

OPV devices based on functionalized lanthanide complexes for application in UV–light detection

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Abstract

Organic photovoltaic (OPV) devices with the general structure of ITO/PEDOT: PSS (60 nm)/*m*-MTDATA (40 nm)/(OXD-Pybm)Ln(DBM)₃ (20 nm)/LiF (1 nm)/Al (120 nm) are demonstrated by utilizing (OXD-Pybm)Ln(DBM)₃ (Ln = Pr, Sm, Eu, Gd, and Tb) as electron acceptors and 4,4',4''-tris(*N*-(3-methylphenyl)-*N*-phenylamino) triphenylamine (*m*-MTDATA) as an electron donor. The performances of these devices are experimentally improved by the introduction of 2,5-diphenyl-1,3,4-oxadiazole (OXD) group into the electron acceptors. Besides, it is found that (OXD-Pybm)Pr(DBM)₃ based device holds the potential application in UV-light detection due to the absence of dark current with the compensatory voltage lower than 1.65 V. The highest power conversion efficiency (η) and the maximum fill factor (FF) among these OPV devices are 2.60% and 0.33, respectively.

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1. Introduction

Intense research has been currently directed to organic photovoltaic (OPV) materials and related device architectures since the donor–acceptor (D–A) heterojunction interface was demonstrated to be an effective exciton–dissociation structure [1], which endows the OPV devices with the advantages of low fabrication cost, simple manufacturing process, potential application in portable products, etc. [2–5]. In order to improve the device performances, some tactics have been applied recently, for example, the materials possessing high mobility [6,7] and/or long exciton lifetimes [2,8–10] are employed as the active materials. Several groups have studied the photophysical properties of lanthanide complexes in detail [11–13] and found the absorption spectra of these complexes mainly located in the ultraviolet (UV) region, indicating that lanthanide complexes possess the potential application in OPV device-based UV–light detectors. It was reported that the OLED

performances can be improved by the incorporation of 2,5-diphenyl-1,3,4-oxadiazole (OXD) group into the emissive materials of rare earth complexes, because both the electron-transporting ability of the materials and the carrier-transporting balance in the devices are improved [14,15]. But as far as we know, there are no reports about the effect of carrier-transporting groups on the performances of the OPV devices based on lanthanide complexes.

In this paper, we studied the performances of the OPV devices with the general structure of ITO/PEDOT: PSS (60 nm)/*m*-MTDATA (40 nm)/(OXD-Pybm)Ln(DBM)₃ (20 nm)/LiF (1 nm)/Al (120 nm), where PEDOT: PSS is poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate), *m*-MTDATA is 4,4',4''-tris-(2-methylphenylphenylamino) triphenylamine and utilized as an electron donor, and (OXD-Pybm)Ln(DBM)₃, presenting [1-(4-5'-phenyl-1,3,4-oxadiazolylbenzyl)-2-pyridinyl benzoimidazole]Ln(1,3-diphenylpropane-1,3-dione) with the central ions of Pr, Sm, Eu, Gd, and Tb for the devices **a**, **b**, **c**, **d**, and **e**, respectively, is employed as the electron acceptor. In order to study the effect of the OXD group on the device performances, the referential device with

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(Pybm)Gd(DBM)₃ (Pybm = 2-pyridinyl-benzoimidazole) as the electron acceptor is also fabricated. The key parameters of these devices are all listed in Table 1.

2. Experimental

All solvent and chemical materials are commercially available and used without further purification. 2-(4-thylphenyl)-5-phenyl-1,3,4-oxadiazole reacted with NBS in refluxing CCl₄ to yield 2-(4-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole, which condensed with 2-pyridinylbenzoimidazole in DMF to synthesize the diimine ligand of OXD–Pybm [15], which was used to prepare the corresponding lanthanide complexes in hot ethanol [16]. The general molecular structure of the organic materials related to this paper, along with the device configuration, is shown in Scheme 1.

The cyclic voltammetry measurements were conducted on a voltammetric analyzer (CH Instruments, Model 620B) with a polished Pt plate as the working electrode, Pt mesh as the counter electrode, and a commercially available saturated calomel electrode (SEC) as the reference electrode, at a scan rate of 0.1 V/s. The voltammograms were recorded using CH₃CN sample solutions with ~10⁻³ M of (OXD–Pybm)Gd(DBM)₃ and (Pybm)Gd(DBM)₃, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Prior to each electrochemical measurement, the solution was purged with nitrogen for ~15 min to remove the dissolved oxygen, and the energy levels of the lowest unoccupied molecular orbital (*E*_{LUMO}) were also calculated according to Ref. [17]. The absorption

spectra of all organic films on quartz substrate were measured with a Shimadzu UV-3101PC spectrophotometer.

