

Available online at www.sciencedirect.com



Journal of Photochemistry Photobiology A:Chemistry

Journal of Photochemistry and Photobiology A: Chemistry 165 (2004) 193-200

www.elsevier.com/locate/jphotochem

# The fluorescent and photoelectric conversion properties of phthalocyanine-perylene tetracarboxylic complexes

Mark O. Liu<sup>a</sup>, Chia-Hung Tai<sup>b</sup>, Andrew Teh Hu<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Tsing-Hua University, Hsinchu 30043, Taiwan, ROC <sup>b</sup> Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan, ROC

Received 2 January 2004; received in revised form 27 February 2004; accepted 24 March 2004

# Abstract

Novel phthalocyanine–perylene tetracarboxylic complexes, which are organo-soluble or water-soluble, have been prepared rapidly under microwave irradiation. Their fluorescent properties and photoelectric conversion properties have also been investigated. The experimental results reveal that introduction of perylene tetracarboxylic derivatives into the peripheral ring of phthalocyanines increases the fluorescence of phthalocyanines and Pc–Pe complexes have larger photocurrent than Pc/Pe blend and laminated Pc/Pe. © 2004 Elsevier B.V. All rights reserved.

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

# 1. Introduction

Phthalocyanines (Pc) have been discovered to be versatile materials and applied in biological as well as electronic areas for many decades [1–4]. They exhibit excellent electrochemical and photochemical properties [5], but poor fluorescent properties. However, perylene tetracarboxylic derivatives (Pe) are not only optoelectronic pigments but also fluorescent materials [6]. Recently, plenty of work with Pc and Pe have been published related to vapor deposited Schottky and p/n heterojunction cells [7–9]. Furthermore, the conventional preparation for both of these two materials are time-consuming [6,10].

In this paper, we have quickly combined these two materials into a single compound via microwave irradiation to form soluble and fluorescent phthalocyanine–perylene tetracarboxylic complexes (Pc–Pe complexes). They are charge-transfer complexes since phthalocyanines and perylene tetracarboxylic derivatives are electron-donors and electron-acceptors [11], respectively. Their photoelectric conversion properties have also been investigated. The experimental results demonstrate that introduction of perylene tetracarboxylic derivatives into the peripheral ring of phthalocyanines increases the fluorescent properties of phthalocyanines and Pc–Pe complexes exhibit better photoelectric conversion effect than Pc/Pe blend and laminated Pc/Pe.

#### 2. Experimental

# 2.1. Materials

# 2.1.1. Preparation of phthalocyanine–perylene

tetracarboxylic complexes (Pc-Pe complexes) (Scheme 1)

Perylene tetracarboxylic dianhydride (1 g, 2.56 mmol), water (10 ml), and 85% aqueous KOH solution (0.678 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 in 4.5–5. Finally, the crude solution was irradiated at 80 W for 10 min. After washing with a water/ethanol (v/v = 1/1) solution and drying, PMONK (1.0903 g) was obtained (yield: 95%). IR (KBr) (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 cm<sup>-1</sup>.

PMONK (0.5 g, 1.12 mmol), 2-amino-6-methylheptane (0.2877 g, 2.24 mmol), and water (5 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 (5 g) was added into the crude solution. The crude solution was finally

<sup>\*</sup> Corresponding author. Tel.: +886-3-5713830; fax: +886-3-5715408. *E-mail address:* athu@che.nthu.edu.tw (A.T. Hu).



Scheme 1.

irradiated at 80 W for 10 min. After washing with water and drying, PAHEP (0.5233 g) was obtained (yield: 93%). IR (KBr) (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 cm<sup>-1</sup>.

PAHEP (0.5 g, 0.99 mmol), 2-bromoethylamine (0.4336 g, 1.98 mmol), zinc acetate (0.15 g, 0.82 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 (v/v = 1/1), PHEEB (0.4936 g) was obtained (yield: 71%).

