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*This study focuses on the syntheses of zinc 5,10,15,20-tetrakis(*p-*tolyl)porphyrin (ZnTTP), silicon dichloride 5,10,15,20-tetrakis(*p-*tolyl)porphyrin ($SiCl_2TTP$), and oxotitanium(IV) 5,10,15,20-tetrakis(*p-*tolyl)porphyrin (TiOTTP) and their photovoltaic properties as additives for use in electrolytes of the DSSC. In order to investigate photovoltaic effects of the DSSC devices, the FTO/TiO_2/N3 Dye/Electrolyte/Pt device was fabricated by using poly (ethylene glycol) (PEG) electrolytes based on TTP metal complexes as an additive. When TiOTTP was introduced into the PEG electrolyte, the power conversion efficiency of DSSC device was shown remarkably a high value compared with values of the others.*

Keywords Dye-sensitized solar cells (DSSCS); porphyrin; poly(ethylene glycol)

1. Introduction

Recently, much effort has been expended to convert solar energy effectively to electric energy by organic solar cell [1–3]. Although inorganic solar cells have been the primary focus, due to the abundance of organic materials having a variety of absorptions, a large number of organic solar cell have been studied today. The organic solar cells have especially attracted attention since Tang et. al reported relatively large power conversion efficiency [4]. The need to develop inexpensive renewable energy sources has continued to stimulate new approaches to production of efficiency

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low-cost solar cell device. In these polymer and organic solar cells, semiconductor particles and an electron acceptor or an electron donor are blended together to create a heterogeneous material that function as a portion of the device. Dye-sensitized solar cells (DSSCs) constructed using dye molecules nanocrystalline metal oxides and organic liquid electrolytes have attractive feature of high energy conversion efficiency and low production coast and energy [5].

This study focuses on the synthesis and photovoltaic properties of zinc 5,10,15,20-tetrakis(*p*-tolyl)porphyrin (ZnTTP), silicon dichloride 5,10,15,20-tetrakis(*p*-tolyl) porphyrin ($SiCl_2$TTP), and oxotitanium(IV) 5,10,15,20-tetrakis(*p*-tolyl)-porphyrin (TiOTTP), as additives for use in DSSCs. In order to investigate the photovoltaic effect of DSSCs based in a poly (ethylene glycol) (PEG) electrolyte, the FTO/TiO_2/Dye/ Electrolyte/Pt device was fabricated using a PEG electrolyte based on TTP metal complexes as an additive.

The chemical structures of TTP metal complexes were measured ^{1}H-NMR spectroscopy. In addition, the photovoltaic effect of the solar cell device was measured using a solar simulator under 100 mW cm^{-2} at AM 1.5. The power conversion efficiency (η) of the DSSC device was calculated from the values of the open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}), and fill factor (FF) was calculated from the values of V_{oc}, J_{sc}, and η.

2. Experimental

2.1. *Materials*

5, 10, 15, 20-Tetra-*p*-tolyl-21H, 23H-porphine (TTP), zinc acetate, titanium(IV) butoxide, silicon tetrachloride, anhydrous *N,N*-dimethylformamide (DMF), were purchased from Aldrich Co. and used without the purification. Dichloromethane (98.8%, ACS. Reagent) was purchased from J.T.Baker Co. and used without the purification.

TiO_2 powders (P-25) were purchased from Degussa AG, Germany. Ruthenium dyes such as *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) dye (N3 dye), fluorine-doped SnO_2 glass (FTO glass, 15 Ω/square), 1-propyl-3-methylimidazolium iodide (PMII), and Pt paste (Pt catalyst T/SP) were purchased from Solaronix. Acetic acid, triton X-100, acetylacetone, deionized water, iodine (I_2), propylene carbonate (PC), ethylene carbonate (EC), poly (ethylene glycol) (PEG, $M_w = 20{,}000$) acetonitrile (AN), and tetrabutylammonium iodide (TBAI) were purchased from Aldrich Co. and used without further purification.

