J. Chem. Sci., Vol. 121, No. 1, January 2009, pp. 75–82. © Indian Academy of Sciences.

Unsymmetrical extended *π*-conjugated zinc phthalocyanine for sensitization of nanocrystalline TiO_2 films

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MS received 11 February 2008; revised 24 October 2008

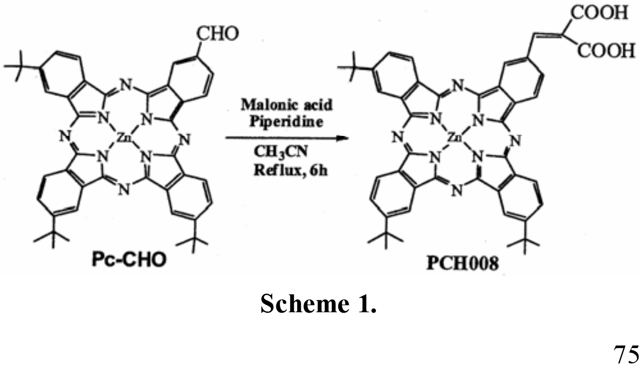
Abstract. We have designed and synthesized a new unsymmetrical zinc phthalocyanine based on '*push-pull*' and extended *π*-conjugation concept, PCH008. The new sensitizer was fully characterized by CHN anlysis, UV-Vis., fluorescence spectroscopies and cyclic voltammetry. The new sensitizer which upon anchoring onto nanocrystalline TiO_2 film exhibit a short circuit current of 5·63 mA cm^{-2}, open circuit potential of 557·0 mV and a fill factor of 0·75 corresponding to an overall conversion efficiency of 2·35% under standard global air mass (AM) 1·5 solar conditions and compared its performance with literature reported phthalocyanine dyes.

Keywords. Dye sensitized solar cells; phthalocyanine; extended *π*-conjugation; unsymmetrical zinc phthalocyanine and redox electrolyte.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductor have intensively studied because of their potential low-cost, easy processing and high performance. In this technology, ruthenium complexes maintained a clear lead in performance in power conversion efficiencies reaching 11%.[1] In the last several years many metal free organic dyes have been developed due to their low cost and environmental compatibility compared to the ruthenium dyes.[2–6] 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. Moreover, phthalocyanine molecules have unique properties in terms of light absorption in the far visible region of the solar spectrum (λ = 690 nm) with molecular extinction coefficients (ε) higher than 100,000 dm^3 M^{-1} cm^{-1} and good chemical stability.[7–10]

Various phthalocyanines have been tested as sensitizers for wide-bandgap oxide semiconductors, although they all have reported power conversion efficiencies below 1% until recently.[11] The low η of cell incorporating phthalocyanines might be due to the poor solubility of the macrocycle in organic solvents, and a strong tendency to aggregate on the film surface, resulting in rapid deactivation of the dye excited state. To overcome these problems, recently, we have reported unsymmetrical zinc phthalocyanines (PCH001 and PCH003) based on '*push-pull*' concept (scheme 1). We have observed an overall cell efficiency of 3·05 and 1·13% for PCH001 and PCH003, respectively, which is a major break through in phthalocyanine based DSSC systems.[12–14] In order to further improve the overall efficiency of PCH003,



Scheme 1.

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one has to increase the molar extinction coefficient (ε) of the Q-band absorption of phthalocyanine macrocycle. During the course of our research work on the development of phthalocyanine based dyes for DSSCs, we have realized by introduction of extended π-conjugation that can increase the ε of the absorption bands of phthalocyanine macrocycle. Grätzel and co-workers have reported in case of ruthenium polypyridyl complexes that the introduction of extended π-conjugation could enhance the ε as well as broaden the absorption bands.[15–17] In the present investigation, we have designed a new unsymmetrical phthalocyanine i.e. PCH008 based on '*push-pull*' and extended π-conjugation concept. The new unsymmetrical phthalocyanine has three bulky *tert*-butyl groups, which act as electron releasing ('*push*'), enhance the solubility of phthalocyanine in common organic solvents, reduce the aggregation and tune the lowest unoccupied molecular orbital (LUMO) level of phthalocyanine. The presence of dicarboxylic acid groups on extended π-conjugation of PCH008 act as electron withdrawing ('*pull*') as well as grafting onto nanocrystalline TiO_2.

