

The fluorescent and photoelectric conversion properties of porphyrin–perylene tetracarboxylic complex

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Abstract

Soluble 5,10,15,20-tetrakis(4-*tert*-butylphenyl)magnesium porphyrins (Mg(TBPor)), perylene tetracarboxylic derivative (*N,N'*-bis(1,5-dimethylhexyl)-3,4,9,10-perylenebis(dicarboximide), PDHEP), and porphyrin–perylene tetracarboxylic complex have been quickly prepared under microwave irradiation. Their fluorescent properties and photoelectric conversion properties have also been investigated. The experimental results reveal that porphyrin–perylene tetracarboxylic complex exhibits better fluorescent quantum yield and photo-electricity conversion effect than Mg(TBPor) and PDHEP, respectively.

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Keywords: Porphyrin; Perylene; Microwave; Fluorescence; Photoelectric conversion

1. Introduction

Porphyrins (Por) have attracted attention for many decades and are well-known optoelectronic as well as biological materials because of their versatile applications such as light-emitting diodes [1], molecular thermometers [2], magnets [3], photodynamic therapy [4], and optical limiting devices [5]. Although they perform excellent photochemical and electrochemical properties, their fluorescent intensity is poor. However, perylene tetracarboxylic derivatives (Pe) are not only optoelectronic pigments but also fluorescent materials [6]. Recently, Por and Pe have been found to be p-type and n-type photoconductors, respectively, and applied for Schottky and p/n heterojunction cells [7–10].

In this paper, soluble and fluorescent porphyrin–perylene tetracarboxylic complex (Por–Pe complex) has been rapidly prepared by the combination of Por and Pe under microwave irradiation. It is a charge-transfer complex since Por and Pe are electron-donor and electron-acceptor [7,8], respectively. Furthermore, we have also investigated their fluorescent and photoelectric conversion properties.

2. Experimental

2.1. Instruments

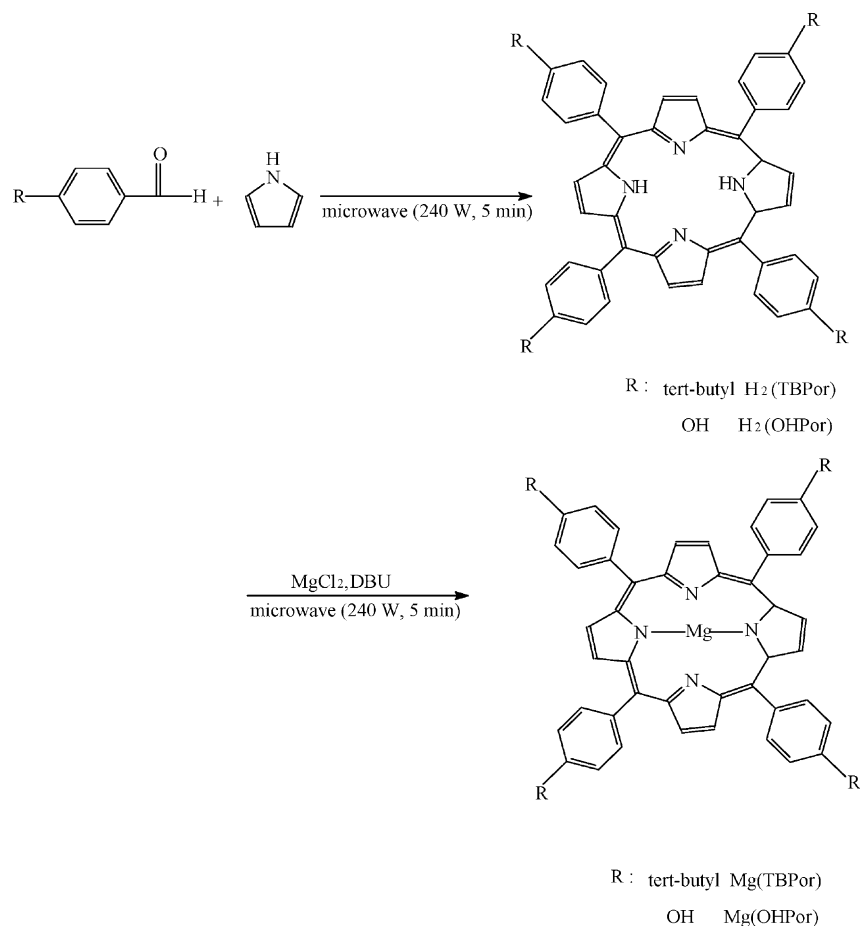
In order to avoid the contamination of metal ion from glass, all of lab-made materials were prepared in the quartz vessel. The microwave oven used in the experiments is Sunpentown SM-1290. UV-Vis and IR spectra were recorded on a HITACHI U-3300 and a Perkin-Elmer RX-1 FT-IR system, respectively. The fluorescent properties were measured by HITACHI F-2500. The short-circuit photocurrents 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 (TECOR P-10).