A pre-patterned indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 20 Ω/□ were cleaned [18], and overlaid with PEDOT: PSS [19]. Other materials were sequentially deposited onto the ITO substrates in a vacuum chamber by thermal evaporation at a pressure of 2 × 10⁻⁴ Pa without breaking the vacuum. The active area of the devices was 2 × 5 mm². The thickness of the depositing film of the above materials was monitored by quartz oscillators. Photocurrent response curves were recorded under a 40 μW/cm² Xe lamp. All measurements were carried out with the incident light admitted through the glass/ITO side in ambient atmosphere at room temperature. FF and η are calculated by the following equations, respectively:

$$FF = \frac{(IV)_{\max}}{V_{OC} \times I_{SC}}, \quad \eta = \frac{(IV)_{\max}}{P_{in} \times L} = \frac{FF \times V_{OC} \times I_{SC}}{P_{in} \times L},$$

where (*IV*)_{max} is the actual maximum power, *V*_{oc} is open-circuit voltage, *I*_{sc} is short-circuit current, *L* is active area, and *P*_{in} is incident light power per square centimeter.

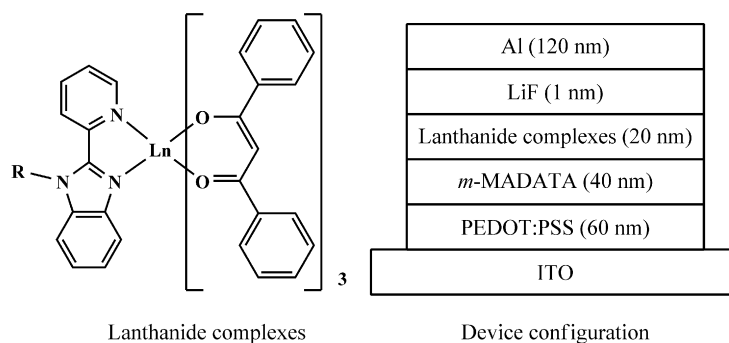
3. Results and discussion

3.1. Photocurrent response and absorption spectra

The absorption spectra of all lanthanide complexes based films are similar to each other, leading to the similar photocurrent response curves of devices a–e. Therefore, only the absorption spectra of (OXD–Pybm)Eu(DBM)₃ film and *m*-MTDATA/(OXD–Pybm)Eu(DBM)₃ double-layer-based film, together with that of *m*-MTDATA film and the photocurrent response curve of the (OXD–Pybm)Eu(DBM)₃-based OPV device, are presented in Fig. 1. Because the ITO glass is not permeable to the light with the wavelength shorter than 300 nm (Fig. 1 inset), devices a–e mainly respond to the UV–light with the wavelength between 300 and 400 nm which inoculates to the UV area of the solar spectrum illuminating earth's surface after the filtration of the atmosphere [20] as presented in Fig. 2. Consequently, these devices hold the potential application in detecting the UV–light, especially those from the sun.

Table 1
Key parameters of devices a–f

| Ions (device) | 4f ⁿ | <i>V</i> _{oc} (V) | <i>I</i> _{sc} (× 10 ⁻⁶ A/cm ²) | FF | η (%) |
|---------------|-----------------|----------------------------|--|------|-------|
| Pr (a) | 4f ² | 1.83 | 77.4 | 0.24 | 1.97 |
| Sm (b) | 4f ⁵ | 1.97 | 86.5 | 0.26 | 2.60 |
| Eu (c) | 4f ⁶ | 1.43 | 40.3 | 0.18 | 0.60 |
| Gd (d) | 4f ⁷ | 1.74 | 93.5 | 0.27 | 2.59 |
| Tb (e) | 4f ⁸ | 1.52 | 79.9 | 0.33 | 2.33 |
| Gd (f) | 4f ⁷ | 1.95 | 86.4 | 0.22 | 2.17 |



Scheme 1. The molecular structures of lanthanide complexes and the device configuration. R = 2-phenyl-5-*p*-tolyl-1,3,4-oxadiazole (devices a–f) and H (device g), and Ln = Pr (device a), Sm (device b), Eu (device c), Gd (devices d and f), and Tb (device e).