2.2. *Measurements*

^{1}H-NMR spectra were measured on a Varian spectrometer (300 MHz) with $CDCl_3$ and DMSO-d_6 as a d-solvent. The UV-Vis spectra were obtained on an Optizen 2120 UV spectrophotometer. Thermogravimetric analysis (TGA) was performed on TA Instruments (TGA-Q 50, -Q 100) thermal analyzer at 10°C min^{-1} of a heating rate under flowing nitrogen (40 ml min^{-1}). The crystal structures of the porphyrins were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (X'Pert PRO) and transmission electron microscope (TEM) with JEOL (JEM-2010). The measurement of I-V characteristics of the DSSC devices was carried out by a Solar Simulator (150 W simulator, PEC-L11/PECCELL) under simulated solar light with ARC Lamp power supply (AM 1.5, 100 mW cm^{-2}). Solar simulator was calibrated to Si

reference cell verified. The active area of DSSC device measured by using a black mask was 0.49 cm^2. The electrochemical properties were measured by Bioanalytical Systems CV-50 W voltametric analyzer. An $Ag/AgNO_3$ reference electrode was employed in the three-electrode arrangement.

2.3. *Syntheses of 5,10,15,20-tetrakis(p-tolyl)porphyrin Metal Complexes*

2.3.1. *Zinc 5,10,15,20-tetrakis(p-tolyl)porphyrin (ZnTTP).* ZnTTP was prepared as literature procedures [6,7]. The chemical structure is shown in Figure 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 12H, CH_3); 7.57 (m, 8H, $H_{m,p}$ of C_6H_4); 8.09 (m, 8H, H_o of C_6H_4); 8.96 (s, 8H, H_β of pyrrole).

2.3.2. *Oxotitanium(IV) 5,10,15,20-tetrakis(p-tolyl) Porphyrin (TiOTTP).* TiOTTP was prepared as literature procedures [8]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (s, 12H, CH_3); 7.57 (m, 8H, $H_{m,p}$ of C_6H_4); 8.12 (m, 8H, H_o of C_6H_4); 8.86 (s, 8H, H_β of pyrrole).

2.3.3. *Silicon Dichloride 5,10,15,20-tetrakis(p-tolyl)porphyrin (3$SiCl_2$TTP).* $SiCl_2$TTP was prepared as literature procedures [9].^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 12H, CH_3); 7.57 (m, 8H, $H_{m,p}$ of C_6H_4); 8.11 (m, 8H, H_o of C_6H_4); 8.92 (s, 8H, H_β of pyrrole).

2.4. *Fabrication of DSSC Devices*

We prepared DSSC devices using the poly (ethylene glycol) (PEG) electrolyte based on ZnTTP, TiOTTP, and $SiCl_2$TTP as the additive and N3 dye as a photosensitizer.

The working electrode was prepared as follows. Thickness of $10 \sim 15$ μm of the TiO_2 paste was spreaded on FTO glass by the doctor blade method [10], followed by sintering at 120°C for approximately 30 min and at 500°C for about 30 min. The sintering process was completed and the TiO_2 deposited electrode was cooled down from 500°C to *ca.* 60°C at the controlled cooling rate (5°C min^{-1}) to avoid any cracking of the glass. The nanostructured TiO_2 electrode was dipped in a concentration of 10 mg of N3 dye per 50 ml of an absolute ethanol solution at room temperature over night. The TiO_2 electrode adsorbed dyes were dipped in the electrolyte solution at room temperature for 24 hours. The electrolyte solution consisted of 0.024 g of I_2, 0.072 g of TBAI, 0.08 g of PMII as an ionic liquid, 0.32 mL of EC, 0.08 mL of PC, 0.4 mL of AN, 0.04 g of PEG as a polymer matrix and 0.04 g of TTP metal complexes as an additive. After that, the electrolyte was casted onto the TiO_2 electrode adsorbed dye and was then dried at about 60°C for 2 hours to evaporate the solvent. The counter electrode was also prepared by a similar method to that which the TiO_2 film was coated. The Pt paste was placed on an FTO glass by sintering to at 100°C for approximately 30 min prior to firing at 400°C for 30 min. In assembling the DSSC devices, the working electrode and the counter electrode were clamped together. The size of active area on DSSC device was 0.49 cm^2. The structure of DSSC device is shown in Figure 2.