2.2. Materials

2.2.1. Preparation of 5,10,15,20-tetrakis(4-*tert*-butylphenyl)magnesium porphyrins (Mg(TBPor)) and 5,10,15,20-tetrakis(hydroxyphenyl)magnesium porphyrins (Mg(HOPor)) (Scheme 1)

4-Tertbutyl benzaldehyde (3 g, 18.5 mmol), and pyrrole (1.34 g, 20 mmol) were irradiated in a quartz vessel of 50 ml by a microwave oven at 240 W for 5 min. The crude product

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Scheme 1.

was washed with distilled water and purified by recrystallization with toluene. After purified by column chromatography (aluminum oxide, chloroform), $\text{H}_2(\text{TBPor})$ (1.7 g) was obtained (yield 44%).

IR (KBr, cm^{-1} , $\text{H}_2(\text{TBPor})$): 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 λ_{max} (nm): 545, 513, 415 (in ethanol). MS (m/z , FAB^+): 840.

$\text{H}_2(\text{TBPor})$ (1 g, 1.2 mmol) and magnesium chloride (0.17 g, 1.79 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) as catalyst, 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), $\text{Mg}(\text{TBPor})$ (0.75 g) was obtained (yield 72%).

IR (KBr, cm^{-1} , $\text{Mg}(\text{TBPor})$): 2941, 2857, 1664, 1644, 1611, 1552, 1535, 1513, 1482, 1465, 1443, 1387, 1359, 1320, 1267, 1233, 1200, 1107, 1020, 990, 956, 914, 883, 836, 794, 716, 665, 647, 536, 514, 464, 441. UV-Vis λ_{max} (nm): 603, 563, 423 (in ethanol), 610, 565, 431

(in 1-methyl-2-pyrrolidone (NMP)). MS (m/z , FAB^+): 861.

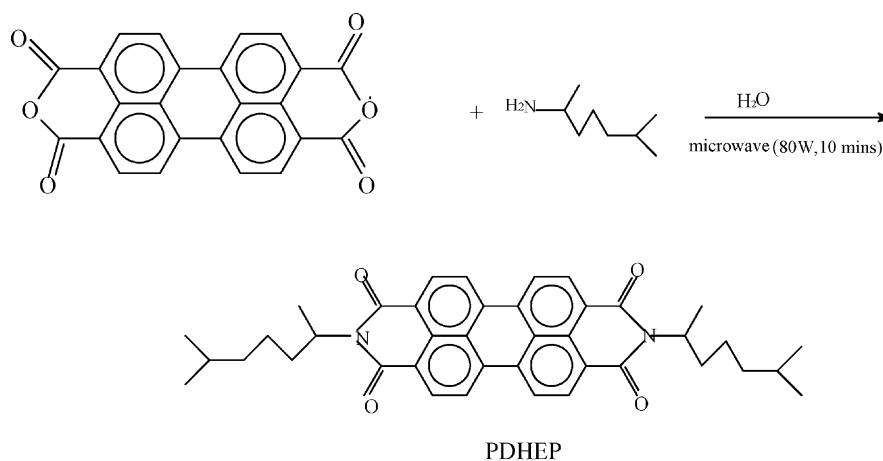
The same procedure was adopted in the preparation of $\text{H}_2(\text{HOPor})$ and $\text{Mg}(\text{HOPor})$. Their yield were 48 and 68%, respectively.

IR (KBr, cm^{-1} , $\text{H}_2(\text{HOPor})$): 3446, 3409, 1663, 1638, 1562, 1462, 1266, 1192, 1106, 1010, 970, 842, 804, 736, 665, 562, 447. UV-Vis λ_{max} (nm): 549, 517, 419 (in ethanol). MS (m/z , FAB^+): 678.

IR (KBr, cm^{-1} , $\text{Mg}(\text{HOPor})$): 3446, 1661, 1646, 1631, 1553, 1535, 1465, 1450, 1321, 1262, 1192, 1163, 1106, 1008, 970, 842, 804, 736, 536, 444. UV-Vis λ_{max} (nm): 604, 561, 425 (in ethanol), 610, 565, 431 (in NMP). MS (m/z , FAB^+): 700.

2.2.2. Preparation of *N,N'*-bis(1,5-dimethylhexyl)-3,4,9,10-perylenebis(dicarboximide) (PDHEP) (Scheme 2)

3,4,9,10-Perylene tetracarboxylic dianhydride (0.5 g, 1.28 mmol) and water (10 ml) were firstly added into a quartz vessel of 50 ml and blended in the ultrasonic bath for 10 min. Then, 2-amino-6-methylheptane (0.66 g, 5.12 mmol) was added into the quartz vessel and blended in the ultrasonic bath for 10 min. Finally, the quartz vessel was irradiated by a microwave oven at 80 W for 10 min. The product was



Scheme 2.

dissolved in methanol and added into water to precipitate. The final precipitate was filtrated, dried, and purified by Soxhelt extraction using toluene and by column chromatography (silica gel, tetrahydrofuran (THF)/*n*-hexane (5/1, w/w)). After drying, 0.64 g PDHEP was obtained (yield 81%).

