



Novel Donor π -Acceptor Conjugates-Functionalized Zinc Phthalocyanines Application in Dye-Sensitized Solar Cells

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New zinc phthalocyanines [2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisethylamino)zinc phthalocyanine (SPC), 2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bispropyl-amino)zinc phthalocyanine (TPC), 2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisbutylamino)zinc phthalocyanine (FPC)], functionalized with donor- π -acceptor conjugates were synthesized. The new compounds were characterized using FTIR, UV-visible, ^1H NMR, cyclic voltammetry, differential pulse voltammetry and elemental analysis. From the reduction and oxidation behaviour, it is proved that SPC, TPC, FPC have negative LUMO levels and positive HOMO levels, satisfying the energy gap rule, they can be employed as sensitizers for dye-sensitized solar cells and their optical, electrochemical and photovoltaic properties were also studied. They exhibited broad absorption adsorbed onto a 6 μm thick TiO films. The photovoltaic devices produced short circuit current densities of 1.53, 2.07, 1.89 mA/cm^2 , the open circuit voltage of 0.48, 0.55, 0.56 V and power conversion efficiency of 1.42, 1.67, 1.64 % respectively under AM1.5G illumination.

Keywords: Dye-sensitized solar cells, Phthalocyanine, Iminodiacetic acid, Carboxy group, Unsymmetrical, Redox electrolyte.