3. Results and Discussion

The UV-Vis absorption spectra were examined in $CHCl_3$. Figure 3 shows the absorption spectra of TTP metal complexes and compared with that of TTP under similar

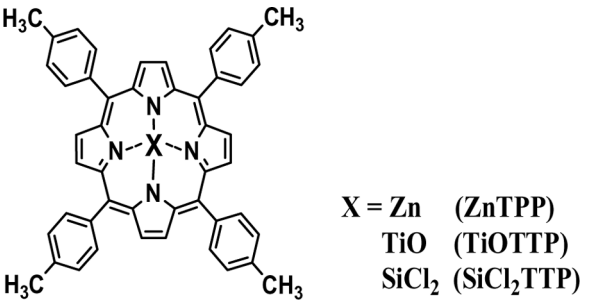

Figure 1. The chemical structure of TTP metal complexes.

conditions. These display common features, with both exhibiting a single Soret-band and two or four Q-bands. According to exciton coupling theory, the transition dipole moments for each moiety interact electrostatically to create two exciton states. The absorption energies of the transitions depend on the angle between the transition dipoles and the relative phase of their excitations. The perturbations sensed in the Q-band region are even less marked due to the much smaller transition dipole moments compared with those of Soret-band. The spectra of the porphyrins exhibit an intense Soret or B-band around 410 nm, assigned to a π-π^* transition to the second electronic excited state [11], and two or four Q-bands between 500 and 700 nm, corresponding to π-π^* transitions to the first electronic excited state.

TGA curves of TTP metal complexes are illustrated in Figure 4. A typical TGA curve demonstrated a high thermal stability, up to 532°C, with a heating rate of 10°C

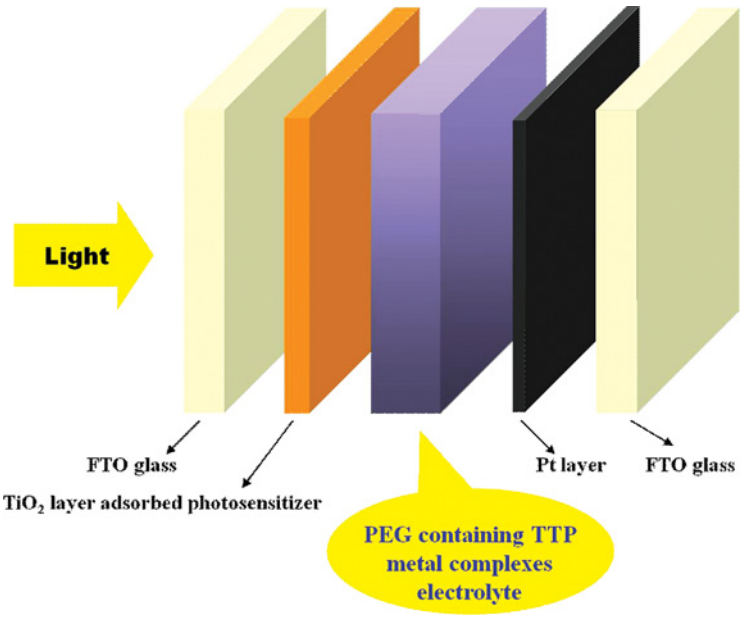

Figure 2. The structure of DSSC device using PEG containing TTP metal complexes electrolyte.