PHEEB (0.4 g, 0.57 mmol), 4-hydroxyphthalonitrile (0.1636 g, 1.14 mmol), potassium carbonate (0.1176 g, 0.855 mmol) and tetrahydrofuran (THF) (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 (v/v = 1/1), PHENI (0.3362 g) was obtained (yield:

77%). IR (KBr) (PHENI): 3105, 2952, 2863, 2214, 1775, 1756, 1741, 1694, 1653, 1631, 1590, 1502, 1454, 1435, 1402, 1354, 1343, 1299, 1233, 1144, 1118, 1023, 934, 857, 805, 790, 757, 731, 639, 602, 569, 521, 499 cm<sup>-1</sup>. UV-Vis  $\lambda_{\text{max}}$  (nm, in 1-methylpyrrolidone (NMP)): 523, 488, 462.

PHENI (0.2 g, 0.26 mmol) and magnesium chloride (0.0702 g, 0.52 mmol) in the presence of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU, 10 ml) as catalyst 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 (v/v = 1/1) and purified by column chromatography (silica gel, 1-methyl-2-pyrrolidone/THF (tetrahydrofuran) = 5/1, wt./wt.), Mg (PHEEO)Pc (0.0781 g) was obtained (yield: 53%).

IR (KBr) (cm<sup>-1</sup>) (Mg(PHEEO)Pc): 2929, 2856, 1767, 1745, 1730, 1694, 1646, 1631, 1616, 1594, 1572, 1553, 1539, 1517, 1502, 1491, 1472, 1450, 1435, 1417, 1391, 1351, 1247, 1188, 1078, 1023, 978, 871, 842, 805, 750, 713,

195

661, 576, 521, 466, 440, 414. UV-Vis  $\lambda_{max}$  (nm, in NMP) 740, 678, 526, 490, 461, 257. MS (*m*/*z*) (MALDI/TOF) 2719. Elemental analysis for C<sub>168</sub>H<sub>132</sub>N<sub>16</sub>O<sub>20</sub>Mg, Calculated: C, 74.20; H, 4.89; N, 8.24. Found: C, 74.08; H, 4.95; N, 8.20.

The same procedure was adopted in the preparation of Mg(PAMEO)Pc, Mg(PTBEO)Pc, and Mg(PSSEO)Pc, respectively. The yields of Mg(PAMEO)Pc, Mg(PTBEO)Pc, and Mg(PSSEO)Pc were 56, 61, and 51%, respectively.

IR (KBr) (cm<sup>-1</sup>) (Mg(PAMEO)Pc): 2922, 2849, 1768, 1749, 1730, 1694, 1646, 1631, 1617, 1595, 1572, 1554, 1535, 1520, 1502, 1488, 1469, 1451, 1432, 1392, 1347, 1248, 1196, 1078, 1023, 979, 890, 842, 809, 747, 665, 570, 525, 470, 433, 418. UV-Vis  $\lambda_{max}$  (nm, in NMP) 739, 677, 525, 489, 458, 259. MS: (*m*/*z*) (MALDI/TOF) 2883. Elemental analysis for C<sub>168</sub>H<sub>132</sub>N<sub>16</sub>O<sub>20</sub>Mg, Calculated: C, 73.31; H, 5.03; N, 9.72. Found: C, 73.44; H, 5.12; N, 9.61.

IR (KBr) (cm<sup>-1</sup>) (Mg(PTBEO)Pc): 2923, 2856, 1768, 1749, 1731, 1694, 1679, 1646, 1631, 1617, 1590, 1569, 1554, 1535, 1517, 1502, 1488, 1469, 1451, 1432, 1418, 1351, 1248, 1196, 1075, 975, 872, 850, 809, 747, 717, 665, 580, 525, 470, 433, 415. UV-Vis  $\lambda_{max}$  (nm, in NMP) 738, 639, 527, 491, 460, 258. MS: (*m*/*z*) (MALDI/TOF) 3244. Elemental analysis for C<sub>208</sub>H<sub>176</sub>N<sub>16</sub>O<sub>20</sub>Mg, Calculated: C, 77.01; H, 5.47; N, 6.91. Found: C, 76.92; H, 5.54; N, 6.86.