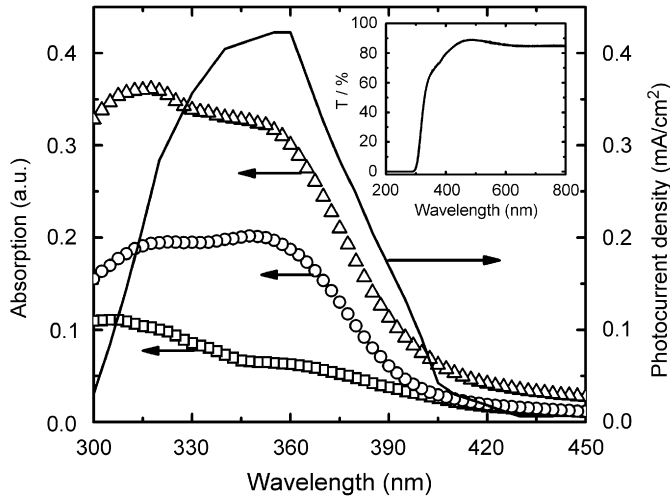


Fig. 1. Absorption spectra of *m*-MTDATA film (open circle), (OXD-Pybm)Eu(DBM)₃ film (open square), *m*-(OXD-Pybm)Eu(DBM)₃ double-layer based films (open triangle), and the photocurrent response of (OXD-Pybm)Eu(DBM)₃-based OPV device (solid line). Inset: the UV-vis transmission spectrum of the ITO glass.

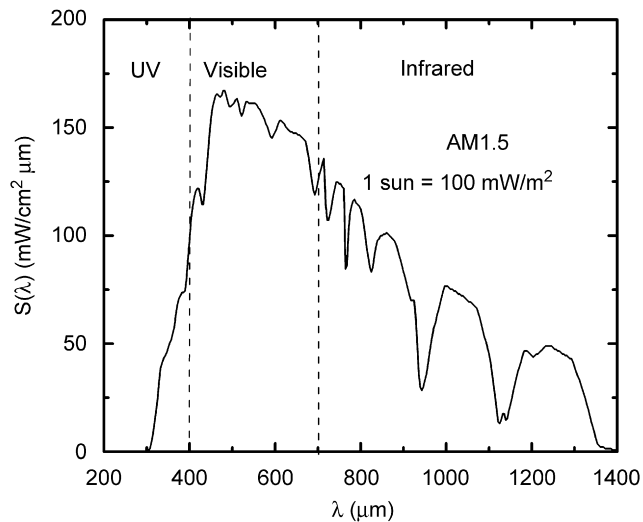


Fig. 2. The standard solar spectrum illuminating earth's surface [20].

In this wavelength range, both *m*-MTDATA film and (OXD-Pybm)Ln(DBM)₃ film show strong absorption ability, suggesting that both of them contribute to the broad band located at 300–420 nm in the absorption spectrum of the double-layer based film as well as the generation of the photocurrent when these devices are exposed to the UV-light illumination.

3.2. Performances of the OPV devices

Fig. 3 presents the current-compensatory voltage (*I*-*V*) characteristics of the OPV devices with UV-illumination (UV-on) (a) and in dark (UV-off) (b). When illuminated by the UV-light (365 nm) with the power density of 1.7 mW/cm², the highest values among the performance