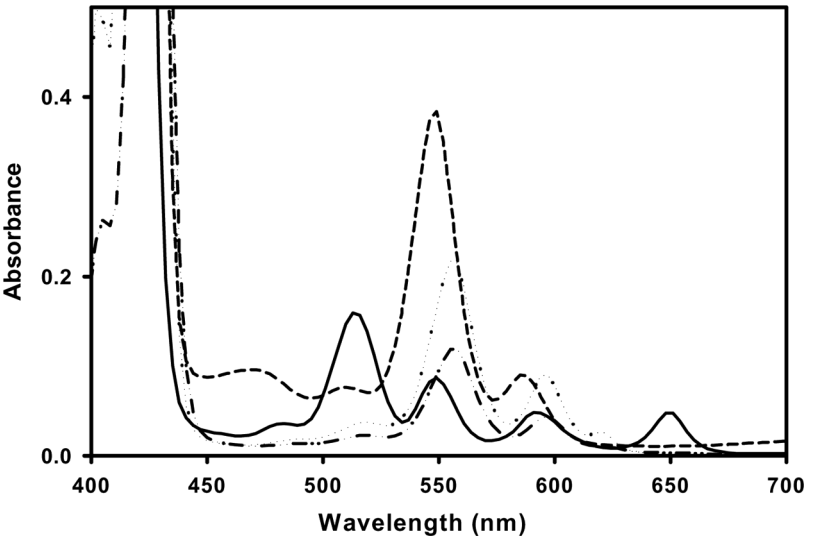

Figure 3. UV-Visible absorption spectra of TTP (solid line), ZnTTP (dotted line), TiOTTP (dashed line), and $SiCl_2TTP$ (dash-dot-dashed line) in chloroform.

min^{-1}. The initial decomposition temperatures (Tds) of ZnTTP and TiOTTP were observed to be around 500°C but TTP and $SiCl_2TTP$ were observed to be each around 300°C and 200°C.

The electrochemistry of the TiOTTP was studied by cyclic voltammetry (CV). All of the porphyrins showed reversible waves for one-electron oxidation and

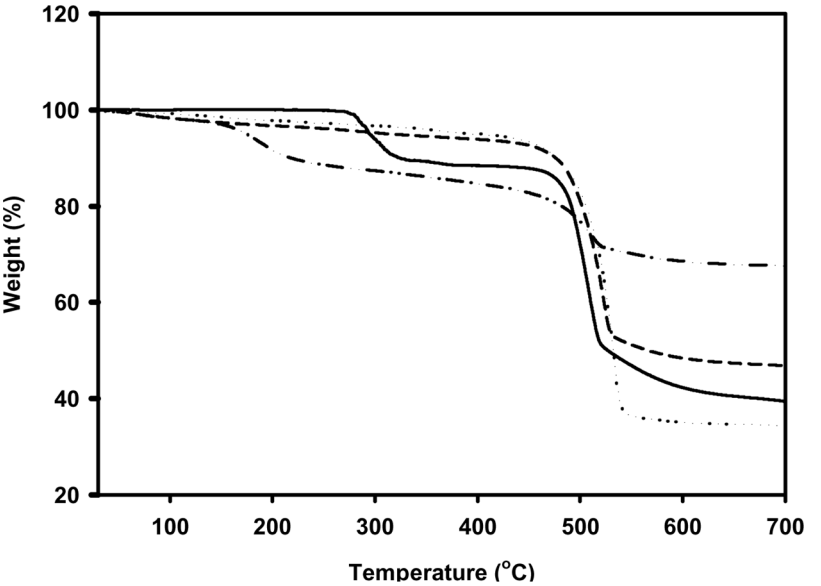

Figure 4. TGA analysis spectra of TTP (solid line), ZnTTP (dotted line), TiOTTP (dashed line), and $SiCl_2TTP$ (dash-dot-dashed line).

reduction. There were small variations in both E_{ox} and E_{red} (+0.45 and −0.54 V with respect to Fc+/Fc, respectively). Cyclic Volrammetry (CV) is a useful method for measuring electrochemical behavior, evaluating the relative HOMO and LUMO energy levels and the band gap of a molecule. In order to calculate the absolute energies of HOMO and LUMO levels, the redox data are standardized with ferrocene,