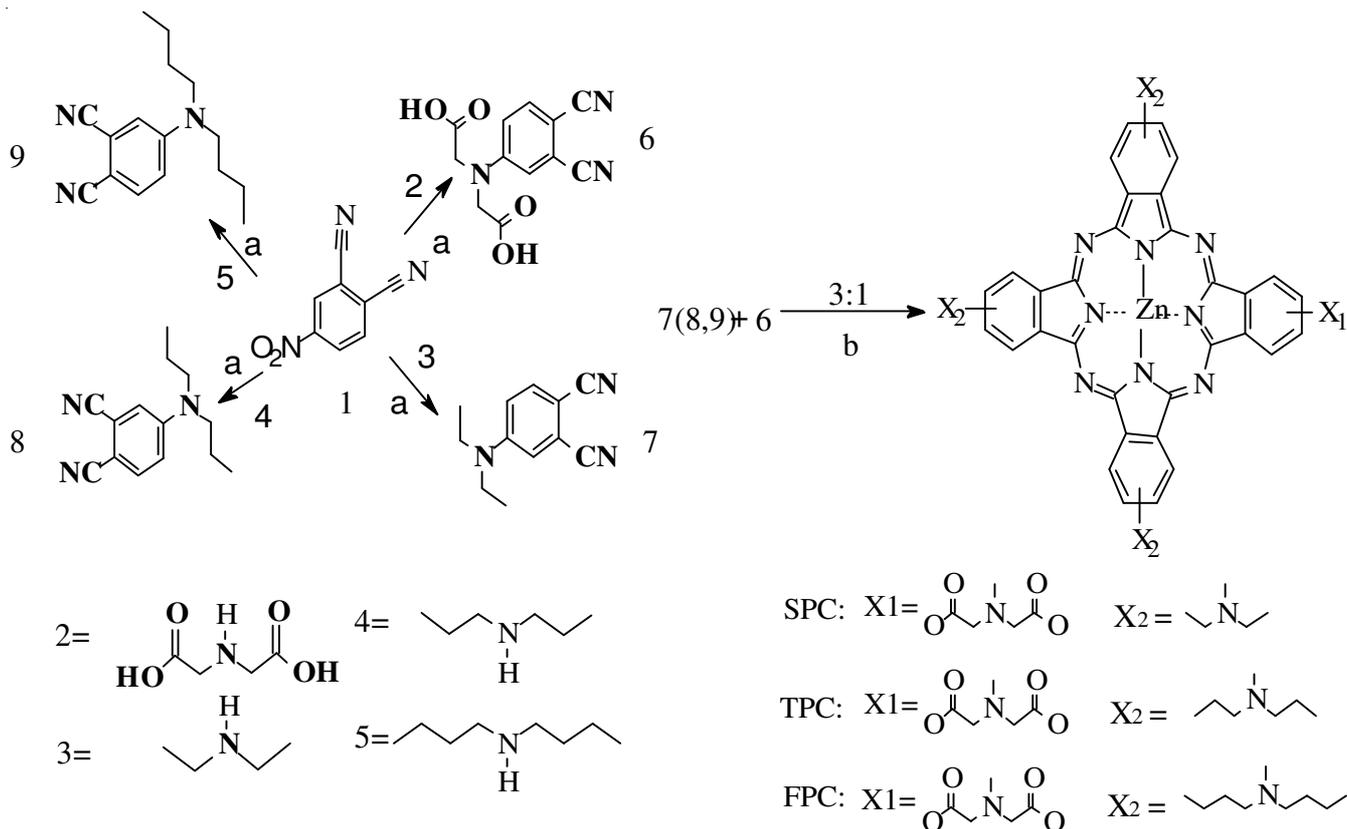
INTRODUCTION

Harvesting energy directly from sunlight using photovoltaic cells is recognized worldwide as an important solution to the growing energy crisis and environmental pollution. In the past decade, low band-gap organic molecules¹⁻⁶ and conjugated polymers⁷⁻¹¹ with internal electron donor- π -acceptor interaction have been developed and received continued interest towards highly efficient dye-sensitized solar cells (DSSCs). In dye-sensitized solar cells the light absorption function is fulfilled by the dye and the electron and hole transporting are fulfilled by the nanocrystalline metal oxide and electrolyte. Therefore the absorption properties of the dye dictate the light-harvesting capacity of the cell.

Phthalocyanines, as planar, two-dimensional aromatics, have emerged as a promising molecular component. The application of phthalocyanines into photovoltaic devices is usually performed in blends together with semiconductor polymers and/or acceptor molecules such as fullerenes *via* vapor deposition technique¹²⁻¹⁴. While, examples based on solution processed bulk heterojunction solar cells using metallophthalocyanine complexes are scarce and the corresponding power conversion efficiencies are still low compared with that of polymer solar cells. In the past, phthalocyanines have been repeatedly tested as photosensitizers for dye-sensitized solar

cells¹⁵⁻¹⁸. However, poor incident photon-to-electric current conversion yields were obtained. This may 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 recombination between injected electron in TiO₂ conduction band and oxidized dye. For this reason, one of the important aims of research on the chemistry of phthalocyanines is to enhance their solubility in common organic solvents. Also, the presence of suitable substituent is known to offer a useful way of regulating the wavelength of the Q band¹⁹⁻²¹.

A series of low band-gap donor- π -acceptor conjugates-functionalized zinc phthalocyanine: 2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisethylamino)zinc phthalocyanine (SPC), 2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bispropyl-amino)zinc phthalocyanine (TPC), 2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisbutylamino)zinc phthalocyanine (FPC) were designed and synthesized and their photovoltaic properties were studied (**Scheme-I**). The central zinc phthalocyanine has high extinction coefficient at around 700 nm, corresponding to the photo flux of solar spectrum, as well as excellent hole-transport ability. The substituents of N,N-bisethylamino, N,N-bispropylamino and N,N-bisbutylamino enhance the solubility of phthalocyanine in common organic solvents, reduce the aggregation. The presence of carboxylic



Scheme-I: (a) K_2CO_3 , DMF and (b) DBU, 1-pentanol, $Zn(CH_3COO)_2$

acid act as electron acceptors for the study of photo induced electron transfer processes as well as grafting onto nanocrystalline TiO_2 . The effects of the substituent are discussed. The solution electrochemistry of the complexes is also investigated.

EXPERIMENTAL

4-Nitro-phthalonitrile, iminodiacetic acid, N,N-diethylamine, N,N-dipropylamine, N,N-dibutylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-pentanol, anhydrous K_2CO_3 , DMF, were purchased commercially. DMF was 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 mesh).