IR (KBr) (cm<sup>-1</sup>) (Mg(PSSEO)Pc): 3439, 2922, 2857, 1790, 1768, 1745, 1731, 1694, 1679, 1646, 1616, 1591, 1572, 1554, 1536, 1517, 1502, 1487, 1469, 1450, 1432, 1413, 1388, 1355, 1259, 1178, 1123, 1038, 1023, 982, 857, 809, 747, 721, 665, 618, 470, 437, 418. UV-Vis  $\lambda_{max}$  (nm) 761, 529, 511, 223 (in water) 731, 526, 491, 463 (in water/ethanol (v/v = 1/1)) MS: (*m*/*z*) (MALDI/TOF) 3204. Elemental analysis for C<sub>160</sub>H<sub>76</sub>N<sub>16</sub>O<sub>44</sub>S<sub>8</sub>Na<sub>4</sub>Mg, Calculated: C, 58.26; H, 2.32; N, 6.79. Found: C, 58.19; H, 2.24; N, 6.84.

Lab-made Mg(PHEEO)Pc, Mg(PAMEO)Pc, and Mg (PTBEO)Pc are soluble in common organic solvents such as *N*,*N*-dimethylformamide (DMF, >1 wt.%), dimethylacetamide (DMAc, >1 wt.%), 1-methylpyrrolidone(NMP, >1 wt.%), dichloromethane (>2 wt.%), chloroform (>2 wt.%), etc. and Mg(PSSEO)Pc is soluble in water (>2 wt.%). They are feasible for spin-coating technology in various industrial applications.

2.1.2. Preparation of magnesium tetrakis(tert-butyl) phthalocyaninate (Mg(TBPc)) and N,N'-bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide) (PDHEP)

Mg(TBPc) and PDHEP, whose chemical structures were depicted in Fig. 1, were synthesized by the microwave procedure [12,13]. Their UV-Vis spectra have been compared with those of lab-made Pc–Pe complexes. The details were described in Section 3.2.

### 2.2. Physical measurement

The microwave oven utilized for heating was Sunpentown SM-1290. The UV-Vis absorption spectra were recorded on a HITACHI U-3300, and IR spectra on a Perkin-Elmer 842. The fluorescent properties were measured by HITACHI F-2500. The photoelectric conversion properties were measured in the air by an instrument (Keithley 238), whose accuracy can reach picoampere. The source of white light was 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).

# 2.3. Film preparation and fabrication of the photoelectric cells

Lab-made Pc–Pe complexes were dissolved in dichloromethane or water (2 wt.%), filtrated with a 0.2  $\mu$ m filter, and deposited onto SnO<sub>2</sub> glass (TEC 10 glass, Hartford Glass Co. Inc.) by spin-coating (1 ml dye solution at 3000 rpm). The counter Al electrode was then put on the top by vacuum evaporation as shown in Fig. 2.

The same procedure was adopted in the fabrication of Mg(PTBEO)Pc/TiO<sub>2</sub> blend photoelectric cell. Mg(PTBEO)Pc was dissolved in dichloromethane (2 wt.%) and filtrated with a  $0.2 \,\mu$ m filter. TiO<sub>2</sub> powder (Degussa P25) was then added into the dichloromethane solution



Mg(TBPc) PDHEP

Fig. 1. The chemical structure of Mg(TBPc) and PDHEP.



Fig. 2. The structures of lab-made photoelectric cell. White light  $(1.2 \text{ mW/cm}^2)$  is irradiated to the SnO<sub>2</sub> glass. The thickness of Pc–Pe complexes, Mg(PTBEO)Pc/TiO<sub>2</sub> blend, Mg(PTBEO)Pc/Mg(PHEPO)Por/TiO<sub>2</sub> blend and Al are 30, 30, 30, and 200 nm, respectively. The active areas are  $2 \text{ cm}^2$  (0.8 cm  $\times$  2.5 cm).

of Mg(PTBEO)Pc (20 wt.%). After blending in the ultrasonic bath, the Mg(PTBEO)Pc/TiO<sub>2</sub> blend was deposited onto SnO<sub>2</sub> glass by spin-coating. Finally, the counter Al electrode was put on the top by vacuum evaporation as shown in Fig. 2. The layer thickness of Pc–Pe complexes, Mg(PTBEO)Pc/TiO<sub>2</sub>, and Al are 30, 30, and 200 nm, respectively. The active areas of all materials are  $2 \text{ cm}^2$ (0.8 cm × 2.5 cm).