2. Experimental

4-*tert*-butyl phthalonitrile, 4-cyano phthalonitrile, malonic acid, 1,8-diazabicyclo [5.4.0]-undec-]-ene (DBU), 1-pentanol and tetrabutylammonium perchlorate (TBAP) are procured from Aldrich. CaH, K_2CO_3, acetonitrile, acetone, chloroform, dichloromethane and hexane are obtained from BDH (India) and were purified prior to use.[18] Column chromatography was performed on Aceme silica gel (60–120).

2.1 *Synthesis*

Formyl phthalocyanine (Pc-CHO) was synthesized as per the procedure reported in the literature.[19]

2.1a *Synthesis of PCH008*: The new sensitizer was synthesized by adopting Knoevenagel condensation method. Pc-CHO (50 mg, 0·06 mmol), malonic acid (10·6 mg, 0·1 mmol) and two drops of piperidine were dissolved in 10 ml of acetonitrile. The reaction mixture was refluxed at 80°C for 6 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The solid material was subjected to silica gel column chromatography and eluted with $CHCl_3/CH_3OH$ (90:10, v/v) mixture and bluish colour band was collected. The solvent was removed under reduced pressure to get the desired product. This PCH008 was characterized by ^1H NMR, IR, UV-Vis, MALDI-TOF spectroscopies and elemental analysis. Elemental analysis of $C_{48}H_{42}N_8O_4Zn$ (calculated mass % in parentheses): C, 67·20 (67·01); H, 4·95 (4·92); N, 13·00 (13·03). IR (KBr pellet): $\nu = 3446$, 2923, 2854, 1721, 1634, 1256, 1582, 1485, 1391, 1280, 1082, 748, 523 cm^{-1}. MALDI-MS: $(C_{48}H_{42}N_8O_4Zn)–CO_2 = 817$ (60%). ^1H NMR (DMSO-d_6, δ, ppm): 7·25–8·10 (*m*, 12H); 6·92 (*d*, 2H, $J = 7{\cdot}8$ Hz); 1·34 (*s*, 27H). UV-Vis, in ethanol (λ_{max}, ε, $mol^{-1}\ cm^{-1}$) 686 (1,33,000), 672 (1,38,000), 638 (54,000), 348 (91,000).

2.2 *Characterization methods*

MALDI-MS spectra were recorded on a TO-4X KOMPACT SEQ, KARTOS, UK, Mass spectrometer. Major fragmentations are given as percentages relative to the base peak intensity. The UV-Vis spectra were recorded with a Shimadzu model 1700 spectrophotometer. Steady state fluorescence spectra were recorded using a Spex model Fluoromax-3 spectrofluorometer for solutions having optical density at the wavelength of excitation (λ_{ex}) ≈ 0·11. ^1H NMR spectra were obtained at 300 MHz using a Brucker 300 Avance NMR spectrometer running X-WIN NMR software. The chemical shifts are relative to tetramethylsilane (TMS). The Fourier transform IR (FTIR) spectra of all the samples were measured using a Thermo Nicolet Nexus 670 spectrometer.

Cyclic- and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. Cyclic voltammetric experiments were performed on 1 mM phthalocyanine dye solution in acetonitrile at scan rate of 100 mV/s using 0·1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode and plantinum wire is an auxillary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured.

Photoelectrochemical data were obtained using a 450 W 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. A sandwich cell was assembled by using the dye anchored TiO_2