Synthesis of 4-(N,N-bisacetic acid amino)phthalonitrile (1): 4-Nitro-phthalonitrile (0.866 g, 5 mmol) and iminodiacetic acid (0.666 g, 5 mmol) were added successively with stirring to dry DMF (10 ml). After dissolution, anhydrous K_2CO_3 (1 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 portionwise 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 dark yellow, crystalline powder. Yield: 0.78 g, 60.2 %, m.p. 140-142 °C. IR (KBr, ν_{max} , cm^{-1}): 3423 (-O-H), 3107 (H-Ar), 2241 (-C=N), 1535 (Ar C=C), 1354 (Ar-O-Ar), 1298 (C-N). 1H NMR (DMSO- d_6) δ , ppm: 7.19-8.35 (m, 3H, Ar-H), 2.53

(s, 4H, $-CH_2$). Anal. calcd. for $C_{12}H_9N_3O_4$ (259.22 g/mol): C, 55.60; H, 3.50; N, 16.21; O, 24.69 Found: C, 55.21; H, 3.92; N, 16.27.

Synthesis of 4-(N,N-bisethylamino)phthalonitrile (2): A similar synthetic and purification procedure as for **1** was followed for **2** using N,N-diethylamine instead of iminodiacetic acid and keeping reaction temperature at 60 °C. Then the brown solid **2** was obtained. Yield: 1.43 g, 71.8 %, m.p. 136-139 °C. IR (KBr, ν_{max} , cm^{-1}): 3107 (H-Ar), 2241 (-C=N), 1537 (Ar C=C), 1354 (Ar-O-Ar), 1298 (C-N). 1H NMR (DMSO- d_6) δ , ppm: 8.64-8.96 (m, 3H, Ar-H), 2.53 (q, 4H, $-CH_2$), 2.94 (t, 6H, $-CH_3$). Anal. Calc. for $C_{12}H_{13}N_3$ (199.26 g/mol): C, 72.34; H, 6.58; N, 21.09; Found: C, 72.57; H, 6.42; N, 21.18.

Synthesis of 4-(N,N-bispropylamino)phthalonitrile (3): A similar synthetic and purification procedure as for **1** was followed for **3** using N,N-dipropylamine instead of iminodiacetic acid and keeping reaction temperature at 60 °C. Then the brown solid **3** was obtained. Yield: 1.52 g, 66.9 %, m.p. 147-149 °C. IR (KBr, ν_{max} , cm^{-1}): 3088 (H-Ar), 2240 (-C=N), 1533 (Ar C=C), 1356 (Ar-O-Ar), 1298 (C-N). 1H NMR (DMSO- d_6) δ , ppm: 8.31-8.93 (m, 3H, Ar-H), 2.53 (q, 4H, $-CH_2$), 2.94 (t, 6H, $-CH_3$), 2.76 (m, 4H, $-CH_2$). Anal. calcd. for $C_{14}H_{17}N_3$ (227.31 g/mol): C, 73.98; H, 7.54; N, 18.49; Found: C, 73.62; H, 7.38; N, 18.13.

Synthesis of 4-(N,N-bisbutylamino)phthalonitrile (4): A similar synthetic and purification procedure as for **1** was followed for **4** using N,N-dibutylamine instead of iminodiacetic acid and keeping reaction temperature at 60 °C. Then the brown solid **4** was obtained. Yield: 1.93g, 75.6%, m.p. 130-133 °C. IR (KBr, ν_{max} , cm^{-1}): 3085 (H-Ar), 2240 (-C=N),

1533 (Ar C=C), 1354 (Ar-O-Ar), 1298 (C-N). ^1H NMR (DMSO- d_6) δ , ppm: 8.25-8.87 (m, 3H, Ar-H), 2.53 (q, 4H, -CH₂-), 2.94 (t, 6H, -CH₃), 2.76 (m, 4H, -CH₂-), 2.54 (m, 4H, -CH₂-). Anal. Calcd. for C₁₆H₂₁N₃ (255.36 g/mol): C, 75.26; H, 8.29; N, 16.46; Found: C, 75.02; H, 8.47; N, 16.19.