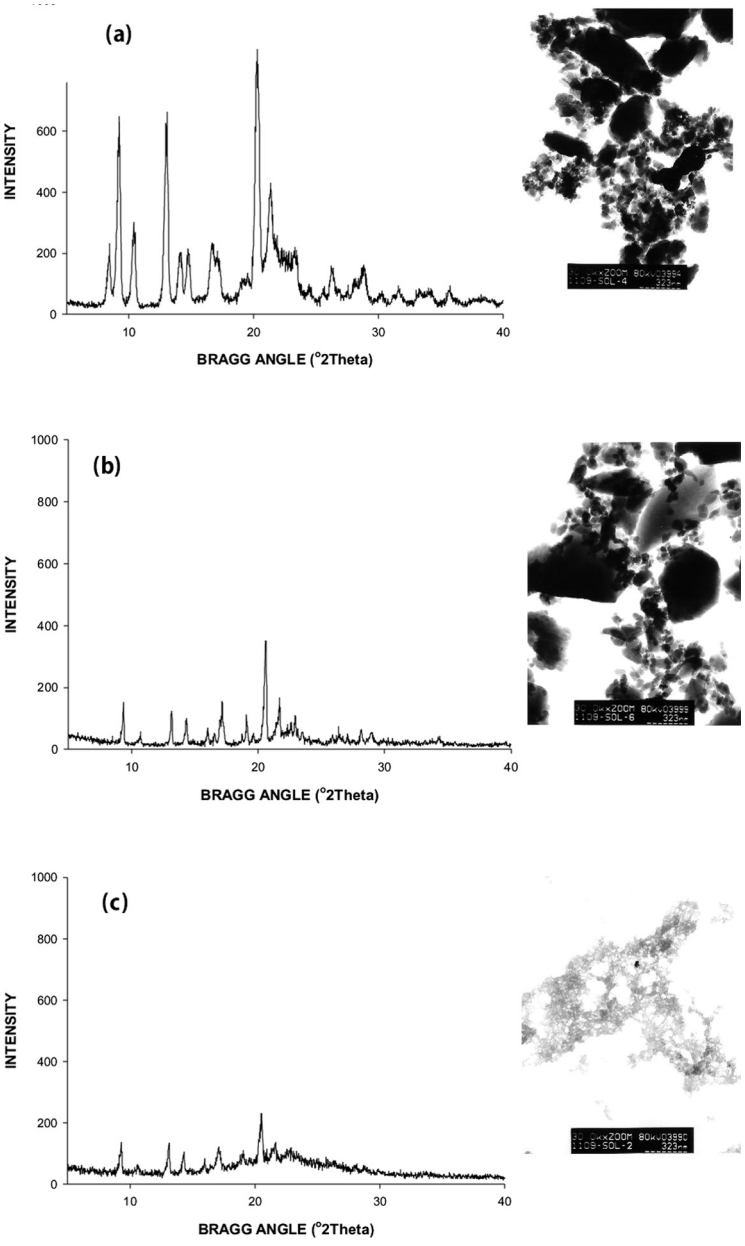

Figure 5. The XRD patterns and the TEM images of TTP metal complexes; ZnTTP (a); TiOTTP (b); $SiCl_2TTP$ (c).

which has a calculated absolute energy of −4.8 eV [12]. The calculated value of TiOTTP for the LUMO level was 2.63 eV and the HOMO level was 5.46 eV (NHE).

Figure 5 shows XRD patterns of metal TTP complexes as their crystal structure and photographs of porphyrin polymorphs were taken by TEM. The particle size and morphology of the synthesized metal TTP complexes were analyzed by TEM measurement. The XRD patterns of porphyrins have the strong peak; ° 2 $\theta = 9.2°$, 13.0° and 20.2°. The similar XRD patterns seen among them were caused by the similar in their particle conditions. In the TEM images, the particle shapes are similar from one another.

