A New Unsymmetrical Zinc Phthalocyanine as Photosensitizers for Dye-sensitized Solar Cells

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A new unsymmetrical zinc phthalocyanine has been designed and synthesized based on the 'push-pull' and extended π-conjugation concept for the dye-sensitized solar cells. Three *tert*-butoxy groups, which act as electron releasing ('push'), enhance the solubility of phthalocyanine in common organic solvents and reduce the aggregation. Hydroxy substituted 9,10-anthraquinones act as electron acceptors ('pull') for the study of photoinduced electron transfer processes as well as grafting onto nanocrystalline TiO_2. The new unsymmetrical zinc phthalocyanine was fully characterized by FTIR, UV-vis, ^{1}H NMR, cyclic voltammetry and differential pulse voltammetry. The new sensitizer was tested in dye-sensitized solar cells, and gave a better performance.

Key Words : Phthalocyanine, Unsymmetrical, Dye-sensitized solar cells, Electrochemistry

Introduction

Dye-sensitized solar cells (DSSC) have attracted significant attention as low-cost, less toxic manufacturing, easy scale-up, and use of flexible panels alternatives to conventional solid state photovoltaic devices.[1-3] Considerable research effort has attended the design of more efficient dyes as these play a very important role in obtaining high power conversion efficiency (η). The most successful charge-transfer sensitizers employed so far in such cells are bis-(tetrabutylammonium)-*cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) (the N719 dye), and trithiocyanato 4,4'4"-tricarboxy-2,2':6',2"-terpyridine ruthenium(II) (the black dye), produced solar-energy-to-electricity conversion efficiencies of up to 11% under AM 1.5 irradiation.[1,4] In spite of this, the main drawback of ruthenium-based sensitizer is their lack of absorption in the red region of the visible spectrum and their high cost. With respect to availability and stability point of view phthalocyanines are excellent sensitizers, which have been an active focus of intense research for the development of efficient light-to-energy conversion devices. Phthalocyanines are well known for their intense absorption in the far visible region and excellent light, thermal and chemical stability, therefore they are an excellent alternative for solar-cell applications.[5,6]

Phthalocyanines have extended π-conjugation system and various central metals, which determine the profile of absorption spectrum.[7] Phthalocyanines have been tested in the past as sensitizers of wide-band gap oxide semiconductors, although poor incident photon-to-electric current conversion yields were obtained.[8,9] The low η of cell incorporating phthalocyanines might be due to the poor solubility of the macrocycle in organic solvent, a strong tendency to aggregation on the film surface, lack of directionality in the excited state and easy electron recombi-

nation between injected electron in TiO_2 conduction band and oxidized dye.[10-12] To achieve higher η, two methods have been studied: elongating the π-system and lowering the symmetry of the macro-cycle, which can lead to a significantly broadened Soret band and a red-shifted Q band absorptions.[13,14] In this study, we have designed a new unsymmetrical zinc phthalocyanine 9,16,23-(*tert*-butoxy)-2-(1-oxy-9,10-anthraquinone-4-carboxylic acid) zinc phthalocyanine (APC) based on 'push-pull' and extended π-conjugation concept. The new complexe has three *tert*-butoxy groups, which cat as electron releasing ('push'), enhance the solubility of phthalocyanine in common organic solvents and reduce the aggregation. Hydroxy substituted 9,10-anthraquinones have been widely used as dispersed dyes for synthetic polymer materials, and as electron acceptors ('pull') for the study of photoinduced electron transfer processes.[15] The Anthraquinone derivative on extended π-conjugation can increase the absorption bands of phthalocyanines macrocycle. The typical phthalocyanines explored for sensitization of wide-band gap are free base or metallic ones substituted by carboxylic or sulphonic acid groups for attachment to the semiconductors surface.[16,17] The presence of carboxylic acid act as electron acceptors for the study of photoinduced electron transfer processes as well as grafting onto nanocrystalline TiO_2.

Experimental

4-Nitro-phthalonitrile, hydroxybenzoic acid, phthalic anhydride, 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU), 1-pentanol, anhydrous K_2CO_3, DMF, $CHCl_3$, anhydrous $AlCl_3$ were purchased commercially. DMF and $CHCl_3$ were dried and distilled by accustomed methods before use. All other solvents and chemicals used in this work were analytical grade and used without further purification. Column chromatography was performed on silica gel (80-100).