films as the working electrode and conducting glass (TEC-15; the glass had been coated with a fluorine-doped stannic oxide layer; sheet resistance, 12–15 Ω/square) coated with chemically deposited platinum from 0·05 M hexachloroplatinic acid as the counter electrode. The two electrodes were held to each other by heating with a hot-melt ionomer film (Surlyn 1702, 25 μm thickness, Du-Pont) as a spacer between the electrodes. A drop of electrolyte solution was placed on the drilled hole in the counter electrode (which had already made) and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Bynel (35 μm) and a cover glass (0·1 mm thickness). We have used two different redox electrolytes for the construction of DSSC test cell device. The composition of electrolytes are 0·6 M 1-butyl-3-methylimidazolium iodide (BMII), 0·025 M LiI, 0·04 M I_2, 0·275 M *tert*-butyl pyridine (TBP) and 0·05 M guanidinium thiocyanate in a 85 : 15 (v/v) mixture of acetonitrile and valeronitrile (M1) and the second redox electrolyte is 0·6 M BMII, 0·1 M LiI, 0·05 M I_2 and 0·5 M *tert*-butyl pyridine in a 85 : 15 (v/v) mixture of acetonitrile and valeronitrile (A7117).

2.3 *Test cell preparation*

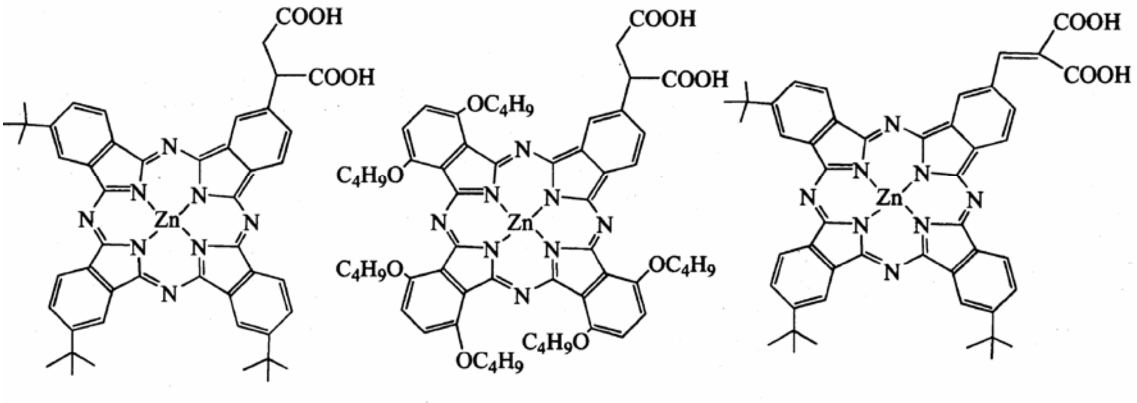
TiO_2 photoelectrode was prepared by screen-printing methods. TiO_2 nanoparticles and an organic TiO_2 paste for screen-printing were prepared by methods reported in the literature.[20,21] Nanocrystalline TiO_2 films were deposited onto transparent conducting glass (Nippon Sheet Glass, which has been coated with a fluorine-doped stannic oxide layer thickness of 4 mm, sheet resistance 8–10 Ω/cm^2) by screen-printing. These films were dried at 125°C for 10 min and then were gradually sintered at 500°C for 20 min.

The heated electrodes were impregnated with a 0·05 M titanium tetrachloride solution in water-saturated desiccator for 30 min at 70°C and then were washed with distilled water. The 0·05 M titanium tetrachloride solution was prepared by adding titanium tetrachloride to ice to make a 2 M solution. This solution was then cooled to –20°C before being diluted to 0·05 M. The electrodes were heated at 500°C for 30 min and were then allowed to cool to 50°C before dipping then into the dye solution. The dye was dissolved in ethanol in the concentration range of 5×10^{-5} M, which contains 10 mM of $3\alpha,7\alpha$-dihydroxy-5β-cholic acid (chenodeoxycholic acid). The TiO_2 films were soaked in the dye solution and then kept at 22°C for 4 h so that the dye was adsorbed onto 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. The dye-adsorbed TiO_2 electrode and thermally platinised counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film (Surlyn 1702, 25 μm thickness, Du-Pont). In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO_2 layer, a light-shading mask was used onto the DSSCs, so active area of DSSCs was fixed to 0·2 cm^2.

