

# Microwave-assisted synthesis of phthalocyanine–porphyrin complex and its photoelectric conversion properties

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## Abstract

A soluble phthalocyanine–porphyrin complex (Lu(TBPor)Pc) has been rapidly synthesized from a lutetium porphyrin (Lu(TBPor)OAc) and a metal-free phthalocyanine (H<sub>2</sub>(TBPC)) under microwave irradiation. Its photoelectric conversion properties have also been investigated. The experimental results reveal that Lu(TBPor)Pc exhibits better photoelectric conversion effect than Lu(TBPor)OAc, H<sub>2</sub>(TBPC), and Lu(TBPor)OAc/H<sub>2</sub>(TBPC) blend. Furthermore, we have also introduced a n-type photoconductor (*N,N'*-bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide)(PDHEP)) and TiO<sub>2</sub> into Lu(TBPor)Pc photoelectric cell to fabricate a SnO<sub>2</sub>/Lu(TBPor)Pc+PDHEP+TiO<sub>2</sub>/Al photoelectric cell, exhibiting the largest short-circuit photocurrent (691.3 μA/cm<sup>2</sup>) among all of lab-made cells under illumination of white light (1.2 mW/cm<sup>2</sup>).

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**Keywords:** Phthalocyanine; Porphyrin; Microwave; Double-decker; Photoelectric conversion

## 1. Introduction

Phthalocyanines (Pc) and porphyrins (Por) are versatile industrial materials and have attracted much attention for many years because of their wide applications such as light-emitting diodes [1,2], photodynamic therapy [3], molecular thermometers [4], magnets [5], and optical limiting devices [6]. Recently, they have been discovered to be p-type photoconductors and applied for solar cells [7,8].

In this paper, a soluble phthalocyanine–porphyrin complex (Pc–Por complex) has been quickly prepared by the combination of Pc and Por under microwave irradiation. Moreover, we have also investigated its photo-

electric conversion properties and demonstrated that it exhibits larger short-circuit photocurrent than Pc, Por, and Pc/Por blend. Finally, a n-type photoconductor (*N,N'*-bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide)) and TiO<sub>2</sub> have been introduced into lab-made photoelectric cell with Pc–Por complex to facilitate the photoelectric conversion properties.

## 2. Experimental

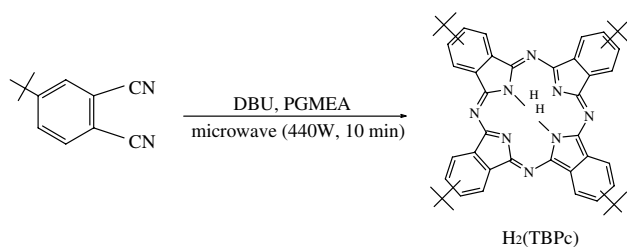
### 2.1. Materials

#### 2.1.1. Preparation of tetrakis(2,9,16,23-*tert*-butyl metal-free phthalocyanines) (H<sub>2</sub>(TBPC)) (Scheme 1)

H<sub>2</sub>(TBPC) was prepared from 4-tetra-*t*-butyl phthalonitrile in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) under microwave irradiation and purified by the procedure reported previously [9].

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Scheme 1.