Synthesis.

1-Hydroxy-9,10-anthraquinone-4-carboxylic Acid: Phthalic anhydride (2 g, 13.5 mmol) and hydroxybenzoic acid (1.87 g, 13.5 mmol) were mixed together and then anhydrous $AlCl_3$ (0.1 g, 0.75 mmol) and concentrated methanesulfonic acid (10 mL, 0.16 mmol) were added to this mixture. The stirred reaction mixture was heated at 110 °C by stirring for the 20 min. After completion of the reaction, reaction mixture was poured on crushed ice and extracted with dichloromethane (3 × 40 mL). The organic layer was washed with 5% sodium hydrogen carbonate solution (150 ml) and dried with $CaCl_2$. The solvent was evaporated to give anthraquinone derivatives as crystalline solid, which was recrystallized from acetone and distillated water. Pale yellow solid. Yield: 2.46 g, 68.1%, mp 130 °C.

4-(1-Oxy-9,10-anthraquinone-4-carboxylic Acid) Phthalonitrile: 4-Nitro-phthalonitrile (0.866 g, 5 mmol) and 1-hydroxy-9,10-anthraquinone-4 -carboxylic acid (1.34 g, 5 mmol) were added successively with stirring to dry DMF (10 mL). After dissolution, anhydrous K_2CO_3 (1.0 g, 7 mmol) was added and the reaction mixture was stirred at 60 °C. Further K_2CO_3 (0.5 g, 3.5 mmol) was added portion-wise after 2 h. Stirring vigorously for 48 h under nitrogen. Then the reaction mass was poured into 150 mL of cold water and stirred for 15 min. The precipitate was filtered, washed several times with cold water until the filtrate became neutral, and crystallized from EtOH-water to give the product as a grey, crystalline powder. Yield: 0.82 g, 43.4%, mp 144-145 °C. IR (KBr), ν (cm^{-1}): 3086 (H–Ar), 2241 (–C≡N), 1587 (Ar C=C), 1253 (Ar–O–Ar). ^{1}H NMR (DMSO-d_6) δ 8.64-8.96 (m, 3H, Ar-H), 8.63 (d, 1H, Ar-H), 8.62 (d, 1H, Ar-H), 8.38 (d, 2H, Ar-H), 8.36 (d, 2H, Ar-H).

4-(*tert*-Butoxy) Phthalonitrile: 4-Nitro-phthalonitrile (1.73 g, 0.01 mol) and tertbutyl alcohol (0.74 g, 0.01 mol) were added successively with stirring to dry DMF (15 mL). After dissolution, anhydrous K_2CO_3 (2.0 g, 0.014 mol) was added and the reaction mixture was stirred at 60 °C. Further K_2CO_3 (1 g, 0.007 mol) was added portion-wise after 2 h. Stirring vigorously for 28 h under nitrogen. Then the reaction mass was poured into 200 mL of cold water and stirred for 15 min. The precipitate was filtered, washed several times with cold water until the filtrate became neutral, and crystallized from EtOH-water to give the product as a yellow, crystalline powder. Yield: 0.87 g, 47.3%, mp 272-273 °C. IR (KBr), ν (cm^{-1}): 3074 (H–Ar), 2233 (–C≡N), 1585, 1569 (Ar C=C), 1254 (Ar–O–Ar). ^{1}H NMR (DMSO-d_6) δ 8.07 (d, 1H, Ar-H), 7.56-7.58 (d, 1H, Ar-H), 7.82 (s, 1H, Ar-H)], 2.48 (s, 9H, -C(CH$_3$)$_3$).