3. Results and discussions

3.1 *Synthesis*

The new sensitizer PCH008 was synthesized by condensing Pc-CHO with malonic acid by refluxing in acetonitrile solvent. The new phthalocyanine was completely characterized by CHN, MALDI-MS, ^{1}H NMR, UV-Vis, and fluorescence spectroscopies as well as cyclic voltammetry. The peak at 817 in MALDI-MS spectrum corresponds to extended π-conjugated unsymmetrical phthalocyanine with loss of CO_2 molecule (figure 1). The electronic absorption spectrum of PCH008 was recorded in ethanol solution and compared to that of the phthalocyanine adsorbed onto 2 μm thick nanocrystalline films (figure 2). The molar extinction coefficient (ε) values of PCH008 are compared with PCH001 and PCH003 and the data are presented in table 1. From table 1, it is clear that the ε values of PCH008 are higher than PCH003. The absorption spectrum of the phthalocyanine adsorbed onto 2 μm thick TiO_2 electrode is similar to that of the solution spectra but exhibit a small 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.[13] Figure 3 shows emission spectrum of PCH008 being excited at 298 K within the charge-transfer (CT) absorption band in an air-equilibrated ethanol solution; it exhibits luminescence maxima at 710 nm and a shoulder at 735 nm. Singlet state (E_{0-0}) energy of PCH008 estimated from the excitation and emission spectra is 1·77 eV. The emission intensity was quenched when the sensitizer adsorbed onto 2 μm thick TiO_2 layer as a consequence of electron injection from excited



PCH001 **PCH003** **PCH008**

Figure 1. Molecular structures of unsymmetrical phthalocyanines used in this study.

Table 1. UV-visible, emission and electrochemical data.

Dye	Absorption[a] λ_{max}, nm[b] (logε, M^{-1}cm^{-1})[c]				Emission[a] λ_{max}, nm[b]		E_{0-0} (eV)	E$_{1/2}$ (V, vs SCE)[d] Oxidation[e]	Reduction[e]
PCH008	348 (4·96)	638 (4·73)	672 (5·14)	686 (5·12)	710	735	1·77	0·80	–1·08
PCH003	343 (4·69)	636 (sh)	697 (4·83)		710	760	1·76	0·51	–1·15
PCH001	347 (4·85)	610 (4·50)	693 (5·28)		698	750	1·78	0·65	–1·31

[a]Solvent Ethanol. [b]error limits: λ_{max} ± 1 nm. [c]logε, ± 10%. [d]Solvent CH_3CN, 0·1 M TBAP. [e]Error limits, ± 0·03 V

singlet state of phthalocyanine macrocycle into the conduction of TiO$_2$.

With a view to evaluate the HOMO–LUMO levels of PCH008, we have carried out the electrochemistry by using cyclic and differential pulse voltammetric techniques. The corresponding cyclic and differential pulse voltammograms were presented in figure 4. PCH008 exhibits a quasi-reversible oxidation at 0.80 V and a quasi-reversible reduction at –1·08 V. With respect to dye-sensitization of wide-bandgap semiconductors, e.g. TiO$_2$, the first oxidation potentials of PCH008 and the E_{0-0} transition energy, the energy levels of the singlet excited states (LUMO) of PCH008 was determined to be –0·97 V vs SCE,[22] whereas the energy level of the conduction band edge of TiO$_2$ is ca. –0·74 V vs SCE.[23] This makes electron injection from the excited state of PCH008 into the conduction band of TiO$_2$ thermodynamically feasible. Furthermore, the HOMO level of the PCH008 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^-

3.2 *Photovoltaic measurements*

The performance of newly synthesized PCH008 as a sensitizer with a sandwich type nanocrystalline TiO$_2$ electrode (10 + 4 μm composed of transparent layer and scattering layer) was determined from measurements on photovoltaic cells using two different redox electrolytes i.e. M1 and A7117 and compared its performance with PCH001 and PCH003 under similar test cell conditions. The M1 redox electrolyte contains 0·6 M 1-butyl-3-methylimidazolium iodide (BMII), 0·025 M LiI, 0·04 M I_2, 0·275 M *tert*-butyl pyridine (TBP) and 0·05 M guanidinium thiocyanate in a 85 : 15 (v/v) mixture of acetonitrile and valeronitrile and A7117 redox electrolyte contains 0·6 M BMII, 0·1 M LiI, 0·05 M I_2 and 0·5 M *tert*-butyl pyridine in a 85 : 15 (v/v) mixture of acetronitrile and valeronitrile. We have added chenodeoxycholic acid to the dye solution to minimize the aggregation of the macrocycle. Earlier, we have reported test cell data of PCH001 and PCH003 with A1376 redox electrolyte with 3·05 and 1·13% efficiency, respectively.[13,14] Figure 5 shows photocurrent action spectra of PCH008 with two different redox electrolytes along with PCH001 and PCH003, where the photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE was calculated according to the following equation.