### 2.1.2. Preparation of Pc–Por complex (Lu(TBPor)Pc) (Scheme 2)

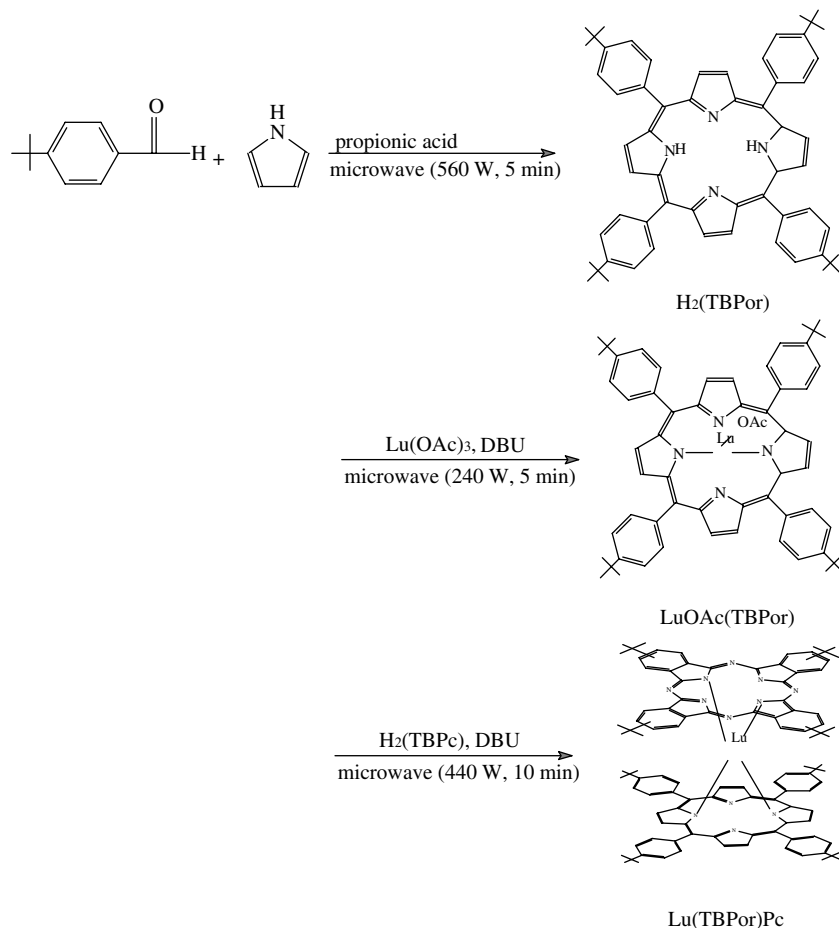
4-*tert*-Butyl benzaldehyde (3 g, 18.5 mmol), pyrrole (1.34 g, 20 mmol), and propionic acid (10 mL) were irradiated in a quartz vessel of 50 mL by a microwave oven at 560 W for 5 min. The crude product was washed with distilled water and purified by recrystallization with toluene. After purified by column chromatography (aluminum oxide, chloroform), H<sub>2</sub>(TBPor) (2.18 g) was obtained (yield: 56%). IR (KBr) (cm<sup>-1</sup>) (H<sub>2</sub>(TBPor)): 3416, 2959, 2853, 1664, 1646, 1601, 1568, 1550, 1531, 1502, 1465, 1410, 1391, 1362, 1329, 1295, 1266, 1196, 1155, 1141, 1107, 1089, 1019, 960, 879, 838, 764, 709,

665, 558, 425. UV/Vis  $\lambda_{\max}$  (nm) 649, 551, 515, 420 (in 1-methyl-2-pyrrolidone (NMP)). MS: (*m/z*) (FAB<sup>+</sup>) 840. Elemental analysis for C<sub>60</sub>H<sub>62</sub>N<sub>4</sub>, Calc.: C, 85.88; H, 7.45; N, 6.68. Found: C, 85.72; H, 7.33; N, 6.52%.

H<sub>2</sub>(TBPor) (1 g, 1.2 mmol) and lutetium acetate (0.42 g, 1.2 mmol) were ground together in a quartz vessel of 50 mL, poured into 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 5 mL), and irradiated in a microwave oven at 240 W for 5 min. The crude product was firstly dissolved in ethanol, and then butyl acetate as well as petroleum ether was added for precipitation. After purified by recrystallization with methanol and by column chromatography (aluminum oxide, chloroform), LuOAc(TBPor) (1.06 g) was obtained (yield=75%).

IR (KBr) (cm<sup>-1</sup>) (LuOAc(TBPor)): 2952, 1762, 1712, 1626, 1561, 1455, 1254, 1177, 1093, 1011, 965, 853, 804, 751, 553. UV/Vis  $\lambda_{\max}$  (nm) 595, 556, 426 (in NMP). MS: (*m/z*) (FAB<sup>+</sup>) 1012. Elemental analysis for C<sub>62</sub>H<sub>63</sub>N<sub>4</sub>O<sub>2</sub>Lu, Calc.: C, 69.52; H, 5.93; N, 5.23. Found: C, 69.68; H, 6.04; N, 5.35%.