IR (KBr, cm^{-1} , PDHEP): 3099, 2952, 1768, 1735, 1697, 1653, 1591, 1510, 1458, 1399, 1340, 1303, 1255, 1182, 1145, 1119, 1019, 964, 853, 806, 735, 621, 488, 433. UV-Vis λ_{max} (nm): 525, 488, 457 (in toluene). MS (m/z , FAB^+): 615.

2.2.3. Preparation of Por–Pe complex ($\text{Mg}(\text{PHEPO})\text{Por}$) (Scheme 3)

Perylene tetracarboxylic dianhydride (1 g, 2.56 mmol), water (10 ml), and 85% aqueous KOH solution (0.68 g) were irradiated in a quartz vessel of 50 ml in a microwave oven at 80 W for 10 min. Then, 37.8 wt.% hydrochloric acid (1 g) was added into the crude solution and kept its pH value 4.5–5. Finally, the crude solution was irradiated at 80 W for 10 min. After washing with a water/ethanol (1/1, v/v) solution and drying, PMONK (1.09 g) was obtained (yield 95%). IR (KBr, cm^{-1} , PMONK): 3106, 2650, 1767, 1741, 1730, 1712, 1690, 1679, 1646, 1590, 1553, 1535, 1502, 1465, 1432, 1402, 1369, 1295, 1233, 1192, 1144, 1118, 1019, 934, 849, 805, 753, 731, 635, 599, 565, 503, 433.

PMONK (1 g, 2.24 mmol), 2-amino-6-methylheptane (0.58 g, 4.48 mmol), and water (10 ml) were irradiated in a quartz vessel of 50 ml in a microwave oven at 80 W for 10 min. Then, 10 wt.% hydrochloric acid (10 g) was added into the crude solution. The crude solution was finally irradiated at 80 W for 10 min. After washing with water and drying, PAHEP (1.04 g) was obtained (yield 93%). IR (KBr, cm^{-1} , PAHEP): 3107, 2922, 2856, 1767, 1745, 1730, 1694, 1682, 1668, 1646, 1594, 1553, 1535, 1502, 1487, 1469, 1454, 1402, 1380, 1299, 1233, 1144, 1118, 1019, 938, 857, 809, 757, 731, 639, 599, 569, 499, 436, 411.

PAHEP (1 g, 1.98 mmol), 2-bromoethylamine (0.43 g, 3.96 mmol), zinc acetate (0.3 g, 1.64 mmol) and quinoline

(10 ml) were irradiated in a quartz vessel of 50 ml by a microwave oven at 440 W for 10 min. After washing with a methanol/water solution (1/1, v/v), PHEEB (0.98 g) was obtained (yield 71%). IR (KBr, cm^{-1} , PAHEP): 3105, 2924, 2856, 1767, 1745, 1730, 1693, 1681, 1668, 1646, 1594, 1553, 1535, 1502, 1487, 1469, 1454, 1402, 1380, 1299, 1233, 1144, 1118, 1019, 938, 857, 809, 757, 731, 639, 599, 569, 499, 436, 411. UV-Vis λ_{max} (nm): 524, 488, 460 (in NMP).

PHEEB (0.81 g, 1.12 mmol), $\text{Mg}(\text{HOPor})$ (0.1 g, 0.14 mmol), potassium carbonate (0.03 g, 0.21 mmol) and *N,N*-dimethylformamide (DMF, 5 ml) were irradiated in a quartz vessel of 50 ml by a microwave oven at 240 W for 30 min. After washing with a methanol/water solution (1/1, v/v) and purifying by column chromatography (silica gel, NMP/THF (3/1, w/w)), $\text{Mg}(\text{PHEPO})\text{Por}$ (0.26 g) was obtained (yield 59%). IR (KBr, cm^{-1} , $\text{Mg}(\text{HOPor})$): 3446, 1661, 1646, 1631, 1553, 1535, 1465, 1450, 1321, 1262, 1192, 1163, 1106, 1008, 970, 842, 804, 736, 536, 444. UV-Vis λ_{max} (nm): 527, 491, 433 (in NMP). MS (m/z , MALDI/TOF): 3128.