2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisethylamino)zinc phthalocyanine (SPC): 4-(N,N-bisacetic acid amino)phthalonitrile (0.13 g, 0.5 mmol), 4-(N,N-bisethylamino)phthalonitrile (0.3 g, 1.5 mmol), Zn(CH₃COO)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:CHCl₃:CH₃OH = 2:8:2 (v/v) and bluish color band was collected. The solvent was removed under reduced pressure to get the desired product. Yield: 0.25 g, 54.2 %, m.p. > 200 °C. IR (KBr, ν_{max} , cm⁻¹): 3431 (-O-H), 2922, 2853, 1720 (-C=O), 1618, 1400, 1650, 1458 (C=C), 1298 (C-N), 1340, 1122, 727. UV-Vis, in DMF (λ_{max} , log ϵ) 686 (4.37), 646 (4.05). ^1H NMR (DMSO- d_6) δ , ppm: 7.15-8.13 (m, 12H, Ar-H), 4.34 (s, 4H, -CH₂-), 2.31-2.85 (m, 30H, -CH₂CH₃). Anal. calcd. for C₄₈H₄₈N₁₂O₄Zn (922.37 g/mol): C, 62.51; H, 5.25; N, 18.22; O, 6.94; Zn, 7.09 Found: C, 62.76; H, 5.37; N, 18.14.

2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bispropylamino)zinc phthalocyanine (TPC): A similar synthetic and purification procedure as for SPC was followed for TPC using 4-(N,N-bispropylamino)phthalonitrile instead of 4-(N,N-bisethylamino)phthalonitrile acid and keeping reaction temperature at 160 °C. Then the desired product was obtained. Yield: 0.23 g, 45.7 %, m.p. > 200 °C. IR (KBr, ν_{max} , cm⁻¹): 3400 (-O-H), 2930, 2856, 1717 (-C=O), 1616, 1398, 1647, 1440 (C=C), 1200 (C-N), 1344, 1080, 721. UV-vis, in DMF (λ_{max} , log ϵ) 690 (4.52), 649 (4.16). ^1H NMR (DMSO- d_6) δ , ppm: 7.15-7.93 (m, 12H, Ar-H), 4.33 (s, 4H, -CH₂-), 2.11-2.89 (m, 42H, -CH₂CH₃). Anal. calcd. for C₅₄H₆₀N₁₂O₄Zn (1006.53 g/mol): C, 64.44; H, 6.01; N, 16.70; O, 6.36; Zn, 6.50 Found: C, 64.23; H, 6.28; N, 16.87.

2-(N,N-bisacetic acid amino)-9,16,23-(N,N-bisbutylamino)zinc phthalocyanine (FPC): A similar synthetic and purification procedure as for SPC was followed for FPC using 4-(N,N-bisbutylamino)phthalonitrile instead of 4-(N,N-bisethylamino)phthalonitrile acid and keeping reaction temperature at 160 °C. Then the desired product was obtained. Yield: 0.24 g, 44.0 %, m.p. > 200 °C. IR (KBr, ν_{max} , cm⁻¹): 3393 (-O-H), 2928, 2858, 1720 (-C=O), 1616, 1398, 1649, 1398 (C=C), 1248 (C-N), 1340, 1094, 723. UV-vis, in DMF (λ_{max} , log ϵ) 687 (4.41), 648 (4.28). ^1H NMR (DMSO- d_6) δ , ppm: 7.25-7.86 (m, 12H, Ar-H), 4.27 (s, 4H, -CH₂-), 2.24-2.81 (m, 54H, -CH₂CH₃). Anal. Calcd. for C₆₀H₇₂N₁₂O₄Zn (1090.69 g/mol): C, 66.07; H, 6.65; N, 15.41; O, 5.87; Zn, 5.99 Found: C, 66.25; H, 6.35; N, 15.53.

The UV-visible 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. ^1H NMR spectra were obtained at

400 MHz using a Varian Inova 400 MHz NMR system. The chemical shifts are relative to tetramethylsilane (TMS). Elemental analyses were performed on a Flash EA1112 Elemental Analyzer.

Cyclic and differential pulse voltammetry measurements were performed on an electrochemical workstation (CHI LK2005A, Tianjin Lanlike Chemistry Electronic High-tech Co., Ltd., P.R. China). Cyclic voltammetry experiments were performed on 1×10^{-4} mol/L phthalocyanine dye solution in DMF at scan rate 100 mV/s using tetrabutylammonium perchlorate (0.1 mol/L) as supporting electrolyte. A platinum wire was used as working electrode, the other platinum as the counter film electrode, the calomel (SCE) as the reference.