9,16,23-(*tert*-Butoxy)-2-(1-oxy-9,10-anthraquinone-4-carboxylic Acid) Zinc Phthalocyanine (APC) 4-(1-Oxy-9,10-anthraquinone-4-carboxylic acid) phthalonitrile (0.197 g, 0.5 mmol), 4-(*tert*-butoxy) phthalonitrile (0.3 g, 1.5 mmol), $Zn(CH_3COO)_2$ (0.11, 0.5 mmol) and a catalytic amount of DBU in dry 1-pentanol (10 mL) was heated at 160 °C with stirring under nitrogen for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding methanol. The product was separated by filtration as a green
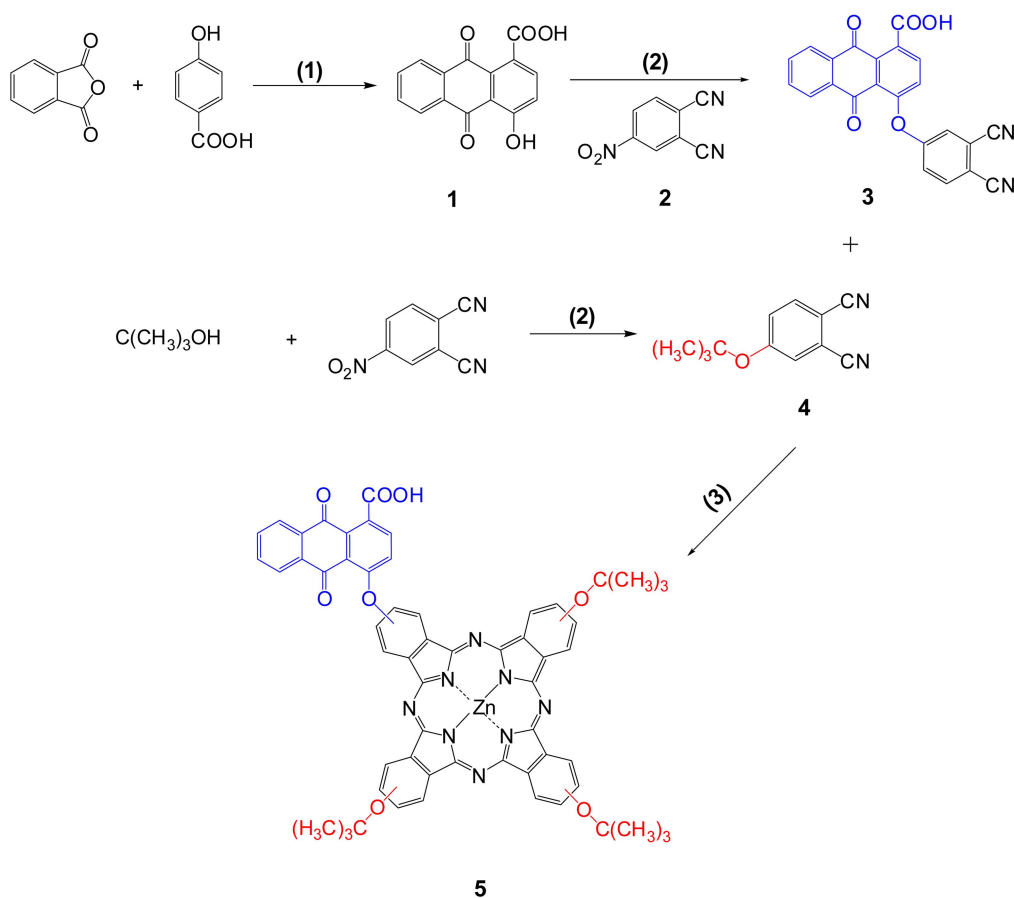
solid which was washed several times with methanol and ethanol to remove any unreacted precursor and then dried in vacuo. The solid material was subjected to silica gel column chromatography and eluted with DMF:CHCl$_3$:CH$_3$OH = 2:8:2 (v/v), and bluish color band was collected. The solvent was removed under reduced pressure to get the desired product. Yield: 0.26 g, 48.5%, mp > 200 °C. IR (KBr), ν (cm^{-1}): 3420 (–O–H), 2926, 2853, 1716 (–C=O), 1616, 1394, 1580, 1468 (C=C), 1230, 1090, 746. ^{1}H NMR (DMSO-d_6) δ 7.15-7.93 (m, 18H, Ar-H), 2.49 (s, 27H, -C(CH$_3$)$_3$). UV-vis, in DMF (λ_{max}, log ε) 681 (4.52), 342 (4.51).