#### 3. Results and discussion

#### 3.1. Microwave heating

In recent years, microwave irradiation has been an important tool for fast chemical synthesis [14]. Nevertheless, only simple reactions have been reported. In this paper, the procedures for preparation of Pc–Pe complexes, including ring-opening of perylene tetracarboxylic anhydride, imidization, dehydrobromination, and tetracyclomerization, as shown in Scheme 1, take only 10 min, however,



Fig. 3. The UV-Vis spectrum of Mg(PHEEO)Pc in NMP.

the conventional methods take several hours to 1 day for completion [6,10]. Microwave irradiation facilitates the polarization of the starting materials to promote the reactions described in this paper. This reveals that microwave heating can also be utilized to accelerate complicated reaction. The reactions mentioned in this paper have been successfully repeated several times with identical results.

#### 3.2. UV-Vis spectra of lab-made Pc-Pe complexes

Rapid characterization of lab-made Pc–Pe complexes can be executed by the UV-Vis spectra as shown in Fig. 3. The characteristic absorption of perylene tetracarboxylic derivative locates in the range 400–600 nm as well as 250–300 nm and that of phthalocyanine locates in the range 600–800 nm (Q band) as well as 250–400 nm (B band), which corresponds to a  $\pi \rightarrow \pi^*$  transition [11]. Generally, the Q band of  $\beta$ -substituted (peripheral substitution) phthalocyanine [15,16] locates in the range 600–700 nm. However, the Q bands of lab-made Pc–Pe complexes are bathochromic (red-shift) and locate in the range 700–800 nm. Compared with the UV-Vis spectrum of Mg(TBPc)/PDHEP blend (mol/mol = 1/4) as shown in Fig. 4, the Q band of the blend locates in the range 600–700 nm rather than 700–800 nm.



Fig. 4. The UV-Vis spectrum of Mg(TBPc)/PDHEP blend (mol/mol = 1/4) in NMP.



Fig. 5. The UV-Vis spectrum of Mg(PSSEO)Pc in water.

Thus, lab-made Pc-Pe complexes are chemically bonded genuinely, not mixtures. We speculate that introduction of perylene tetracarboxylic derivatives at the periphery of the phthalocyanine ring may enhance the delocalization of  $\pi$ electrons. Since the effect of the delocalization lowers the energy level of the  $\pi^*$  orbital [17], the O band of lab-made Pc-Pe complexes are shifted to longer wavelengths. Furthermore, the B band of  $\beta$ -substituted phthalocyanine generally splits into two peaks, which corresponds to  $a_{2u} \rightarrow e_g$  and  $b_{2u} \rightarrow e_g$  transition, respectively [18]. Nevertheless, the B band of lab-made Pc-Pe complexes are hypsochromic (blue-shift) and combine with the absorption of pervlene tetracarboxylic derivative in the range 250-300 nm to generate a strong absorption band. Pc-Pe complexes are charge-transfer complexes since phthalocyanines and perylene tetracarboxylic derivatives are electron-donors and electron-acceptors [11,18], respectively. Therefore, we speculate that the observed blue-shift is because the charge transfer and  $\pi \to \pi^*$  transition overlap to result in the extensive configurational mixing between the B band and the charge-transfer state [19].

In case of Mg(PSSEO)Pc, the absorption bands in water and in aqueous ethanol solution differ. The absorption band of Mg(PSSEO)Pc in water is very broad, as shown in Fig. 5, with respect to those of phthalocyanine and perylene tetracarboxylic derivative because aggregation takes place in water [20,21]. With addition of ethanol to the aqueous solution, however, the absorption band becomes not only sharp but also hypsochromic (blue-shift) since deaggregation occurs. We speculate that the aggregation of Mg(PSSEO)Pc in water may be parallel in arrangement [22].

The UV-Vis spectra of lab-made Pc-Pe complexes in solution and dry films, as shown in Figs. 3 and 6, are quite different. Their absorption bands in the dry film become broad and the Q bands were diminished because of aggregation [22].