LuOAc(TBPor) (1 g, 0.99 mmol) and H<sub>2</sub>(TBPc) (0.73 g, 0.99 mmol) were ground together in a quartz vessel of 50 mL, poured into DBU (5 mL), and irradiated in a microwave oven at 440 W for 10 min. The product was



Scheme 2.

washed with a methanol/water solution (v/v, 1/2) and purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/3, wt/wt). After drying, Lu(TBPor)Pc (1.14 g) was obtained (yield: 66%).

IR (KBr) ( $\text{cm}^{-1}$ ) Lu(TBPor)Pc: 2946, 2924, 2857, 1758, 1708, 1683, 1650, 1633, 1622, 1574, 1558, 1518, 1507, 1488, 1474, 1457, 1437, 1418, 1384, 1362, 1323, 1261, 1200, 1107, 1082, 1046, 1018, 917, 830, 797, 752, 718, 696, 671, 618, 556. UV/Vis  $\lambda_{\text{max}}$  (nm) 686, 641, 422 (in NMP). MS: ( $m/z$ ) ( $\text{FAB}^+$ ) 1749. Elemental analysis for  $\text{C}_{108}\text{H}_{108}\text{N}_{12}\text{Lu}$ , Calc.: C, 74.16; H, 6.22; N, 9.61. Found: C, 73.82; H, 6.30; N, 9.73%.

### 2.1.3. Preparation of *N,N'*-bis(1,5-dimethylhexyl)-3,4,9,10-perylenebis(dicarbox-imide) (PDHEP) (Scheme 3)

PDHEP was prepared from 3,4,9,10-perylenetetracarboxylic dianhydride and 2-amino-6-methylheptane in the presence of water under microwave irradiation and purified by the procedure reported previously [10].

### 2.2. Film preparation and fabrication of the photoelectric cells

$\text{H}_2(\text{TBPc})$  or LuOAc(TBPor) or Lu(TBPor)Pc was dissolved in dichloromethane (2 wt%), filtrated with a 0.2  $\mu\text{m}$  filter, and deposited onto  $\text{SnO}_2$  glass (TEC 10 glass, Hartford Glass Co. Inc.) by spin-coating technique. The counter Al electrode was then put on top by vacuum evaporation as shown in Fig. 1. The same procedure was adopted in the fabrication of  $\text{H}_2(\text{TBPc})/\text{LuOAc}(\text{TBPor})$  or Lu(TBPor)Pc/PDHEP (mol. ratio = 1/1) blend photoelectric cell. The layer thickness of  $\text{H}_2(\text{TBPc})$ , LuOAc(TBPor), Lu(TBPor)Pc, blend, and Al are 30, 30, 30, 30, and 200 nm, respectively. The active areas of all dyes are 2  $\text{cm}^2$  (0.8  $\text{cm} \times 2.5 \text{ cm}$ ).

The Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  photoelectric cell was fabricated by the similar procedure. The Lu(TB-