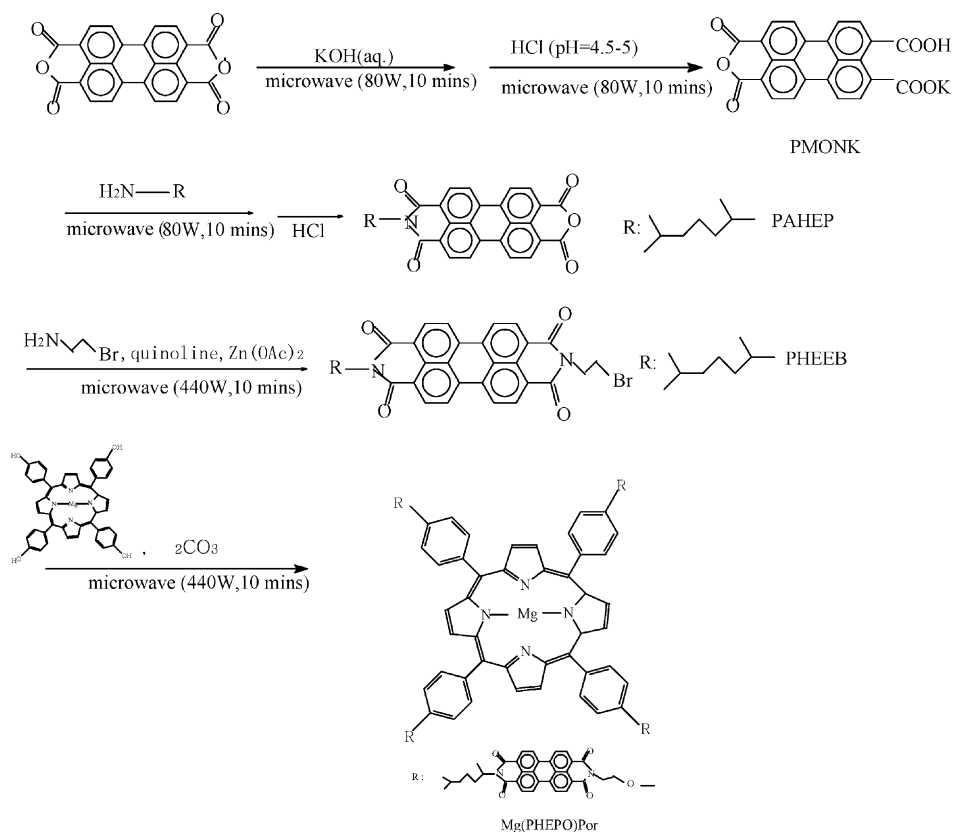
2.3. The quantum yield of fluorescence

The quantum yield was calculated from the following equation [11]:

$$\Phi_{\text{sample}} = \Phi_{\text{standard}} \times \frac{\text{area}_{\text{sample}} / (1 - \exp(-A_{\text{sample}}))}{\text{area}_{\text{standard}} / (1 - \exp(-A_{\text{standard}}))} \quad (1)$$

where Φ_{sample} and Φ_{standard} represent the quantum yields of sample and standard, respectively; $\text{area}_{\text{sample}}$ and $\text{area}_{\text{standard}}$ the area of fluorescent emission band for sample and standard, respectively; A_{sample} and A_{standard} the UV-Vis absorbances of sample and standard, respectively.

The standard in this study is Rose Bengal ($\Phi_{\text{standard}} = \Phi_{\text{Rose Bengal}} = 0.14$). The concentrations of samples are 10^{-6} M.



2.4. Film preparation and fabrication of the photoelectric cells

Mg(TBPor), PDHEP or Mg((PHEPO)Por was dissolved in dichloromethane (2 wt.%), filtrated with a 0.2 μm filter, and deposited onto SnO₂ glass (TEC 10 glass, Hartford Glass Co. Inc.) by spin-coating. The counter Pt or Al electrode was then put on top by vacuum evaporation as shown in Fig. 1. The same procedure was adopted in the fabrication of Mg(TBPor)/PDHEP (mole ratio = 1/1) blend photoelectric cell. The layer thickness of Mg(TBPor), PDHEP, blend,

Pt, and Al are 30, 15, 30, 200, and 200 nm, respectively. The active areas of all dyes are 2 cm² (0.8 cm \times 2.5 cm).

The Mg(PHEPO)Por/TiO₂ photoelectric cell was fabricated by the similar procedure. Mg(PHEPO)Por was dissolved in dichloromethane (2 wt.%) and filtrated with a 0.2 μm filter. TiO₂ powder (Degussa P25) was then added into the dichloromethane solution of dye (20 wt.%). After blending in the ultrasonic bath, the Mg(PHEPO)Por/TiO₂ blend was deposited onto SnO₂ glass by spin-coating. Finally, the counter Al electrode was put on the top by vacuum evaporation as shown in Fig. 1. The layer thickness of Mg(PHEPO)Por/TiO₂ blend and Al were 30 nm and 200 nm, respectively. The active areas of Mg(PHEPO)Por/TiO₂ were 2 cm² (0.8 cm \times 2.5 cm).