$$\mathrm{IPCE}(\lambda) = 1240\left(\frac{I_{\mathrm{SC}}}{\lambda\phi}\right), \qquad (1)$$

where λ is the wavelength, I_{SC} the current at short circuit (mA/cm^2) and ϕ is the incident radiative flux (W/m^2). We have observed an IPCE value of 47% with both M1 and A7117 redox electrolytes. Under similar test cells conditions, we have observed an IPCE of 71 and 16% in case of PCH001 and PCH003, respectively. The photocurrent action spectrum resembles the absorption spectra except for a slight red shift by ca. 10 nm. The photoresponse of thin films displays a broad spectral response covering almost the entire visible spectrum extends from 500 to 800 nm in case of PCH001 and PCH008 where as in case of PCH003, it was only from 575 to 800 nm.

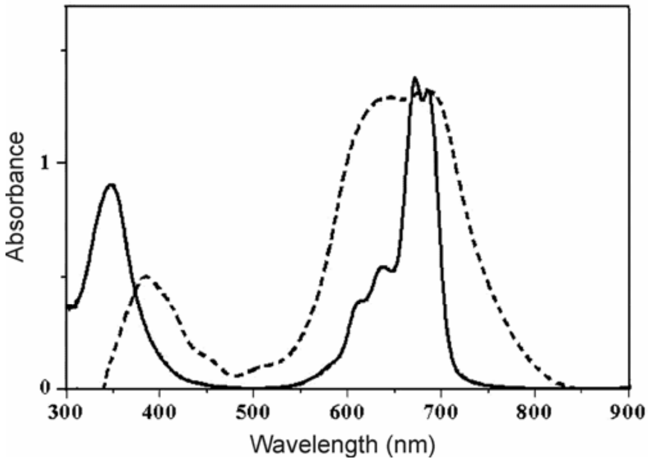


Figure 2. UV-visible absorption spectra of PCH008 (——) in ethanol and (-----) adsorbed onto a 2 μm thick TiO$_2$ film.

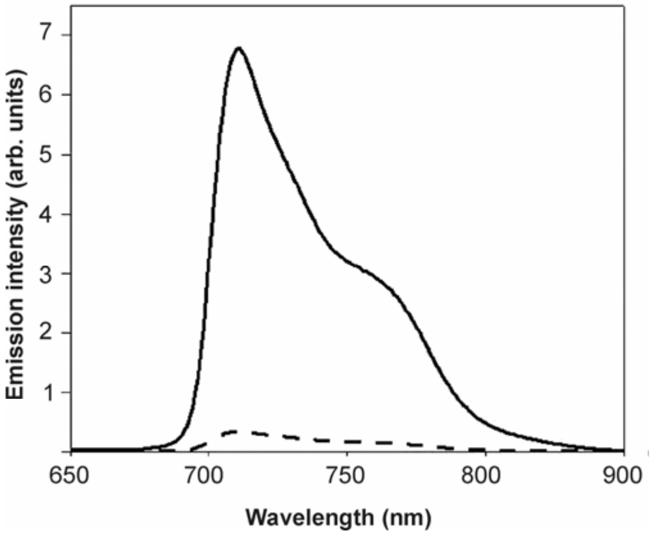


Figure 3. Fluorescence spectra of PCH008 (——) in CH$_3$CN and (-----) adsorbed onto a 2 μm thick TiO$_2$ film. The excitation wavelength λ_{ex} = 686 nm.

The photovoltaic performance of DSSC based on PCH008 with two different redox electrolytes along with PCH001 and PCH003 under 1 sun (1000 W/m^2) irradiation is shown in table 2. The solar energy-to-electricity conversion efficiency, η, under white-light irradiation can be obtained from the following equation.