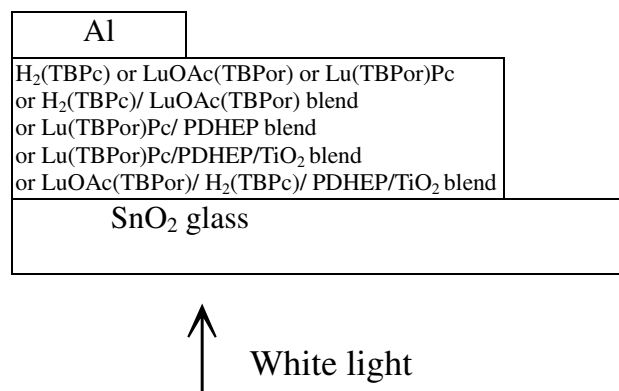
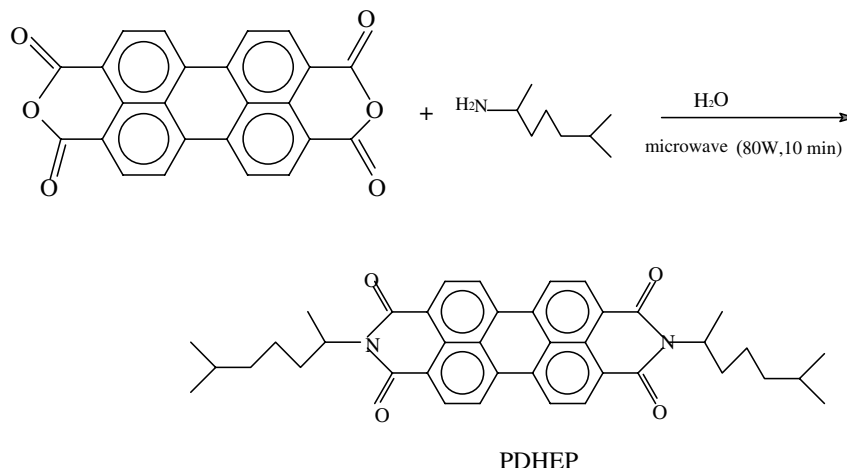


Fig. 1. The structure of lab-made photoelectric cell. White light (1.2  $\text{mW}/\text{cm}^2$ ) is irradiated on the  $\text{SnO}_2$  glass.

Por)Pc/PDHEP blend was dissolved in dichloromethane (2 wt%) and filtrated with a 0.2  $\mu\text{m}$  filter.  $\text{TiO}_2$  powder (Degussa P25) was then added into the dichloromethane solution of dye (20 wt%). After blending in the ultrasonic bath, the Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  blend was deposited onto  $\text{SnO}_2$  glass by spin-coating technique. Finally, the counter Al electrode was put on the top by vacuum evaporation as shown in Fig. 1. The LuOAc(TBPor)/ $\text{H}_2(\text{TBPc})/\text{PDHEP}/\text{TiO}_2$  photoelectric cell was also fabricated by the similar procedure. The layer thickness of Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  blend, LuOAc(TBPor)/ $\text{H}_2(\text{TBPc})/\text{PDHEP}/\text{TiO}_2$  blend and Al were 30, 30, and 200 nm, respectively. The active areas of Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  and LuOAc(TBPor)/ $\text{H}_2(\text{TBPc})/\text{PDHEP}/\text{TiO}_2$  cell were 2  $\text{cm}^2$  (0.8  $\text{cm} \times 2.5 \text{ cm}$ ).

### 2.3. Instruments

In order to avoid the contamination of metal-ion from glass, all of lab-made materials were prepared in the quartz vessel. The microwave oven used in the experiments was Sunpentown SM-1290. UV/Vis and IR



Scheme 3.

spectra were recorded on a HITACHI U-3300 and a Perkin–Elmer RX-1 FT-IR System, respectively. The photoelectric conversion properties were measured in the air by an instrument (Keithley 238), whose accuracy can reach picoampere, under illumination of white light from a 300 W halogen lamp (Saturn Co.) whose intensity was recorded on a radiometer (IL-1700). The thickness of the films were measured by a surface profiler (TENCOR P-10).

### 3. Results and discussion

#### 3.1. Microwave-assisted procedure

Microwave irradiation has recently been a fast procedure for chemical synthesis [11]. In this paper, the process for preparation of Pc, Por, Pc–Por complex, and PDHEP as shown in Schemes 1–3, take only 5–10 min. However, the conventional methods take several hours to one day for completion [12,13]. Microwave-assisted procedure promotes the polarization of the starting materials to accelerate the reactions described above and reduces the production cost. All the reactions in this paper have been successfully repeated several times with identical results.