3. Results and discussion

3.1. Microwave-assisted procedure

Microwave-assisted procedure has recently been a facile tool for chemical synthesis [12]. In this paper, the process for preparation of porphyrin, perylene tetracarboxylic derivative, and porphyrin–perylene complex, including dehydration, replacement of protons to metal ions, imidization, ring-opening of perylene tetracarboxylic anhydride, and dehydrobromination as shown in Schemes 1–3, take

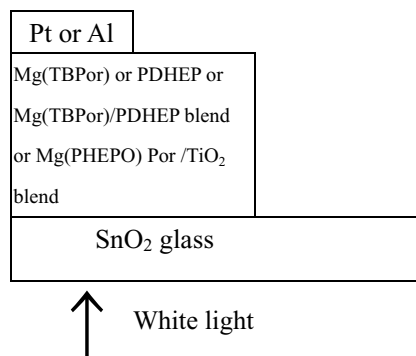


Fig. 1. The structure of lab-made photoelectric cell. White light (1.2 mW/cm²) is irradiated on the SnO₂ glass.

Table 1
The fluorescent properties of lab-made Mg(TBPor), PDHEP, and Mg(PHEPO)Por

Compound	Emitting wavelength (nm)	Excited wavelength (nm)	Quantum yield (Φ)
Mg(TBPor)	625	431	0.11
PDHEP	542	524	0.27
Mg(PHEPO)Por	621	433	0.12
Mg(PHEPO)Por	535	527	0.38

only 5–30 min. Nevertheless, the conventional methods take several hours to 1 day for completion [6,13]. Microwave irradiation accelerates the polarization of the starting materials to proceed the reactions described earlier.

Furthermore, no acid as well as oxidant are necessary in the microwave procedure for the preparation of porphyrins and the reaction condition is mild. These advantages are paramount to fit the demand in the clean and low-cost production of soluble porphyrins.

The reactions mentioned in this paper have also been successfully repeated several times with identical results.

3.2. Fluorescent properties

Generally, porphyrin exhibits poor fluorescent properties. However, introduction of perylene tetracarboxylic derivatives into porphyrin increases the fluorescence. The fluorescent properties of lab-made Mg(TBPor), PDHEP, and Mg(PHEPO)Por are summarized in Table 1.

In case of Mg(PHEPO)Por, its characteristic absorption locates in 433 and 527 nm, as shown in Fig. 2, which represent the absorptions of porphyrin and perylene tetracarboxylic derivative, respectively. When the excited wavelength is 433 nm, its fluorescence comes from the contribution of porphyrins as shown in Fig. 3. Compared with the fluorescence of Mg(TBPor), the quantum yield of Mg(PHEPO)Por ($\Phi = 0.12$) is slightly larger than that

of Mg(TBPor) ($\Phi = 0.11$). When the excited wavelength is 528 nm, however, its fluorescence comes from the contribution of perylene tetracarboxylic derivative as shown in Fig. 4. Compared with the fluorescence of PDHEP, the quantum yield of Mg(PHEPO)Por ($\Phi = 0.38$) is larger than that of PDHEP ($\Phi = 0.27$). This reveals that introduction of perylene tetracarboxylic derivatives into the porphyrin not only extends the range of excited wavelengths but also increases the fluorescent intensity.

3.3. Photoelectric conversion properties

The conversion of sunlight into electrical energy attracts much attention recently because sunlight is an inexhaustible, clear, and environment-friendly 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]. Because Por are synthetic analogues of chlorophyll [15] and the absorptions of Por and Pe locate in the range of 400–450 and 450–600 nm, respectively, they are suitable materials for photoelectric conversion. In order to promote the photoelectric performance, Por and Pe have been combined into a single compound, Por–Pe complex.

As shown in Figs. 5–8, the photons in the range of 400–450 nm are absorbed by Mg(TBPor), those in the range of 450–600 nm by PDHEP, and those in the range of 400–600 nm by the Mg(TBPor)/PDHEP blend and Mg(PHEPO)Por. Under illumination of white light (1.2 mW/cm^2), the photo-absorptions of these dyes cause photo-excitation of electrons from the valence band to the conduction band [16], producing a short-circuit photocurrent in the external circuit. Without illumination of white light, no significant current can be detected. Their photoelectric performances are summarized in Table 2.