Characterization Methods. The UV-vis spectra were recorded with a Techcomp 2300 spectrophotometer. The Fourier transform IR (FTIR) spectra of all the samples were measured using a Shimadzu 4800S spectrophotometer. ^{1}H NMR spectra were obtained at 400 MHz using a Varian Inova 400 MHz NMR system. The chemical shifts are relative to tetramethylsilane (TMS).

Cyclic and differential pulse voltammetry measurements were performed on an electrochemical workstation (CHI LK2005A, Tianjin Lanlike Chemistry electronic high-tech Co., Ltd., PR China). Cyclic voltammetry experiments were performed on 1×10^{-4} mol phthalocyanine dye solution in DMF at scan rate 100 mV/s using tetrabutylammonium perchlorate (0.1 mol/L) as supporting electrolyte. Cyclic voltammetry with a platinum wire was used as working electrode, the platinum as the counter film electrode, the calomel as the reference. Purge the solution with nitrogen for 1 h before the experiment.

Dye-solar Cell Preparation. TiO$_2$ photoelectrode was prepared by screen-printing methods. TiO$_2$ photoelectrode (area: *ca.* 0.8 cm × 1.2 cm) was prepared by a similar method reported in the literature.[18-20] Nanocrystalline TiO$_2$ films of 8 ìm thickness were deposited onto transparent conducting glass (which has been coated with a fluorine-doped stannic oxide layer, thickness of 4 mm, sheet resistance of 18-20 Ω). These films were dried at 150 °C for 20 min and then were gradually sintered at 500 °C for 20 min. The sensitizer was dissolved in ethanol at a concentration of 1×10^{-4} mol. The photoelectrode was dipped into the dye solution immediately after the high-temperature annealing and it was still hot (80 °C) and then kept at room temperature for 24 h so that the dye was adsorbed onto the TiO$_2$ films. After completion of the dye adsorption, the photoelectrode was withdrawn from the solution and washed thoroughly with ethanol to remove non-adsorbed dye under a stream of dry air or nitrogen.

A sandwich cell was assembled by using the dye anchored TiO$_2$ films as the working electrode and conducting glass coated with carbon as the counter electrode. The two electrodes were placed on top of each other using a thin polyethylene film (50 μm) thick as a spacer to form the space for electrolyte. The empty cell was tightly held, and the edges were heated to 65 °C to seal the two electrodes together. The active surface area of TiO$_2$ film electrode was *ca.* 0.96 cm^2. The electrolyte was introduced into cell through pre-drilled whole of the counter electrode and later covered by cover

Scheme 1. (1) AlCl$_3$, H$_2$SO$_4$; (2) K$_2$CO$_3$, DMF; (3) DBU, 1-pentanol, Zn(CH$_3$COO)$_2$.

glass to avoid the leakage of the electrolyte solution. The composition of electrolyte is 0.05 mol/L iodine, 0.5 mol/L LiI in acetonitrile. Photoelectrochemical data were obtained using a 450W xenon light source focused to give 1000 W/m^2, the equivalent of one sun at AM 1.5 (the luminance of the lamp has normalized and corrected by the supplier), at the surface of the test cell.

Results and Discussion

Design and Synthesis. The synthesis of new unsymmetrical zinc phthalocyanine was illustrated in the Scheme 1. 4-(1-Oxy-9,10-anthraquinone-4-carboxylic acid) phthalonitrile 3 was prepared through the displacement reaction of 1-hydroxy-9,10-anthraquinone-4-carboxylic acid 1 with 4-Nitro-phthalonitrile 2 in DMF solution in a moderate yield. APC was prepared through 4-(1-oxy-9,10-anthraquinone-4-carboxylic acid) phthalonitrile 3 with 4-(*tert*-butoxy) phthalonitrile 4 in 1-pentanol solution in the presence of DBU and metal salts.