#### 3.2. Photoelectric conversion properties

In recent years, the conversion of sunlight into electrical energy has become an important topic because sunlight is a clean, environment-friendly, and inexhaustible energy source. Furthermore, over half the energy that reaches the earth's surface from the sun is in the form of visible radiation (400–800 nm) [14]. Since Por and Pc are synthetic analogues of chlorophyll [15] and the absorptions of Por and Pc locate in the range of 400–450 and 600–800 nm, respectively, they are proper materials for photoelectric conversion. In order to increase the photoelectric performance, we have combined Por and Pc to form a single compound, Pc–Por complex. In our previous research [9,16], we have discovered that the double-decker lutetium tetrakis(*tert*-butyl)bisphthalocyaninate ( $\text{Lu}(\text{TBPC})_2$ ) exhibits photoelectric conversion properties and its short-circuit photocurrent is larger than other double-decker lanthanide tetrakis(*tert*-butyl)bisphthalocyaninate ( $\text{Ln}(\text{TBPC})_2$ , Ln = Tb, Dy, ... etc.) Therefore, we prepared Lu Pc–Por complex ( $\text{Lu}(\text{TBPor})\text{Pc}$ ) and investigated its photoelectric conversion properties.

As shown in Figs. 2 and 3, the photons in the range of 400–450 nm are absorbed by  $\text{LuOAc}(\text{TBPor})$ , and those in the range of 600–800 nm by  $\text{H}_2(\text{TBPC})$ . Under illumination of white light ( $1.2 \text{ mW}/\text{cm}^2$ ), the photo-absorptions of these dyes cause photo-excitation of electrons from the valence band to the conduction band [17], producing a short-circuit photocurrent in the external cir-

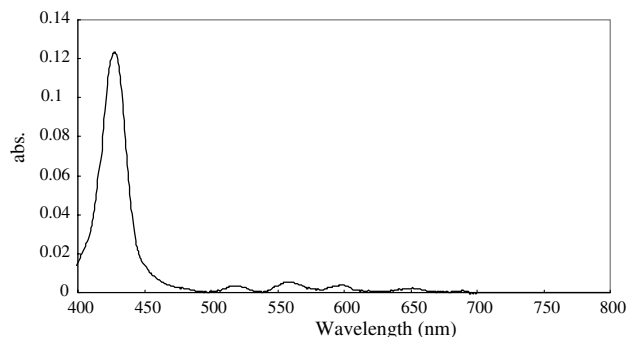


Fig. 2. The UV/Vis spectrum of  $\text{LuOAc}(\text{TBPor})$  thin film.

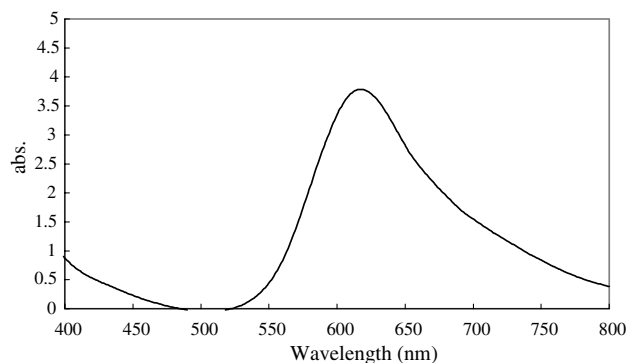


Fig. 3. The UV/Vis spectrum of  $\text{H}_2(\text{TBPC})$  thin film.

cuit. Without illumination of white light, no significant current can be detected. Their photoelectric performances are summarized in Table 1.

The experimental results reveal that  $\text{LuOAc}(\text{TBPor})$  has poorer short-circuit photocurrent than  $\text{H}_2(\text{TBPC})$  because of larger band gaps [1,18]. In order to promote the photoelectric properties of the cell with  $\text{LuOAc}(\text{TBPor})$  and  $\text{H}_2(\text{TBPC})$ , we have mixed these two materials and fabricated a blend-type photoelectric cell. The  $\text{SnO}_2$  glass/ $\text{LuOAc}(\text{TBPor})$  and  $\text{H}_2(\text{TBPC})$  blend (mol. ratio = 1/1)/Al blend-type cell exhibits better photoelectric properties than  $\text{LuOAc}(\text{TBPor})$  or  $\text{H}_2(\text{TBPC})$  owing to wider photo-absorptions consisted of 400–