The experimental results reveal that M(TBPor) exhibits poorer short-circuit photocurrent than PDHEP because of larger band gaps [8,17]. In order to increase the

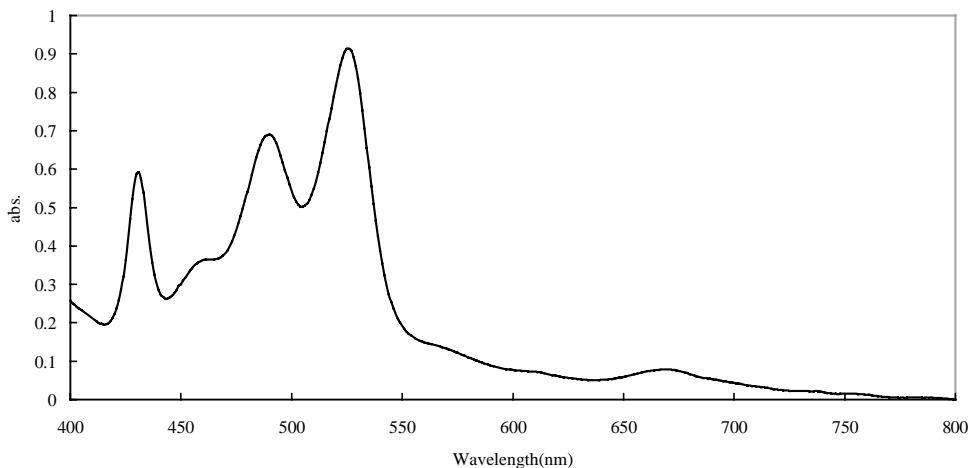


Fig. 2. The UV-Vis spectrum of Mg(PHEPO)Por in NMP.

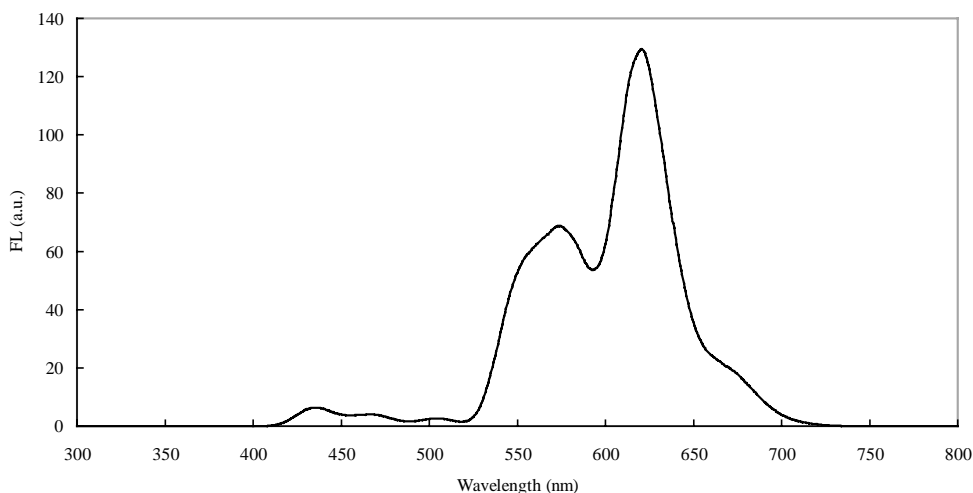


Fig. 3. The fluorescent spectrum of Mg(PHEPO)Por in NMP (0.001 wt.%). The excited wavelength is 433 nm.

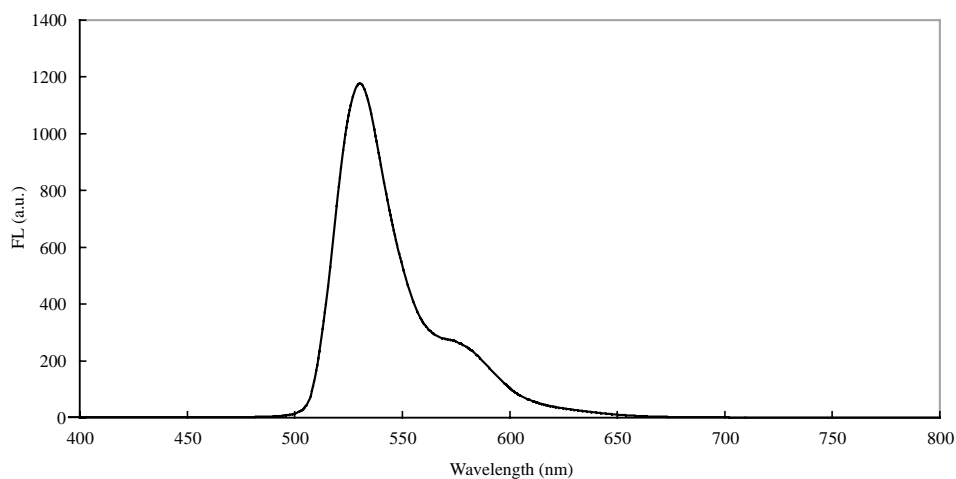


Fig. 4. The fluorescent spectrum of Mg(PHEPO)Por in NMP (0.001 wt.%). The excited wavelength is 528 nm.