UV-vis Measurements. The electronic absorption spectrum of APC was recorded in DMF solution and compared to that of the phthalocyanine adsorbed onto 6 μm thick nanocrystalline TiO$_2$ films (Fig. 1). The absorption spectrum in solution showed characteristic absorptions around 681 nm in the Q band region. The Q band observed was attributed

to π-π* transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the conjugated macrocycle. The other bands (Soret band) around 342 nm were observed due to the transitions from the deeper π levels to the LUMO. Analysis of UV-vis spectra shows no evidence of aggregation in solution as demonstrated by a sharp unperturbed phthalocyanine Q band at 681 nm.[21] In the case of APC, the
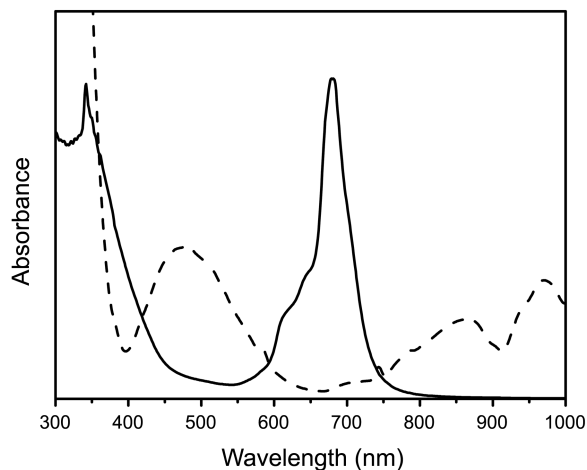

Figure 1. UV-vis absorption spectra of APC (—) in DMF and (----) adsorbed onto a 6 μm thick TiO$_2$ films.

anthraquinone group is fused to the planar phthalocyanine core and its π-electrons are integrated into the aromatic system of the main core. The consequence of this structure is some bathochromic shift to the near IR region.[22]

The absorption spectrum of the phthalocyanine adsorbed onto 6 μm thick TiO$_2$ electrode exhibit an obvious red shift. This may be due to the presence of carboxylic protons of phthalocyanine, which on adsorption on TiO$_2$ release the proton and bind to Ti^{4+}. The Ti^{4+} acts as electron withdrawing and produces a red shift in the absorption bands.[23] Dyes are known to form aggregation, which is due to the strong coupling between the molecules that causes either a red shift or a blue shift in the absorption band of the aggregate. For a J-type aggregate the absorption band is red shifted relative to the monomer, while a blue shift in the absorption band is observed for an H-aggregate.[24] APC adsorbed onto nanocrystalline TiO$_2$ to obtain a red shift in comparsion with that of the solution spectra, which should result from the formation of the J-type aggregate of APC on the TiO$_2$ surface.[13,25] APC adsorbed onto nanocrystalline TiO$_2$ films not only broaden the range of nanocrystalline TiO$_2$ films spectral response, but also conducive to inject electrons into the conduction band of TiO$_2$. $E_{0\text{-}0}$ energy of APC estimated from absorption maximum is 1.82 eV. The $E_{0\text{-}0}$ was calculated according to the following equation.

$$E_{0-0} = \frac{1240}{\lambda_{max}} \qquad (1)$$

λ_{max} is the absorption maximum.

Electrochemical Measurements. The reduction and oxidation behavior of metallophthalocyanine derivatives is due to the interaction between the phthalocyanine ring and the central metal. First-row transition metal phthalocyanines differ from those of the main-group metal phthalocyanines due to the fact that metal 'd' orbitals may be positioned between the HOMO and LUMO of the phthalocyanine ligand.[26] The HOMO and LUMO levels of APC must match with the conduction-band-edge energy level of the TiO$_2$ and the redox potential of electrolyte for efficient electron injection and APC regeneration. The electrochemical behavior of APC was investigated using cyclic and differential pulse voltammetric techniques in DMF solvent. The oxidation potentials were determined from half-wave potentials ($E_{1/2}$) ($E_{ox}-E_{red}$)/2 by cyclic voltammetry or peak potentials by differential pulse voltammetry. The corresponding cyclic and differential pulse voltammograms are presented in Figure 2. The oxidation potentials ($E_{1/2(ox)}$) correspond to the HOMO level of phthalocyanines. The unsymmetrical zinc phthalocyanine exhibits a quasi-reversible oxidation at 0.90 V. With respect to dye-sensitization of wide-band gap semiconductors, e.g. TiO$_2$, the first oxidation potentials of APC and the $E_{0\text{-}0}$ transition energy, the energy levels of the LUMO was determined to be −0.92 V *vs* SCE,[27] whereas the energy level of the conduction band edge of TiO$_2$ is *ca.* −0.74 V *vs* SCE.[28] This makes electron injection from the excited state of APC into the conduction band of TiO$_2$ thermodynamically feasible. Furthermore, the HOMO level
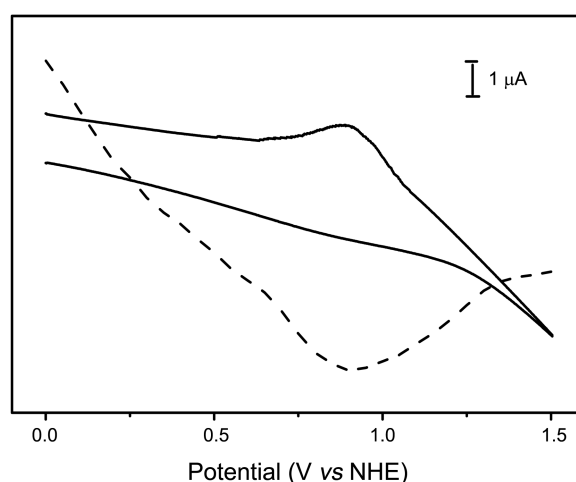