Table 1  
The photoelectric performances of lab-made cells

Lab-made photoelectric cells	Short-circuit photocurrent ( $\mu\text{A}/\text{cm}^2$ )
$\text{SnO}_2/\text{Lu}(\text{TBPor})\text{Pc} + \text{PDHEP} \text{ blend} + \text{TiO}_2/\text{Al}$	691.3
$\text{SnO}_2/\text{LuOAc}(\text{TBPor}) + \text{H}_2(\text{TBPC}) + \text{PDHEP} \text{ blend} + \text{TiO}_2/\text{Al}$	493.5
$\text{SnO}_2/\text{Lu}(\text{TBPor})\text{Pc} + \text{PDHEP} \text{ blend}/\text{Al}$	240.3
$\text{SnO}_2/\text{Lu}(\text{TBPor})\text{Pc}/\text{Al}$	50.6
$\text{SnO}_2/\text{LuOAc}(\text{TBPor}) + \text{H}_2(\text{TBPC}) \text{ blend}/\text{Al}$	47.8
$\text{SnO}_2/\text{H}_2(\text{TBPC})/\text{Al}$	42.0
$\text{SnO}_2/\text{LuOAc}(\text{TBPor})/\text{Al}$	20.6

450 and 600–800 nm as shown in Fig. 4. However, its short-circuit photocurrent was still unsatisfying since our goal is to reach  $100 \mu\text{A}/\text{cm}^2$ .

Thus, the photoelectric cell of Pc–Por complex (Lu(TBPor)Pc) has been fabricated to further increase the photoelectric conversion properties. As shown in Table 1 the photoelectric cell of Lu(TBPor)Pc has larger short-circuit photocurrent than those of  $\text{H}_2(\text{TBPC})$ , Lu(TBPor)Pc, and  $\text{H}_2(\text{TBPC})/\text{Lu}(\text{TBPor})\text{Pc}$ . This reveals that combination of Por and Pc into a single compound not only extends the range of absorptions but also prevents the resistance of random grain arrangement of Lu(OAc)(TBPor)/ $\text{H}_2(\text{TBPC})$  blend [18]. Finally, we blend PDHEP into the cell of Lu(TBPor)Pc to form Lu(TBPor)Pc/PDHEP blend-type cell  $\text{SnO}_2$  glass/Lu(TBPor)Pc and PDHEP blend (mol. ratio = 1/1)/Al. As shown in Table 1 the photoelectric conversion properties of Lu(TBPor)Pc/PDHEP blend-type cell are larger than those of Lu(TBPor)Pc cell because the former has broader photo-absorption (400–800 nm) than the latter (600–800 and 400–450 nm) as shown in Figs. 5, 6 and p/n heterojunction takes place in the case of the former since Lu(TBPor)Pc and PDHEP are p-type and n-type semiconductor, respectively [7,8,18].

Recently,  $\text{TiO}_2$  has been utilized in photoelectrochemical cells [19]. Therefore, we have introduced  $\text{TiO}_2$  into the Lu(TBPor)Pc/PDHEP blend-type cell to fabricate nanocrystalline dye sensitized photoelectric

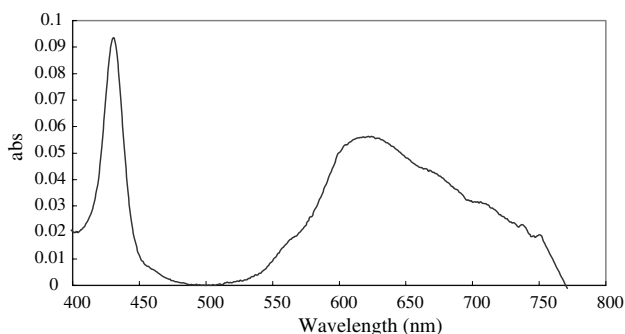


Fig. 4. The UV/Vis spectrum of LuOAc(TBPor)/ $\text{H}_2(\text{TBPC})$  blend thin film.