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

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.

$$ff = \frac{J_{\mathrm{PH(max)}} \cdot V_{\mathrm{PH(max)}}}{J_{\mathrm{SC}}V_{\mathrm{OC}}}, \qquad (3)$$

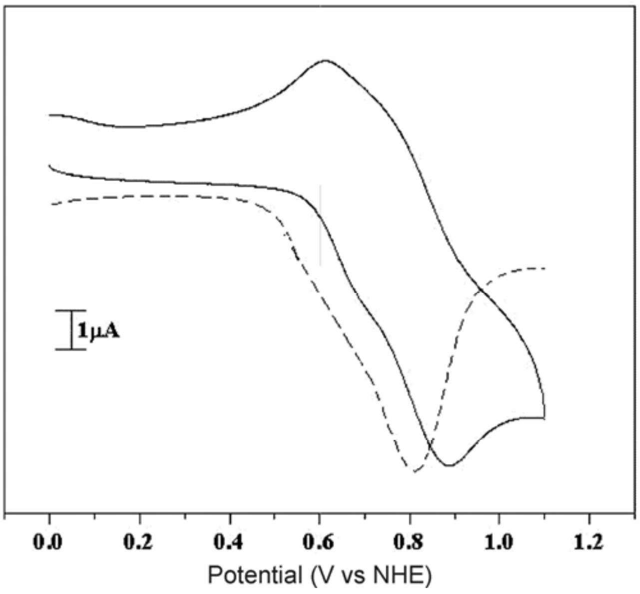


Figure 4. Cyclic (——) and differential pulse voltammograms (----) of PCH008.

Table 2. Photovoltaic performance data.[a]

Dye	Electrolyte	J_{SC}[e] (mA/cm^2)	V_{OC} (V)	Fill factor (ff)	η [%]
PCH008	A7117[b]	5·63	0·557	0·75	2·35
PCH003	A7117	1·94	0·517	0·77	0·77
PCH001	A7117	6·20	0·620	0·73	2·80
PCH008	M1[c]	5·31	0·562	0·74	2·22
PCH003	M1	1·33	0·510	0·77	0·52
PCH001	M1	6·25	0·633	0·74	2·86

[a]Photoelectrode: TiO_2 (10 + 4 μm and 0·2 cm^2); [b]A7117 = 0·6 M 1-butyl-3-methylimidazolium iodide (BMII), 0·1 M LiI, 0·05 M I_2 and 0·5 M *tert*-butyl pyridine in a 85 : 15 (v/v) mixture of acetonitrile and valeronitrile. [c]M1 = 0·6 M BMII, 0·025 M LiI, 0·04 M I_2, 0·275 M *tert*-butyl pyridine (TBP) and 0·05 M guanidinium thiocyanate in a 85 : 15 (v/v) mixture of acetronitrile and valeronitrile. [d]A1376 = A1376, 0·6 M 1-butyl-3-methylimidazolium iodide, 0·05 M iodine, 0·05 M LiI and 0·5 M *tert*-butylpyridine in a 50 : 50 (v/v) mixture acetonitrile and valeronitrile. [e]Error limits, J_{SC}, ±0·1 mA/cm^2; V_{OC}, ± 30 mV and ff, ± 0·03