## 3.3. Fluorescent properties

In general, phthalocyanines exhibit poor fluorescent properties. However, as shown in Fig. 7, introduction of pervlene tetracarboxylic derivatives into the peripheral ring of phthalocyanines increases the fluorescence. Their fluorescent properties are summarized in Table 1. In case of Mg(PHEEO)Pc, we choose 740, 678, 526, and 257 nm, in which its characteristic absorption locates, as the excited wavelength, respectively. No significant fluorescence can be detected when 740, 678, and 257 nm were chosen as the excited wavelength, respectively. Nevertheless, the observed fluorescence is produced when the excited wavelength is 526 nm only. The similar experimental results take place in case of Mg(PAMEO)Pc, Mg(PTBEO)Pc, and Mg(PSSEO)Pc, respectively. This reveals that the fluorescence is contributed from the side chain, perylene tetracarboxylic derivative, rather than the backbone, phthalocyanine ring. Furthermore, the quantum yields of fluorescence for Mg(PTBEO)Pc and Mg(PSSEO)Pc are much larger than those for Mg(PHEEO)Pc and Mg(PAMEO)Pc because the peripheral aromatic substitution of perylene tetracarboxylic



Fig. 6. The UV-Vis spectrum of Mg(PHEEO)Pc dry film.



Fig. 7. The fluorescent spectrum of Mg(PHEEO)Pc in NMP (0.001 wt.%). The excited wavelength is 526 nm.

Table 1 The fluorescent properties of lab-made phthalocyanine-perylene tetracarboxylic complexes

Compound	Emitting wavelength ( $\lambda_{max}$ , nm)	Excited wavelength (nm)	Quantum yield <sup>a</sup>
Mg(PHEEO)Pc	538	526	0.18 (in NMP)
Mg(PAMEO)Pc	537	525	0.19 (in NMP)
Mg(PTBEO)Pc	546	527	0.25 (in NMP)
Mg(PSSEO)Pc	539	533	0.24 (in water)
Mg(TBPc)	Not detected	675, 611, 350	Approximately 0 (in NMP)
PDHEP	542	524	0.27 (in NMP)

<sup>a</sup> The quantum yield is calculated from the following equation [28]:  $\Phi_{sample} = \Phi_{standard}[Area_{sample}/(1 - exp(-A_{sample}))]/[Area_{standard}/(1 - exp(-A_{standard}))]]$ , where  $\Phi_{sample}$  and  $\Phi_{standard}$  represent the quantum yields of sample and standard, respectively. (The standard in this study is Rose Bengal  $\Phi_{standard} = \Phi_{Rose Bengal} = 0.14$ .) Area\_{sample} and Area\_{standard} represent the area of fluorescent emission band for sample and standard, respectively,  $A_{sample}$  and  $A_{standard}$  represent the UV-Vis absorbances of sample and standard, respectively (the concentrations in this study are  $10^{-6}$  M).

derivatives for the former exhibit lower-energy  $\pi \rightarrow \pi^*$  transition levels than the peripheral aliphatic substitution of perylene tetracarboxylic derivatives for the latter [23].

In comparison with the fluorescent properties of PDHEP, Pc–Pe complexes exhibit poorer quantum yields. This reveals that the Pc ring may quench the fluorescent intensity.

#### 3.4. Photoelectric conversion properties

Table 2

Since sunlight is clean, environment-friendly, and inexhaustible energy source, the applications in its conversion into electrical energy become an essential requirement. Over half the energy that reaches the earth's surface from the sun is in the form of visible radiation (400–800 nm) [24]. Because phthalocyanines are close synthetic analogues

Mg(PHEPO)Por

Fig. 8. The chemical structure of Mg(PHEPO)Por.