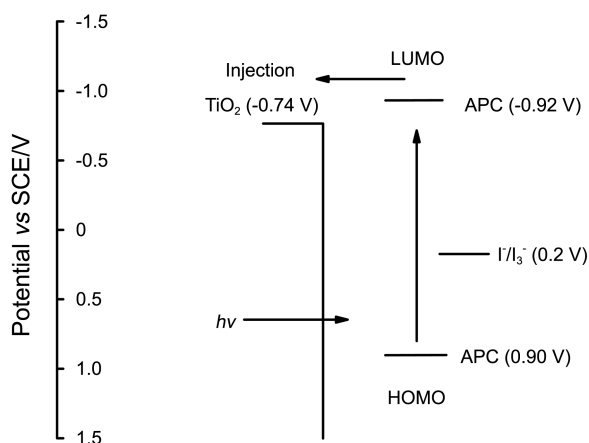**Figure 2.** Cyclic (—) and differential pulse voltammograms (----) of APC.

Figure 3. Energy level diagram for APC.

of APC is lower than the energy level of the redox couple I$^-$/I$_3^-$ (0.2 V *vs* SCE) in the electrolyte, enabling the dye regeneration by electron transfer from I$^-$.[11] Energy level diagram for APC is shown in Figure 3. APC has negative LUMO level and positive HOMO level, satisfying the energy gap rule. This means that, the APC can be employed as sensitizers for DSSC applications.[15]

Photovoltaic Characterization. Figure 4 shows a representative photocurrent action spectrum obtained from a sandwich cell using sensitizer APC. The photocurrent action spectrum resembles the absorption spectra except for a slight red shift by *ca.* 3 nm. The photoresponse of thin films extends up to 750 nm. The IPCE was calculated according to the following equation.

$$\text{IPCE}(\lambda) = 1240\left(\frac{I_{ph}}{\lambda P_{in}}\right) \qquad (2)$$

Where λ is the wavelength, I_{ph} is the photocurrent of the incident radiation (mA/cm^2) and P_{in} is the incident radiative flux (W/m^2). We have observed an IPCE value of 31%.

