Fig. 2. Photocurrent response curves (solid lines) and the absorption spectra (short dashed lines) of some of the PV diodes.

film, a Sm(DBM)$_3$ bath film, a TPD/Y(DBM)$_3$ bath film and a TPD/Sm(DBM)$_3$ bath film. It has been proved in our previous paper [8] that PV performances of diodes containing RE complexes as electron acceptors are related with exciplex-formation in these diodes. The stronger the exciplex formed at the interface is, the better the performance of the PV diode is. Fig. 3 shows EL spectra of Ln(DBM)$_3$ bath series PV diodes driven by dc bias voltage. It has been found that there are basically exciplex emissions in these PV diodes, which coincides with our original prediction.

For the Y(DBM)$_3$ bath film and the Sm(DBM)$_3$ bath film, the absorption bands showing a peak at 350 nm are assigned to π–π^* transition of the ligand moiety (DBM). Ln(DBM)$_3$ bath system exhibits the same absorption spectra due to the same ligand moiety. By comparing the photocurrent response curves with the absorption spectra of the TPD/Y(DBM)$_3$ bath film and TPD/Sm(DBM)$_3$ bath film, it can be found that generation of photocurrents should be attributed to the total absorption of both the TPD layer and the Ln(DBM)$_3$ bath layer, which is the same as the previous result incompletely [8]. But the absorption of the TPD layer played an important role for the generation of the photocurrent since it was stronger than that of the Ln(DBM)$_3$ bath layer. The most sensitive response wavelengths are at about 355–365 nm, so these PV diodes containing Ln(DBM)$_3$ bath series are very suitable for fabricating photodetectors to detect UV light.

According to the parameters shown in Table 1, all PV diodes divided into three groups in the main. For the first group (G_I), Ln represents La, Y, Gd, and Lu; G_I possesses the best PV properties and their I_{sc}s are high up to 43.58–48.62 μA cm^{-2}. For the second group (G_{II}), Ln is pointed to Pr, Yb, and Sm; G_{II} has the moderate performances comparing to other diodes, and their I_{sc}s (20.90–25.25μA cm^{-2}) are about half of G_I's. For the third group (G_{III}), Ln represents Nd, Eu, Tb, Dy, Ho, Er, and Tm; G_{III} shows poor PV properties and their I_{sc}s (5.95–16.28 μA cm^{-2}) are only quarter of G_I's or so.

Although all PV diodes containing Ln(DBM)$_3$ bath series showed obvious PV effects due to exciplex-formation which was resulted from the interaction between the donor and the acceptor, these PV diodes showed distinct PV performances. It is well known that the biggest open voltage is determined by the difference between the energy levels of donor and acceptor materials [21]. Energy levels of HOMO and LUMO of these RE complexes are almost equal because Ln-complexes have the same ligand, however, the diodes show different PV performances. The dissimilarities are probably attributed to different 4f electrons and 4f^n configurations of Ln^{3+} ions [22]. For G_I, the central ions are inert structures, that is, $n = 0$ for La^{3+} and Y^{3+}, 7 for Gd^{3+} and 14 for Lu^{3+} in 4f^n orbital, respectively. Because of their relatively stable 4f electron structure, Ln^{3+} ions could give less effect on properties of the ligand which should react with TPD molecules to form exciplexes [17]. PV effects in RE-diodes are strongly dependent on the exciplex-formation, so G_I shows the best PV effects among of them in Table 1. The nuclear charges and trivalent ion radii are 59 and 101.3 pm for Pr^{3+} and 57 and 101.6 pm for La^{3+}, and 70 and 85.8 pm for Yb^{3+} and 71 and 85.0 pm for Lu^{3+}, respectively, which are very close to each other. Pr^{3+} is near to La^{3+} though they are separated by Ce^{3+}, and Yb^{3+} is adjacent to Lu^{3+}. Pr^{3+} and Yb^{3+} have the similar 4f configurations with La^{3+} and Lu^{3+}, respectively, and are close to the stable states. Thus, Pr^{+} and Yb^{3+} should have the similar coordinating characteristics with La^{3+} and Lu^{3+}, respectively. Then, it is considered that the properties of PV