The photoelectric performances of lab-made cells			
Lab-made photoelectric cells	Short-circuit photocurrent (µA/cm <sup>2</sup> )	Energy conversion efficiencies (%)	
SnO <sub>2</sub> /Mg(PTBEO)Pc + Mg(PHEPO)Por + TiO <sub>2</sub> blend/Al	3478.7	0.283	
$SnO_2/Mg(PTBEO)Pc + TiO_2$ blend/Al	2432.7	0.198	
SnO <sub>2</sub> /Mg(PTBEO)Pc/Al	167.9	0.0154	
SnO <sub>2</sub> /Mg(PHEEO)Pc/Al	164.2	0.0103	
SnO <sub>2</sub> /Mg(PAMEO)Pc/Al	161.7	0.00999	
SnO <sub>2</sub> /Mg(PSSEO)Pc/Al	158.1	0.00991	
SnO <sub>2</sub> /MgPc(SO <sub>3</sub> Na) <sub>4</sub> /PDHEP/A1	116.0	0.00520	
SnO <sub>2</sub> /Mg(TBPc) and PDHEP blend/Al	89.6	0.00501	



Fig. 9. The UV-Vis spectrum of Mg(PTBEO)Pc/Mg(PHEPO)Por blend dry film.

of chlorophyll [25] and the absorptions of phthalocyanines and perylene tetracarboxylic derivatives locate in the range 600–800 and 400–600 nm, respectively, they are suitable materials for photoelectric conversion. Therefore, we combined these two materials into a single compound to increase the photoelectric performance.

As shown in Fig. 6, the absorptions of lab-made Pc–Pe complexes dry films locate in the entire visible spectrum (400–800 nm). These photoabsorptions can convert into electrical energy while white light  $(1.2 \text{ mW/cm}^2)$  was irradiated on the SnO<sub>2</sub> glass, as summarized in Table 2.

Compared with our recent research [12] for the double-layer photoelectric cell  $(SnO_2/MgPc(SO_3Na)_4$  (sodium salt of sulfonated magnesium phthalocyanine, p-type)/PDHEP (n-type)/Al) and blend-type photoelectric cell  $(SnO_2/Mg(TBPc) (p-type)$  and PDHEP (n-type) blend/Pt), their short-circuit photocurrents are higher. This reveals that combination of phthalocyanine and perylene tetracarboxylic derivative into a single compound not only spreads the range of absorptions to the entire visible spectrum but also avoids the resistance of interface between p- and n-type materials while the double-layer cell was fabricated with these two materials.

Recently, paper about Pcs on  $TiO_2$  in photoelectrochemical cells has been published [26]. In order to promote the photoelectric performances of the cell with Pc–Pe complexes, we have introduced  $TiO_2$  into the cell of Mg(PTBEO)Pc to fabricate a nanocrystalline dye sensitized photoelectric cell. As shown in Table 2, the SnO<sub>2</sub>/Mg(PTBEO)Pc + TiO<sub>2</sub> blend/Al cell dramatically performs the best photoelectric conversion properties among lab-made cells. We speculate that the photoelectric conversion may proceed by the following procedure [27]:

$$Dye + white light \rightarrow Dye^*$$
 (1)

$$Dye^* + TiO_2 \rightarrow e^- (TiO_2) + Dye^+$$
(2)

$$e^{-}$$
 (TiO<sub>2</sub>) + SnO<sub>2</sub> glass  $\rightarrow$  TiO<sub>2</sub> + electrical energy (3)

where Dye<sup>\*</sup> represents that Dye is photo-excited,  $e^{-}$  (TiO<sub>2</sub>) represents that TiO<sub>2</sub> carries electrons.

Firstly, the Mg(PTBEO)Pc is photo-excited. Then the excited electrons of Mg(PTBEO)Pc, 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.

In our recent research, we have added porphyrin–perylene complex (Mg(PHEPO)Por) [13], whose chemical structure is shown in Fig. 8, into the cell to fabricate Mg(PTBEO)Pc/Mg(PHEPO)Por/TiO<sub>2</sub> blend photoelectric cell (Mg(PTBEO) Pc/Mg(PHEPO)Por = 1/1, mol/mol). The experimental results reveal that Mg(PTBEO)Pc/Mg(PHEPO)Por/TiO<sub>2</sub> blend cell performs the best photoelectric conversion performance among all of lab-made cells since it exhibits the broadest photoabsorptions (400–800 nm, the entire visible spectrum), as shown in Fig. 9.

