

Synthesis and photovoltaic properties of new europium complex $\text{Eu}(\text{DBM})_3(\text{CPyBM})$

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Abstract

A new europium(III) complex, tris(dibenzoylmethanate){1-[9-hexyl-9-carbazole]-2-(2-pyridyl)-benzimidazole}europium(III) [$\text{Eu}(\text{DBM})_3(\text{CPyBM})$] was synthesized and used as an electron-acceptor and electron-transport layer in organic photovoltaic (PV) device. Power conversion efficiency achieved from the device was 1.04% under illumination with 365 nm UV light at 1.6 mW/cm². Compared with the previous reported devices based on Eu(III) complexes, the PV performances were improved. The working mechanism of the organic PV device was discussed.

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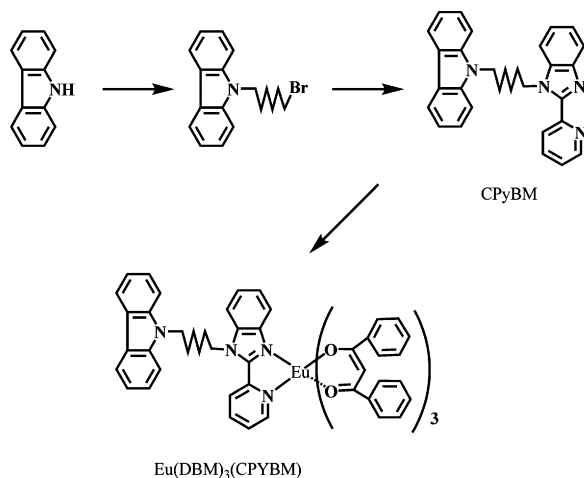
Keywords: Organic photovoltaic device; Europium complex; Synthesis

Organic PV devices have attracted much attention due to their excellent properties such as light weight, low cost and compatibility with flexible substrates [1]. Most efforts, made in the past two decade, focused on improvement of power conversion efficiency (η_p) [2,3]. Unfortunately, η_p and the lifetime of organic PV devices are far from satisfactory. Both materials choice and device processing techniques are crucial for improving η_p [2,4]. Conjugated polymers, such as poly(phenylene vinylene) and its derivatives [5], have become the most interesting materials in the organic PV field, and in recent years attention has also been paid to some small molecules [5,6]. Chu et al. [7] have reported a PV device using yttrium complex as electron-acceptor with open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and η_p of 2.15 V, 46 $\mu\text{A}/\text{cm}^2$, 0.3, 0.7%, respectively.

In order to explore highly efficient organic PV materials, herein we report the synthesis of an Eu(III) complex $\text{Eu}(\text{dibenzoylmethanate})_3(\text{CPyBM})$ (Scheme 1). CPyBM containing 2-(2-pyridyl)benzimidazole fragment was selected as the second ligand, since it is thought to enhance the electron-transport capability of material [8], and the PV device using $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ as an electron-acceptor and electron-transport layer was fabricated simultaneously. The PV properties of $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ were investigated. The synthetic routes of the ligand CPyBM and the complex $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ are presented in Scheme 1.

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Scheme 1. Synthesis routes of the ligand CPyBM and the complex Eu(DBM)₃(CPyBM).

1. Experimental

9-(6-Bromohexyl)-9H-carbazole was prepared according to a literature method [8].

Synthesis of CPyBM. A mixture of 9-(6-bromohexyl)-9H-carbazole (1.67 g, 5 mmol), 2-(2-pyridyl)benzimidazole (0.98 g, 5 mmol), NaOH (0.22 g, 5.5 mol) and DMF (30 mL) was stirred and heated at 120 °C for 15 h under N₂. It was subsequently poured into water, extracted with CH₂Cl₂. The resulting residue after removal of the solvent was purified by chromatography to give 1.8 g of product. Yield: 80%. mp: 50 °C. ¹H NMR (CDCl₃, δ ppm): δ 1.27–1.39 (m, 4H, alkyl protons), 1.68–1.85 (m, 4H, alkyl protons), 4.25–4.29 (t, 2H, *J* = 6.83 Hz, –NCH₂–), 4.77–4.81 (t, 2H, *J* = 7.46 Hz, –NCH₂–), 7.27 (t, 2H, *J* = 8.01 Hz, aromatic protons), 7.31 (t, 2H, *J* = 8.25 Hz, aromatic protons), 7.32 (t, 2H, *J* = 6.98 Hz, aromatic protons), 7.35 (d, 2H, *J* = 7.82 Hz, aromatic protons), 7.37 (d, 2H, *J* = 7.64 Hz, aromatic protons), 7.45 (d, 2H, *J* = 7.54 Hz, aromatic protons), 8.10 (d, 1H, *J* = 7.62 Hz, aromatic proton), 8.17 (t, 1H, *J* = 8.23 Hz, aromatic proton), 8.29 (t, 1H, *J* = 7.93 Hz, aromatic proton), 8.501 (d, 1H, *J* = 8.06 Hz, aromatic proton). EI-MS: *m/z* 444 (*M*⁺).