We have made of SnO_2:F/TiO_2/N3 Dye/Electrolyte/ Pt devices using PEG electrolyte with TTP or metal TTP complexes as the additive. The I-V curves of the DSSC devices using various porphyrins are shown in Figure 6, and theirs characteristics are summarized in Table 1. When TiOTTP was introduced into the PEG electrolyte, the power conversion efficiencies on DSSC devices were shown remarkably a high value compared with the value of that others. This result was caused by the HOMO energy level of TiOTTP was higher than the ground state energy of N3 dye and lower than work function of Pt counter electrode. But other porphyrins are not and the adsorption on the interface between nanocrystalline porous TiO_2 films and polymer electrolyte. Due to the interface adsorption by TiOTTP mediator, the electron transfer distance between nanoporous TiO_2 film and PEG matrix decrease, and it can attribute to make PEG matrix close to dye molecules. This behavior can improve the electron transfer from PEG matrix toward to dyes adsorbed nanoporous TiO_2 surface.

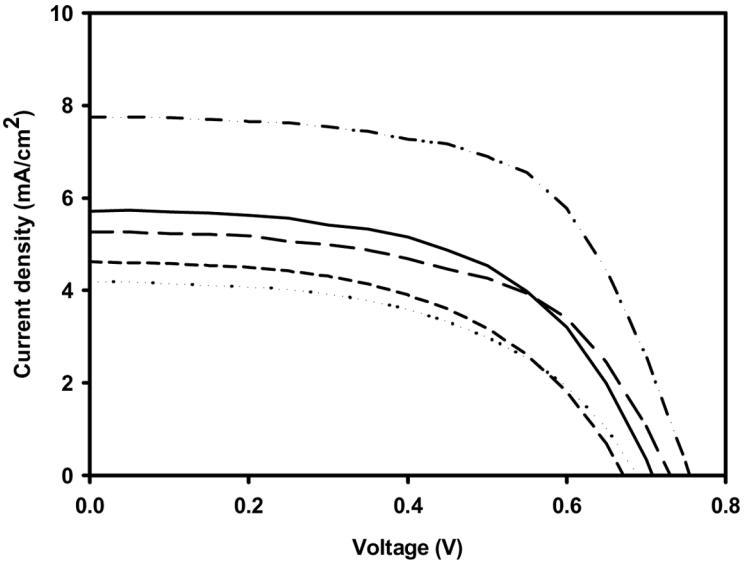

Figure 6. The I-V characteristics for DSSC devices using TTP metal complexes as the additive under AM 1.5; light intensity: 100 mW/cm^2; active area: 0.49 cm^2; PEG (solid line), PEG + TTP (dotted line), PEG + ZnTTP (short dashed line), PEG + TiOTTP (dash-dot-dashed line), and PEG + $SiCl_2$TTP (long dashed line).

Table 1. The photovoltaic performances of DSSC devices using TTP metal complexes as the additive under AM 1.5; light intensity: 100 mW/cm^2; active area: 0.49 cm^2

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Eff. (%)
PEG	0.71	5.71	0.56	2.27
PEG + TTP	0.69	4.19	0.52	1.49
PEG + ZnTTP	0.67	4.62	0.52	1.62
PEG + TiOTTP	0.76	7.75	0.62	3.60
PEG + $SiCl_2$TTP	0.72	5.26	0.59	2.23

4. Conclusion

Metal TTP complexes have successfully synthesized and studied the photovoltaic properties of this compound to apply on DSSCs. We have confirmed their chemical structures by ^{1}H-NMR and FT-IR. And the crystal structures are confirmed by XRD and TEM measurement.

Photovoltaic characteristics of DSSC devies using PEG electrolytes based on TTP metal complexes as the additive were measured by Solar Simulator. In SnO_2:F/TiO_2/Dye/ Electrolyte/Pt device system using the PEG electrolyte based on TiOTTP as the additive, the J_{sc} was 7.75 mA cm^{-2} and the V_{oc} was 0.76 V and the FF was 0.62, leading to a calculated power conversion efficiency of 3.60% under 100 mW cm^{-2} at AM 1.5. DSSC device using the PEG electrolyte based on TiOTTP as the additive showed higher photovoltaic performance than the devices using other porphyrin, due to the interface adsorption by TiOTTP mediator, the electron transfer distance between nanoporous TiO_2 film and PEG matrix decrease, and it can attribute to make PEG matrix close to dye molecules. This behavior can improve the electron transfer from PEG matrix toward to dyes adsorbed nanoporous TiO_2 surface.

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