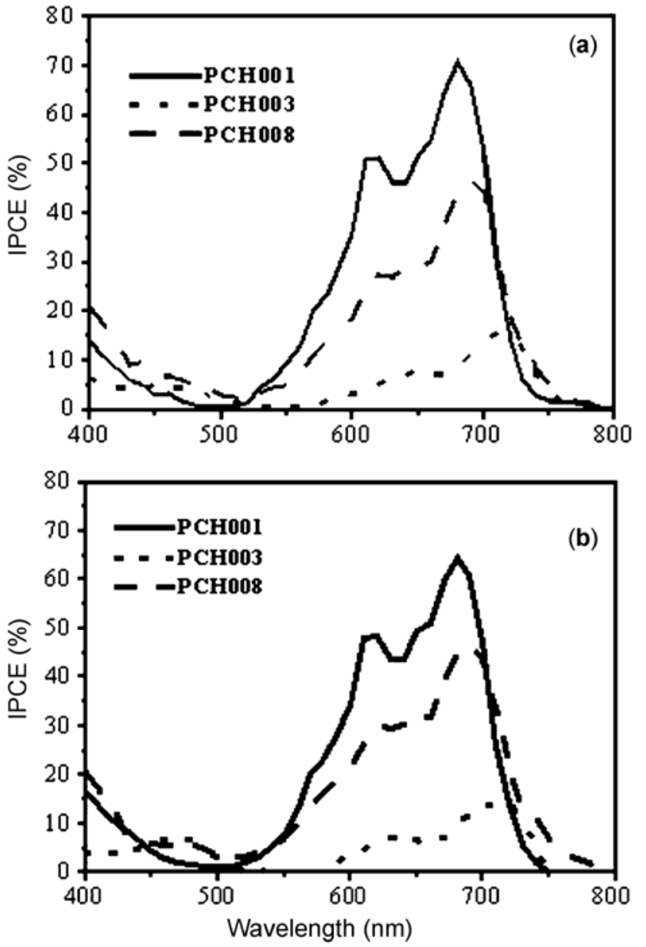


Figure 5. Photocurrent action spectra of PCH001 (——), PCH003 (·······), and PCH008 (-----) with (**a**) M1, (**b**) A7117 redox electrolytes and the cell's active area 0·2 cm^2.

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 6 shows photocurrent-voltage of PCH008 dye grafted onto nanocrystalline TiO_2 films along with PCH001 and PCH003 with two different redox electrolytes and related parameters are listed in table 2. We have observed an overall efficiency 2·35% under 1 sun irradiation with a DSSC based on PCH008 using A7117 redox electrolyte (J_{SC} = 5·63 mA cm^{-2}, V_{OC} = 0·557 V and *ff* = 0·75). Under similar test cell conditions, PCH003 has shown 0·77% efficiency.

In order to further improve the efficiency of test cell device, we have added guanidinium thiocyanate (GuSCN) to the redox electrolyte (M1) as an additive. The effect of GuSCN as additive on photovoltaic performance of the DSSC was first reported by Grätzel.[24] It was concluded that co-adsorption of GuSCN with dyes such as N719 and N3 improved the V_{OC} of the DSSC obviously due to the reduction of dark current.[25] In this study, we have also investigated the effect of addition of 0·05 M of GuSCN to the redox electrolytes and results are shown in table 2. With M1 redox electrolyte, we have observed an efficiency of 2·22% with PCH008 (J_{SC} = 5·31 mA cm^{-2}, V_{OC} = 0·562 V and *ff* = 0·74). We observed a slight increase in V_{OC} of the DSSC with the presence of GuSCN but lost J_{SC}. Thus, no increase in the efficiency of the DSSC was observed. Under similar test cell conditions, we have observed an efficiency of 2·86% with PCH001 and 0·52% with PCH003. In our phthalocyanine-based dyes, we have not observed any increase in the efficiency of test cell with co-adsorbent GuSCN unlike in the case of ruthenium polypyridyl complex and organic based dyes. The reasons for not increased in photovoltaic properties of DSSC with GuSCN for which the studies are in progress.