The solar energy-to-electricity conversion efficiency, η, under whitelight irradiation can be obtained from the follow-
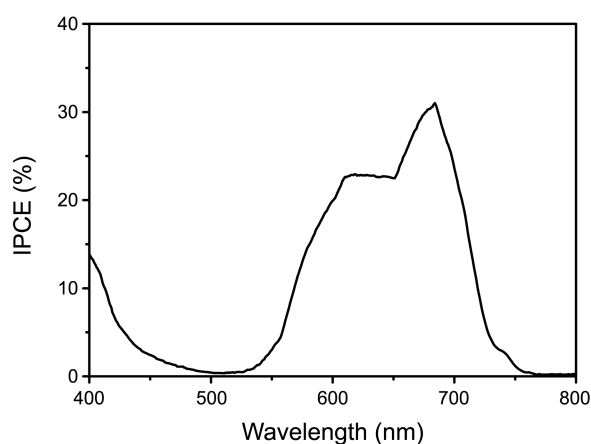
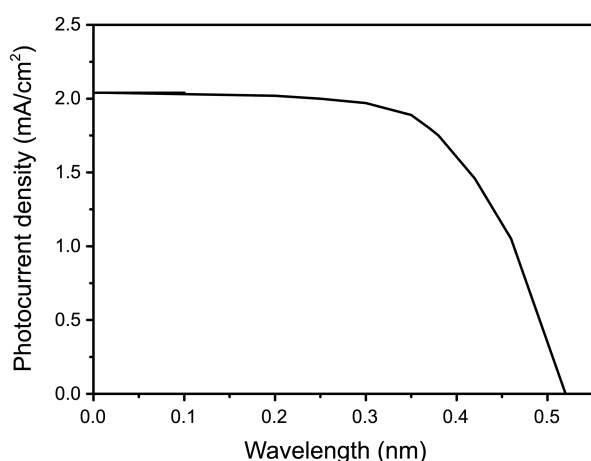**Figure 4.** Photocurrent action spectra of APC.

Figure 5. Current-voltage characteristics.

ing equation.

$$\eta[\%] = \frac{J_{SC}[mAcm^{-2}]V_{OC}[V]Xff}{I_0[WM^{-2}]} \times 100 \qquad (3)$$

Where I_0 is the photon flux (e.g. 1000 W m^{-2} for 1.0 sun), J_{SC} is the short-circuit photocurrent density under irradiation, V_{OC} is the open-circuit voltage, and ff represents the fill factor. The fill factor is defined by the following equation.

$$ff = \frac{J_{PH(max)}.V_{PH(max)}}{J_{SC}V_{OC}} \qquad (4)$$

Where $J_{PH(max)}$ and $V_{PH(max)}$ are the photocurrent and photovoltage for maximum power output and J_{SC} and V_{OC} are the short-circuit photocurrent density and open-circuit photovoltage. Figure 5 shows photocurrent-voltage of APC dye grafted onto nanocrystalline TiO$_2$ films. We have observed an overall efficiency 0.71% under 1 sun irradiation, $J_{SC} = 2.04$ mA cm^{-2}, $V_{OC} = 0.52$ V, and $ff = 0.67$.

The low overall conversion efficiency of APC adsorbed onto TiO$_2$ was due to the solubility, aggregation and poor electron injection from excited state of phthalocyanine into the conduction band of TiO$_2$.[8,9,15,29,30]

Conclusion and Perspectives

We were successful in the preparation and characterization of a new unsymmetrical zinc phthalocyanine, APC based on 'push-pull' and π-conjugation concept. It was shown that the extension of phthalocyanine π-conjugation by anthraquinone can increase the absorption bands and shift to near infrared, three *tert*-butoxy groups enhance the solubility of phthalocyanine in common organic solvents and also act as electron releasing ('push'). The presence of carboxylic acid act as electron acceptors ('pull') and server to graft onto nanocrystalline TiO$_2$. However, the surface aggregation of APC adsorbed onto TiO$_2$ was not significantly avoided. The new photosensitizer was tested in DSSC by using I$^-$/I$_3^-$ redox electrolyte. The DSSC with about 0.71% power conversion efficiency have been fabricated.

To further improve the efficiency of test cell device, some additives should be added to the redox electrolyte *i.e.* 1-butyl-3-methylimidazolium iodide (BMII), *tert*-butyl pyridine (TBP), guanidinium thiocyanate (GuSCN).[11,31,32] These additives can suppress dark current and improve cell conversion efficiency. Because *i.e.* TBP can coordinate with incomplete coordination of Ti on the surface of TiO$_2$ film by nitrogen atoms of pyridine ring, and hinder recombination between the conduction band electrons of the surface of TiO$_2$ film with I$_3^-$ in solution. The results significantly improve solar cell of open-circuit voltage, fill factor and the photoelectric conversion rates.[33] Furthermore, for the future performance of phthalocyanine-based TiO$_2$ solar cells, some other redox-active substituents that are asymmetrically should be incorporated into the phthalocyanine macrocycle.

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