photoelectric performances of the cell with porphyrins (electron-donors) and perylene tetracarboxylic derivatives (electron-acceptors), we have mixed these two materials to form charge-transfer complex and fabricated a blend-type

photoelectric cell. The SnO₂ glass/Mg(TBPor) and PDHEP blend (mole ratio = 1/1)/Pt blend-type cell performs better photoelectric properties than Mg(TBPor) or PDHEP owing to wider photo-absorptions and formation of p/n

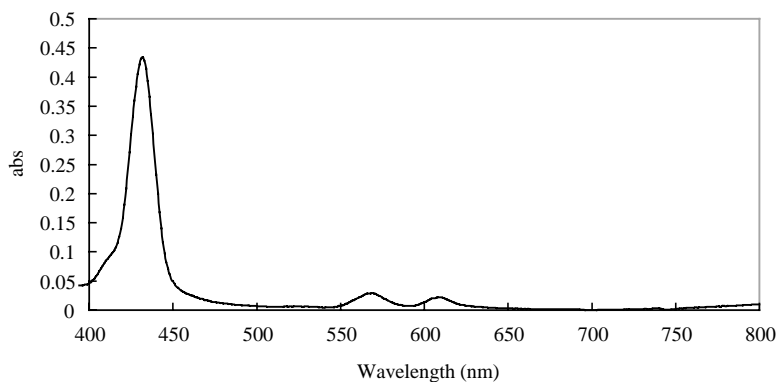


Fig. 5. The UV-Vis spectrum of Mg(TBPor) thin film.

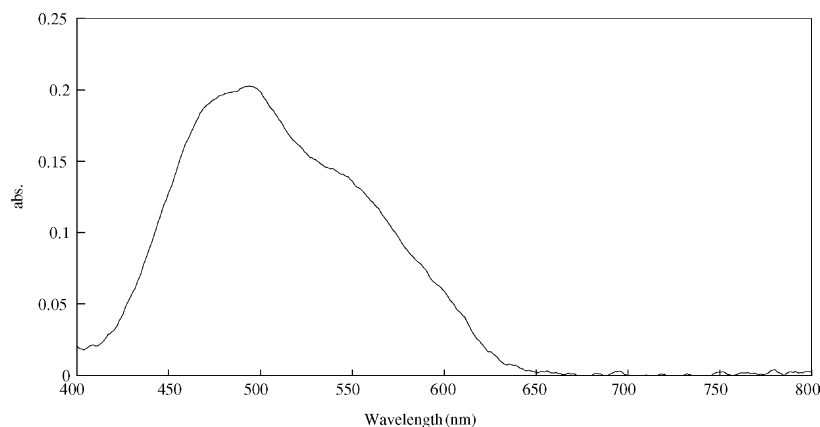


Fig. 6. The UV-Vis spectrum of PDHEP thin film.

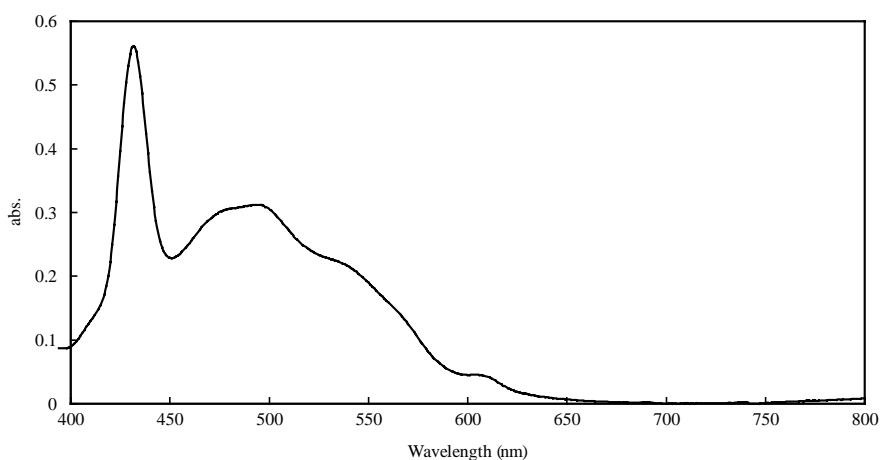


Fig. 7. The UV-Vis spectrum of Mg(TBPor)/PDHEP blend thin film.

heterojunction. The p/n heterojunction in the blend-type cell results from molecular contact of Mg(TBPor) and PDHEP. The blended region has an aggregation of small grains for both materials [8]. When the electrons and holes are photo-generated, they diffuse into the different dye grains (i.e. the

electrons to the PDHEP and the holes to the Mg(TBPor)) [8]. It is difficult for electrons and holes to be close to each other due to the p/n heterojunction barriers formed at the contact of Mg(TBPor) and PDHEP [8]. Nevertheless, its short-circuit photocurrent was still small and discontented.