# 4. Conclusion

We have successfully synthesized soluble and fluorescent Pc–Pe complexes by microwave irradiation. They are feasibly used for spin-coating technology in the preparation of the thin film. Furthermore, their photoelectric conversion properties have also been investigated. The photoelectric performances of Pc–Pe complex are better than those of Pc/Pe blend and laminated Pc/Pe. Among lab-made Pc–Pe complexes, Mg(PTBEO)Pc exhibits the largest photocurrent. In order to further increase their photoelectric performances, we have fabricated Mg(PTBEO)Pc/Mg(PHEPO)Por/TiO<sub>2</sub>

blend cell, which have the best photoelectric conversion effect among all of lab-made cells.

#### References

- J. Griffiths, J. Schofield, M. Wainwright, S.B. Brown, Dyes Pigments 33 (1997) 65.
- [2] H. Kojima, J. Electrochem. Soc. 144 (1997) 3628.
- [3] Y. Liu, K. Shigehara, M. Hara, A. Yamada, J. Am. Chem. Soc. 113 (1991) 440.
- [4] F.Z. Henari, J. Callaghant, W.J. Blau, P. Haisch, Pure Appl. Opt. 6 (1997) 741.
- [5] Ph. Ghosez, R. Gote, L. Gastonguay, G. Veilleux, G. Denes, J.P. Dodelet, Chem. Mater. 5 (1993) 1581.
- [6] Y. Nagao, T. Naito, Y. Abe, T. Misono, Dyes Pigments 32 (1996) 71.
- [7] D. Wöhrle, D. Meissner, Adv. Mater. 3 (1991) 129.
- [8] M. Hiramoto, H. Fujiwara, M. Yokoyama, J. Appl. Phys. 72 (1992) 3781.
- [9] D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller, D. Schlettwein, J. Mater. Chem. 5 (1995) 1819.
- [10] H. Tomoda, S. Saito, S. Shiraishi, Chem. Lett. (1983) 313.
- [11] C.C. Leznoff, A.B.P. Lever, Phthalocyanines Properties and Applications, VCH, New York, 1989, p. 147.
- [12] L.C. Liu, A.T. Hu, J. Porphyrins Phthalocyan. 7 (2003) 565.
- [13] M.O. Liu, C.H. Tai, C.W. Chen, W.C. Chang, A.T. Hu, J. Photochem. Photobiol. A: Chemistry 163 (2004) 259.
- [14] A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, Daniel Mathe, Synthesis (1998) 1213.

- [15] N.B. McKeown, Phthalocyanine Materials Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998, p. 89.
- [16] C.C. Leznoff, A.B.P. Lever, Phthalocyanines Properties and Applications, VCH, New York, 1989, p. 140.
- [17] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Harcourt Brace & Company, Philadelphia, 1998, p. 333.
- [18] N.B. McKeown, Phthalocyanine Materials Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998, p. 112.
- [19] C.C. Leznoff, A.B.P. Lever, Phthalocyanines Properties and Applications, VCH, New York, 1989, p. 153.
- [20] J.D. Spike, Photochem. Photobiol. 43 (1986) 691.
- [21] X.Y. Li, X. He, A.C.H. Ng, C. Wu, D.K.P. Ng, Macromolecules 33 (2000) 2119.
- [22] N.B. McKeown, Phthalocyanine Materials Synthesis, Structure and Function, Cambridge University Press, Cambridge, 1998, p. 92.
- [23] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Harcourt Brace & Company, Philadelphia, 1998, p. 361.
- [24] R.J. Komp, Practical Photovoltaics, aatec Publications, Ann Arbor, MI, 1981, p. 109.
- [25] P. Gregory, High-Technology Applications of Organic Colorants, Plenum Press, New York, 1991, p. 46.
- [26] M.K. Nazeeruddin, R. Humphry-Baker, M. Gratzel, D. Wohrle, G. Schnurpfeil, G. Schneider, A. Hirth, N. Trombach, J. Porphyrins Phthalocyan. 3 (1999) 230.
- [27] A. Kay, M. Gratzel, J. Phys. Chem. 98 (1994) 952.
- [28] M.H. Miles, R.A. Henry, D.A. Fine, US Patent 5 516 462 (1996).