Photoelectrode preparation: TiO₂ photoelectrode (area: 0.74 cm²) was prepared by a similar method reported in the literature²²⁻²⁴. TiO₂ anatase nanoparticles of 19 nm were procured from Solaronix. Nanocrystalline TiO₂ films of 6 μm were deposited onto transparent conducting glass (the glass had been coated with a fluorine-doped stannic oxide layer (FTO); sheet resistance 8-10 Ω /square) by screen-printing technique. Nanocrystalline TiO₂ films were heated to 450 °C in an oxygen atmosphere and calcinated for 45 min. The dye was dissolved in organic solvents at a concentration of 0.5×10^{-4} M. The TiO₂ films were soaked in the dye solution and then kept at room temperature for 16 h so that the dye was adsorbed onto TiO₂ films. The photoelectrode was dipped into the dye solution while it was still hot, its temperature was 80 °C. After completion of the dye adsorption, the photoelectrode was withdrawn from the solution and washed thoroughly with either THF or ethanol to remove non-adsorbed dye under a stream of dry air or argon. A sandwich cell was prepared using the dye-sensitized electrode and platinum coated conducting glass electrode as the counter electrode. The latter was prepared by chemical deposition of platinum from 0.05 M hexachloroplatinic acid. The two electrodes were placed on top of each other using a thin polyethylene film (50 μm thick) as a spacer to form the electrolyte space. The empty cell was tightly held and edges were heated to 130 °C to seal the two electrodes together. The active surface area of the TiO₂ film electrode was 0.74 cm². The redox electrolyte was introduced into the cell through a predrilled hole of the counter electrode, which was later closed by a cover glass to avoid the leakage of the electrolyte solution. The composition of redox electrolyte is 0.05 mol/L iodine, 0.5 mol/L lithium iodide in acetonitrile.

RESULTS AND DISCUSSION

The synthesis of SPC, TPC and FPC were illustrated in **Scheme-I**. The phthalonitrile derivatives (**6-9**) were obtained through displacement reaction of 4-nitrophthalonitrile with iminodiacetic acid, N,N-diethylamine, N,N-dipropylamine, N,N-dibutylamine, respectively. SPC, TPC and FPC were prepared through 4-(N,N-bisethylamino)phthalonitrile (**7**), 4-(N,N-bispropylamino)phthalonitrile (**8**) and 4-(N,N-bisbutylamino)phthalonitrile (**9**) with 4-(N,N-bisacetic acid-amino)phthalonitrile (**6**), (molar ratio of 3:1), respectively, in 1-pentanol solution in the presence of DBU and metal salts.

Compounds SPC, TPC and FPC were characterized by ^1H NMR, UV-visible, IR and elemental analysis. For the IR spectra of SPC, TPC and FPC, it is clear that the strong imido-

groups vibration was appeared at about 1700 cm^{-1} . Further, the following UV-visible spectra reveal some special properties of SPC, TPC and FPC in terms of the impact of substituent. These characteristic results were consistent with the proposed structures (**Scheme-I**).

UV-visible and electrochemical measurements: Figs. 1-3 show absorption spectrum of SPC, TPC and FPC in DMF solution and compared to that of the phthalocyanines adsorbed onto 6 μm thick nanocrystalline TiO_2 films. The absorption spectrum in solution showed characteristic absorptions between 690 and 646 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 LUMO of the conjugated macrocycle. The other bands (Soret band) in the ultraviolet (UV) region at 343-356 nm were observed due to the transitions from the deep levels to the LUMO. The absorption spectrum of the phthalocyanines adsorbed onto 6 μm thick TiO_2 electrode exhibit obvious red shift. The interaction between the carboxylate group and the surface Ti^{4+} ions may lead to increased delocalization of the π^* orbital of the conjugated framework. The energy of the π^* level is decreased by this delocalization, which explains the red shift for the absorption

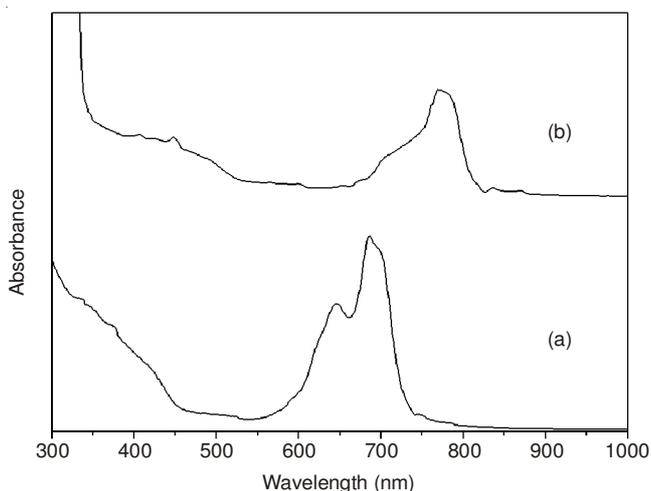


Fig. 1. UV-visible absorption spectra of SPC (a) in DMF and (b) adsorbed onto a 6 μm thick TiO_2 films