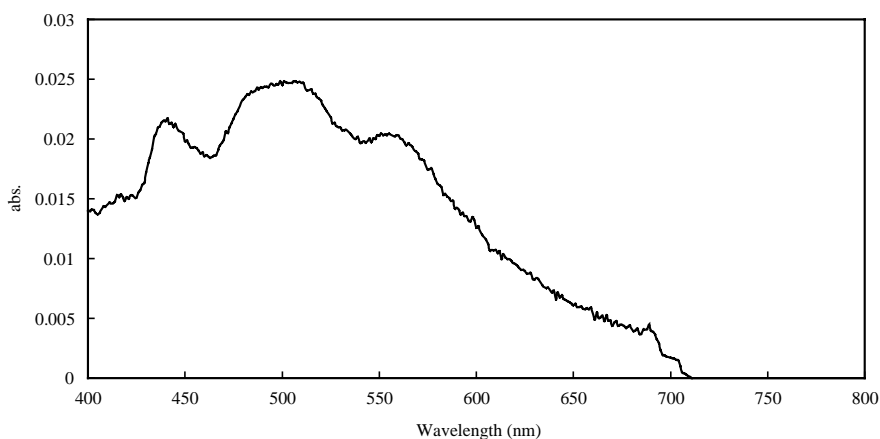


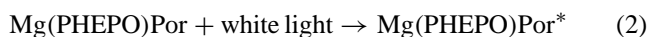
Fig. 8. The UV-Vis spectrum of Mg(PHEPO)Por thin film.

Table 2
The photoelectric performances of lab-made cells

Lab-made photoelectric cell	Short-circuit photocurrent ($\mu\text{A}/\text{cm}^2$)
$\text{SnO}_2/\text{Mg}(\text{PHEPO})\text{Por} + \text{TiO}_2$ blend/Al	1057.7
$\text{SnO}_2/\text{Mg}(\text{PHEPO})\text{Por}/\text{Al}$	126.5
$\text{SnO}_2/\text{Mg}(\text{TBPor}) + \text{PDHEP}$ (1/1)/Pt	69.4
$\text{SnO}_2/\text{PDHEP}/\text{Pt}$	37.4
$\text{SnO}_2/\text{Mg}(\text{TBPor})/\text{Pt}$	26.7

Therefore, we have fabricated the photoelectric cell of $\text{Mg}(\text{PHEPO})\text{Por}$ to further improve the photoelectric performances. Compared with $\text{Mg}(\text{TBPor})$, PDHEP, and blend cell, $\text{Mg}(\text{PHEPO})\text{Por}$ exhibits higher short-circuit photocurrent, as shown in Table 2. This reveals that combination of Por and Pe into a single compound not only broadens the range of absorptions but also averts the resistance of random grain arrangement of $\text{Mg}(\text{TBPor})/\text{PDHEP}$ blend [8].

In recent years, paper about TiO_2 used in photoelectrochemical cells has been published [18]. Thus, we have introduced TiO_2 into the cell of $\text{Mg}(\text{PHEPO})\text{Por}$ to fabricate nanocrystalline dye sensitized photoelectric cells in order to promote the photoelectric properties. As shown in Table 2, the $\text{Mg}(\text{PHEPO})\text{Por}/\text{TiO}_2$ cells dramatically exhibit better photoelectric conversion properties than other cells because TiO_2 facilitates the electron transfer in the cell. The photoelectric conversion may proceed by the following procedure [19].



where $\text{Mg}(\text{PHEPO})\text{Por}^*$ represents that $\text{Mg}(\text{PHEPO})\text{Por}$ is photo-excited and $\text{e}^-(\text{TiO}_2)$ represents that TiO_2 carries electrons.

Firstly, the $\text{Mg}(\text{PHEPO})\text{Por}$ is photo-excited. Then, the excited electrons of $\text{Mg}(\text{PHEPO})\text{Por}$, which are generated by light absorption, were transferred into the TiO_2 . Finally, the electrons flow from the TiO_2 -coated SnO_2 glass through the external circuit to generate the electrical energy.

4. Conclusion

Soluble and fluorescent Por–Pe complex has been successfully synthesized by microwave irradiation and is feasibly utilized for spin-coating technology in the preparation of the thin film. Furthermore, we have also investigated its fluorescent and photoelectric conversion properties. The fluorescent and photoelectric performances of Por–Pe complex are better than that of Por, Pe, and Por/Pe blend. Under illumination of white light ($1.2 \text{ mW}/\text{cm}^2$), Por–Pe complex/ TiO_2 blend photoelectric cell exhibits the best photo-electricity conversion effect with a short-circuit photocurrent ($1057.7 \mu\text{A}/\text{cm}^2$).

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