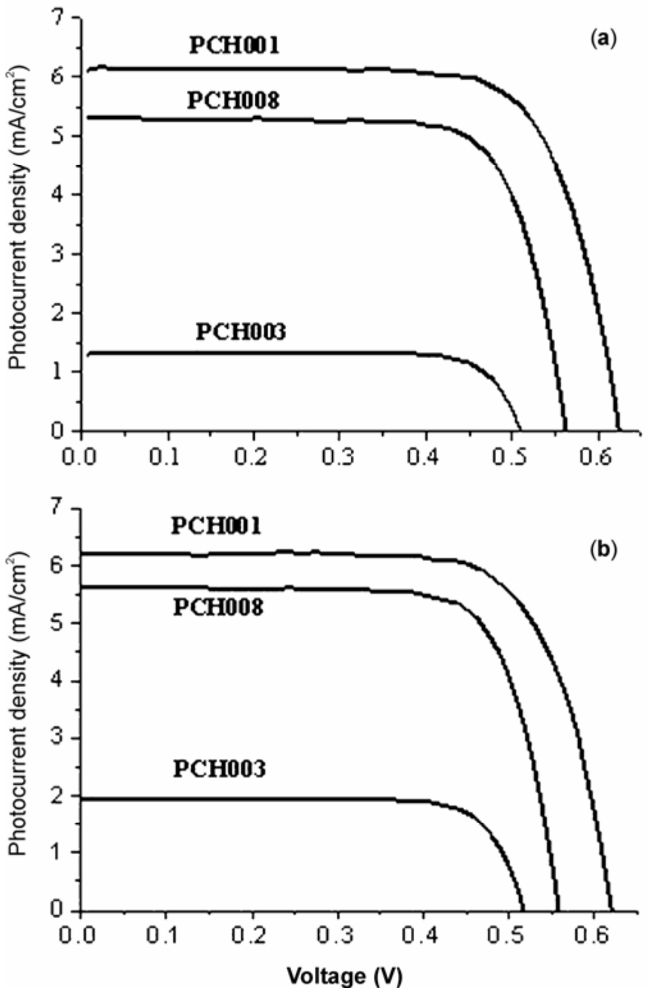


Figure 6. Current-voltage characteristics (**a**) M1, (**b**) A7117 redox electrolytes and the cell's active area 0·2 cm^2.

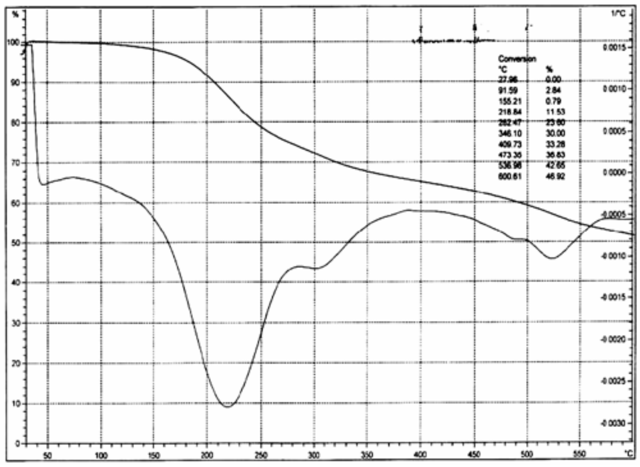


Figure 7. TG/DTG curves of PCH008 with heating rate of 10°C min^{-1} under nitrogen.

Thus the new sensitizer, PCH008 is showing improved performance in both M1 and A7117 redox electrolytes when compared to PCH003. This is probably due to the change in the energy levels of PCH008.

3.3 *Thermal stability*

In order to use for rooftop applications phthalocyanine dyes based DSSC, the dye should be stable to higher temperatures. For this reason, we have carried out the thermogravimetric analysis of PCH008 to study the stability of new sensitizer. It was well known in the literature that phthalocyanines and their metallo derivatives are stable up to 400°C.[26] From the figure 7, it is apparent that the thermal behaviour of PCH008 is stable up to 150°C. The initial weight loss (11·53%) between 150 and 225°C is attributed to the removal of carboxyl group. From the thermal data, it is clear that DSSC based phthalocyanine dyes are potentially useful for rooftop applications.

4. Conclusions

In conclusion, we have designed and synthesized an unsymmetrical zinc phthalocyanine, PCH008 based on '*push-pull*' and extended π-conjugation concept. The new photosensitizer was tested in DSSC by using M1 and A7117 redox electrolytes. The new sensitizer has shown η of 2·35% with A7117 redox electrolyte, which is second best phthalocyanine for DSSC applications. Thermal stability studies show that the sensitizer is stable up to 150°C and suitable for roof top applications.

Acknowledgements

We are thankful to IICT-Aisin Cosmos collaborative project for financial support to carry out this work. The EPFL group acknowledges financial support for this work by the Swiss Federal Office for Energy (OFEN). Ch. V is thankful to Council of Scientific and Industrial Research (CSIR) for a research fellowship.

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