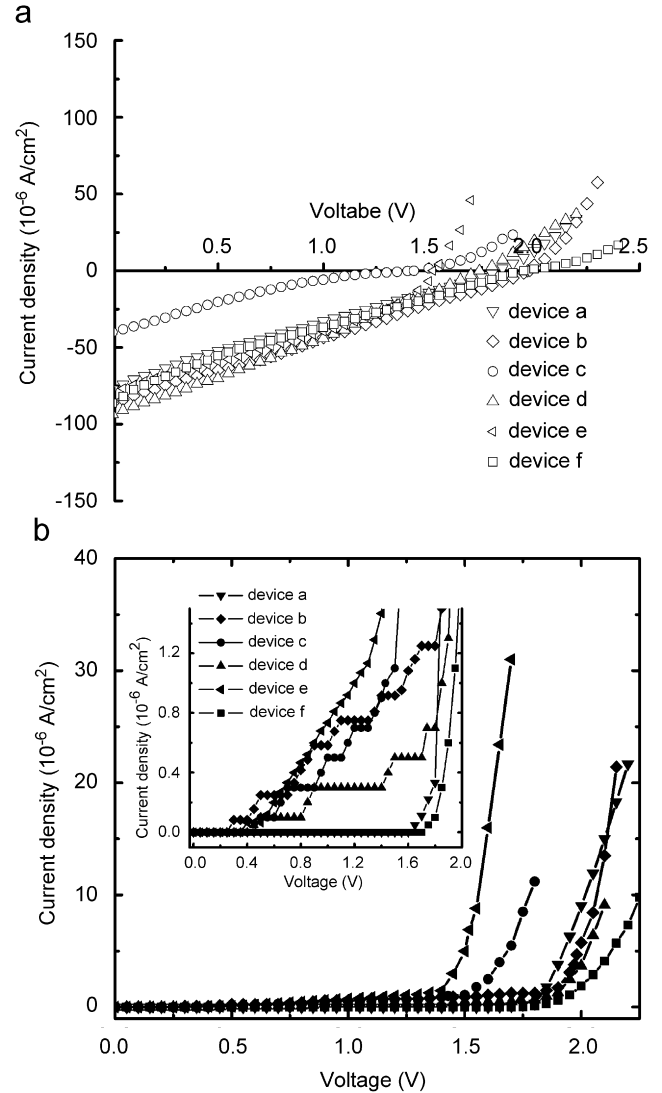


Fig. 3. *I*-*V* characteristics of the devices a-f with UV-on (a) and UV-off (b). Inset (b): the dark current with the compensatory voltage lower than 1.65 V.

parameters of these devices are: V_{oc} of 1.97 V and η of 2.60% for device b; I_{sc} of 93.5 $\mu\text{A}/\text{cm}^2$ for device d; and FF of 0.33 for device e. Device a does not give out dark current when the compensatory voltage is lower than 1.65 V, indicating that it holds the potential application in UV-light detection. As can be seen from Table 1, the devices based on (OXD-Pybm)Gd(DBM)₃ and (OXD-Pybm)Sm(DBM)₃ are the best ones, and those based on (OXD-Pybm)Pr(DBM)₃ and (OXD-Pybm)Gd(DBM)₃ are the moderate ones. When (OXD-Pybm)Eu(DBM)₃ is used as the electron acceptor, device c shows poor performance, for example, the values of V_{oc} , FF, and η of device c are only 1.43 V, 0.18, and 0.6%, respectively. These results present that the 4f electrons and 4fⁿ configurations of Ln³⁺ ions affect the device performance greatly. Device e is experimentally found to exhibit better performance than device a, which disagrees with the result from the Ln(DBM)₃ bath based OPV devices [21],

suggesting the properties of the diimine ligand can also influence the OPV device performances.

3.3. Effect of the OXD group on the performances of the OPV devices

For the purpose of studying the influence of electron-transporting group of OXD on the OPV device performances, (Pybm)Gd(DBM)₃ is used as electron acceptor to construct the referential device with the structure of ITO/PEDOT: PSS (60 nm)/*m*-MTDATA (40 nm)/(Pybm)Gd(DBM)₃ (20 nm)/LiF (1 nm)/Al (120 nm) (device **f**). The *I*–*V* characteristics of device **f** were also measured with UV-on and UV-off conditions (Fig. 2). The *E*_{LUMO} of (OXD–Pybm)Gd(DBM)₃ was measured to be –3.41 eV, which is 0.02 eV lower than that (–3.39 eV) of (Pybm)Gd(DBM)₃. As a result, the *V*_{oc} (1.74 V) of device **d** is 0.21 V lower than that of device **f** (1.95 V). At the same time, the η and *I*_{sc} of device **d** are 2.59% and 93.5 μ A/cm², respectively, which are slightly higher than those (2.17% and 86.4 μ A/cm²) of device **f**. The higher current of device **d** is attributed to high transport characteristics, because the OXD group in the electron acceptors of lanthanide complexes possesses higher electron-affinity which is helpful for the excitons dissociation at the D–A interface and meanwhile endows the electron acceptor higher transport ability.

4. Conclusion

In summary, a series of OPV devices are fabricated by utilizing (OXD–Pybm)Ln(DBM)₃ as the electron acceptors. The device performances are generally improved by the introduction of electron-transporting group of OXD into lanthanide complexes which also makes the devices more sensitive to the UV-light illumination. As a result, the devices based on (OXD–Pybm)Sm(DBM)₃ and (OXD–Pybm)Gd(DBM)₃ show the highest power conversion efficiency of ca. 2.6%, whereas (OXD–Pybm)Pr(DBM)₃ based device holds the potential application in UV-light detection. It also indicates that with the help of molecular engineering and optimal architectures to purposely design

novel metal complexes is an efficient method to improve the performances of OPV devices.

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