Eu(DBM)₃(CPyBM) was prepared according to a literature method [9]. Elemental analysis for C₇₅H₆₁N₄O₆Eu. Calcd: C, 71.14; H, 4.85; N, 4.42. Found: C, 71.20; H, 4.61; N, 4.34.

PV device with structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) (20 nm)/4,4',4''-tris-[3-methylphenyl (phenyl) amino]triphenyl amine (*m*-MTDATA) (30 nm)/Eu(dibenzoylmethanate)₃ (CPyBM) (60 nm)/LiF (1 nm)/Al (100 nm) was fabricated as shown in Fig. 1. Eu(DBM)₃(CPyBM) and *m*-MTDATA were used as electron-acceptor and electron-donor, respectively. The ITO coated glass substrate was pre-coated with PEDOT:PSS, which acted as hole injection layer to lower the hole barrier at the ITO anode and increase the short circuit current. The light-state *I*–*V* characteristics of the PV device were measured under UV illumination at 365 nm of 1.6 mW/cm². The absorption spectra were measured with Shimadzu UV-3101PC spectrophotometer. Photocurrent response curves were recorded under 40 μA/cm² Xe lamp.

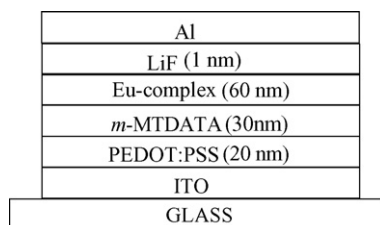


Fig. 1. The configuration of the PV device.

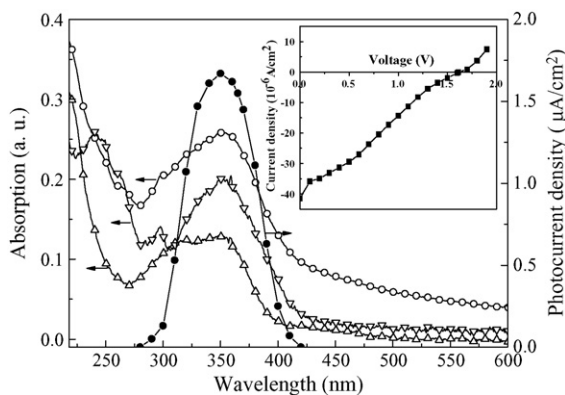


Fig. 2. The absorption spectra of $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ film (down triangle), m -MTDATA film (up triangle), m -MTDATA/ $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ film (open circle), and photocurrent response of PV device (solid circle). Inset the I - V characteristics of the PV device.

2. Results and discussion

Fig. 2 exhibits the absorption spectra of m -MTDATA, $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ and m -MTDATA/ $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ films, and the photovoltaic spectral response of the PV device. For the $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ film, the band at 297 nm is attributed to the absorption of carbazole fragment, the absorption band centering at 350 nm is assigned to π - π^* transition of the DBM ligand. By compared the photocurrent response curve of the device with the absorption spectra of $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ and m -MTDATA films, it is found that their maximum peaks are nearly at the same position, and the total absorption of m -MTDATA/ $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ films consists of $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ film and m -MTDATA film, indicating that the generation of photocurrent is attributed to the total absorption of both the m -MTDATA layer and the $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ layer. The most sensitive response wavelength of the device is about 310–390 nm, so this PV device containing $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ is suitable for fabricating photodetectors to detect UV light.

Both $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ and m -MTDATA have contributed to the PV effects of the device, and $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ should play electron-acceptor role, while m -MTDATA played electron-donor role in our PV device. Dissociations of the excitons must take place at the interface between $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ layer and m -MTDATA layer. The typical parameters, V_{oc} , I_{sc} , and FF of the PV device reached about 1.61 V, 41.5 $\mu\text{A}/\text{cm}^2$, and 0.25, respectively, and η_{p} was about 1.04% under illumination with 365 nm UV light at 1.6 mW/cm^2 , as shown in the inset of Fig. 2. These parameters are superior, compared with the previously reported PV device based on Eu(III) complex [10].

In conclusion, an Eu(III) complex $\text{Eu}(\text{DBM})_3(\text{CPyBM})$ was synthesized and used as electron-acceptor and electron-transport layer in organic PV device. The typical parameters, V_{oc} , I_{sc} , and FF of the PV device reached about 1.61 V, 41.5 $\mu\text{A}/\text{cm}^2$, and 0.25, respectively, and η_{p} was about 1.04% under illumination with 365 nm UV light at 1.6 mW/cm^2 . Our results demonstrated that the PV performance based on lanthanide complex can be effectively improved by molecular design and superior device architecture.

Acknowledgments

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