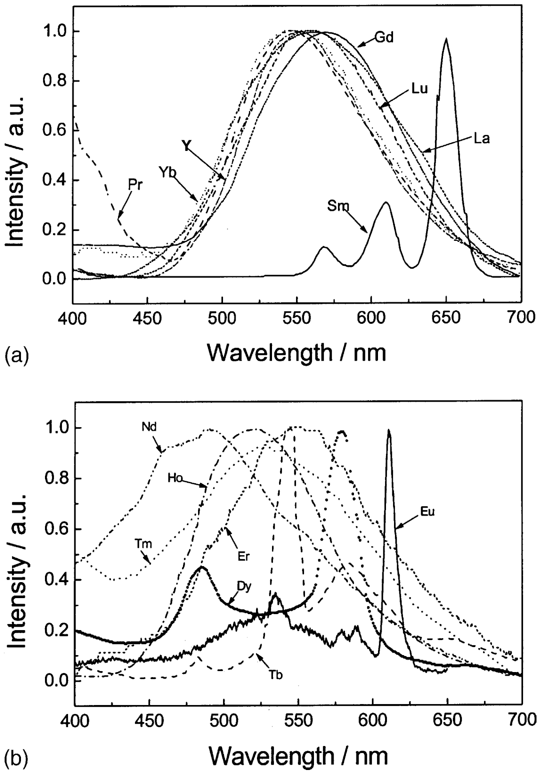

Fig. 3. EL spectra of Ln(DBM)$_3$ bath series PV diodes driven by dc bias voltage. (a) La: short dashed line, Y: dotted line, Gd: dash dot dotted line, Lu: dashed line, Pr: dash dotted line, Yb: short dotted line, Sm: solid line; (b) Nd: dash dot dotted line, Eu: solid line, Tb: dashed line, Dy: solid circle, Ho: dash dotted line, Er: short dashed line, Tm: dotted line.

diodes containing Pr^{3+}- and Yb^{3+}-complexes are supposed to resemble with those of La^{3+}- and Lu^{3+}-diodes. They also have better PV effects, just like shown in Table 1.

We have proved that PV effects of diodes containing RE complexes as electron acceptors are dependent on an exciplex formation of these diodes. However, there is a special case of $Sm(DBM)_3$ bath in these PV diodes. There is hardly an exciplex emission in the EL spectrum of a $Sm(DBM)_3$ bath diode in Fig. 3a, but in Table 1 this diode also has the better PV effect closed to Pr^{3+}- and Yb^{3+}-diodes. We think that there is a competing process between exciplex emission and Ln^{3+} emission [23]. It is considered that the exciplex level of a Sm^{3+}-containing diode just lies at the appropriate position between the excited state level ($T1 \sim 20{,}500\,cm^{-1}$) [24] of the ligand and $^4G_{5/2}$ emission level ($\sim 17{,}600\,cm^{-1}$) of a Sm^{3+} ion. So, the exciplex level is more matched with the Sm^{3+}resonance level, $^4G_{5/2}$ level, and the energy transfer from exciplex level to $^4G_{5/2}$ seems more efficiently so that the emission of the exciplex could not be almost observed. In other words, an exciplex should be also formed between intermolecular indeed though its emission could not be observed. So, PV effects of the diode with Sm^{3+}-complex are also better and the Sm^{3+}-containing diode is classified to G_{II}.

For G_{III}, the diodes containing $Ln(DBM)_3$ bath (Ln: Nd, Eu, Tb, Dy, Ho, Er, and Tm) show the poor PV performances probably due to their characteristic ion emissions competing with an exciplex emission. The reason has been not clear yet.

4. Summary

In conclusion, we fabricated bilayer PV diodes containing $Ln(DBM)_3$ bath series and TPD molecules as an electron acceptor and a donor, respectively. They all have obvious PV effects under illumination of UV light because exciplexes are formed and benefit to dissociation of excitons generated by light. The dissimilar PV effects of these diodes are probably resulted by slightly different properties of RE-complexes due to 4f electrons and ion radii of central ions. The PV effects of diodes containing $Ln(DBM)_3$ bath (Ln: La, Y, Gd, and Lu) having stable configurations are best among of them, and I_{sc} and η_{ex} values of the diodes were about $46\,\mu A\,cm^{-2}$ and over 4%, respectively. The diodes containing Pr^{3+}-, Yb^{3+}-, and Sm^{3+}-complexes had the better PV properties, and the other diodes containing $Ln(DBM)_3$ bath (Ln: Nd, Eu, Tb, Dy, Ho, Er, and Tm) only had the poor PV performances. The excellent RE materials will be chosen to improve PV effects in the future.

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