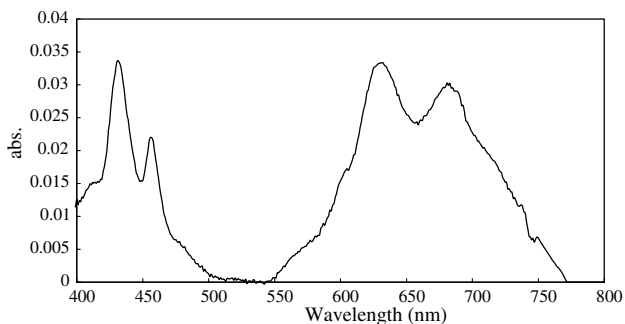


Fig. 5. The UV/Vis spectrum of Lu(TBPor)Pc thin film.

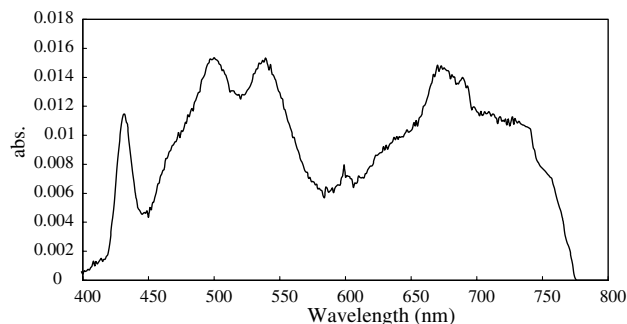
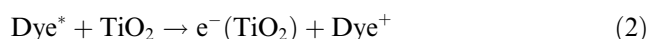
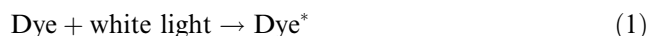


Fig. 6. The UV/Vis spectrum of Lu(TBPor)Pc/PDHEP thin film.

cells in order to promote the photoelectric performances. As shown in Table 1 Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  cell dramatically exhibits better photoelectric conversion properties than other lab-made cells because  $\text{TiO}_2$  assists the electron transfer in the cell. The photoelectric conversion may proceed by the following process [20].



where Dye represents Lu(TBPor)Pc/PDHEP blend; Dye\* represents that Lu(TBPor)Pc/PDHEP blend is photo-excited; and  $\text{e}^-(\text{TiO}_2)$  represents that  $\text{TiO}_2$  carries electrons.

First, the Lu(TBPor)Pc/PDHEP blend is photo-excited. Then the excited electrons of Lu(TBPor)Pc/PDHEP blend, which are generated by light absorption, were transferred into the  $\text{TiO}_2$ . Finally, the electrons flow from the  $\text{TiO}_2$  through the external circuit to generate the electrical energy.

Moreover, we have also fabricated LuOAc(TBPor)/ $\text{H}_2(\text{TBPC})/\text{PDHEP}/\text{TiO}_2$  cell and investigated its photoelectric conversion properties. As shown in Table 1, the short-circuit photocurrent of LuOAc(TBPor)/ $\text{H}_2(\text{TBPC})/\text{PDHEP}/\text{TiO}_2$  cell is lower than that of Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  cell. Although p/n heterojunction takes place in both cases, the grain arrangement of the former is more random than that of the latter, increasing the resistance of electrons flowing through one molecule to another [9,18]. As a result, Lu(TBPor)Pc/PDHEP/ $\text{TiO}_2$  cell exhibits better photoelectric conversion properties than LuOAc(TBPor)/ $\text{H}_2(\text{TBPC})/\text{PDHEP}/\text{TiO}_2$  cell.

#### 4. Conclusion

We have synthesized a soluble Pc–Por complex (Lu(TBPor)Pc) by microwave irradiation and it is feasibly utilized for spin-coating technology in the prepara-

tion of the thin film. Furthermore, its photoelectric conversion properties have also been investigated. We demonstrate that Pc–Por complex exhibits better photoelectric performances than that of Por, Pc, and Por/Pc blend. Under illumination of white light (1.2 mW/cm<sup>2</sup>), Pc–Por complex/PDHEP/TiO<sub>2</sub> blend photoelectric cell has the best photoelectric conversion effect with a short-circuit photocurrent (691.3 μA/cm<sup>2</sup>) among all lab-made cells.

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