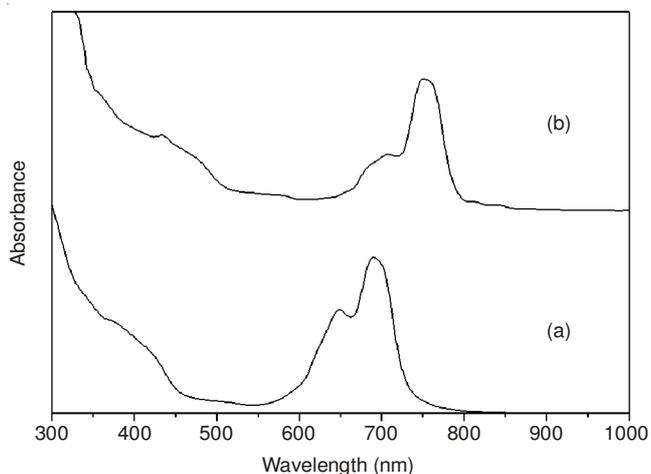


Fig. 2. UV-visible absorption spectra of TPC (a) in DMF and (b) adsorbed onto a 6 μm thick TiO_2 films

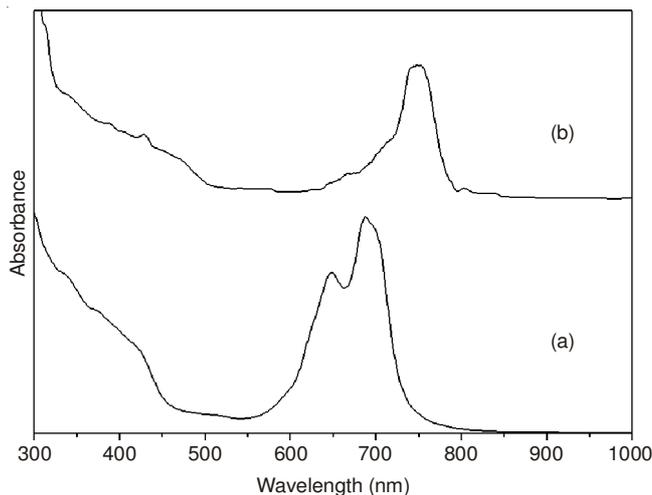


Fig. 3. UV-visible absorption spectra of FPC (a) in DMF and (b) adsorbed onto a 6 μm thick TiO_2 films.

threshold^{25,26}. SPC, TPC and FPC 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 . The E_{0-0} was calculated according to the following equation.

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

λ_{max} is the absorption maximum.

UV-visible data for SPC, TPC and FPC in DMF is shown in Table-1. E_{0-0} energy of SPC, TPC and FPC estimated from absorption maximum is 1.81, 1.80, 1.80 eV, respectively.

TABLE-1 UV-Visible DATA FOR SPC, TPC AND FPC IN DMF		
Compound	Absorption λ_{max} , nm (log ϵ , $\text{mol}^{-1} \text{cm}^{-1}$)	E_{0-0} (eV)
SPC	646 (4.05) 686 (4.37)	1.81
TPC	649 (4.16) 690 (4.52)	1.80
FPC	648 (4.28) 687 (4.41)	1.80

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^{27,28}. To get an efficient charge separation, the HOMO and LUMO levels of SPC, TPC and FPC must match with the conduction-band-edge energy level of the TiO_2 and the redox potential of electrolyte for efficient electron injection and SPC, TPC and FPC regeneration. The electrochemical behavior of SPC, TPC and FPC were investigated using cyclic and differential pulse voltammetric techniques in DMF solvent. The oxidation potentials were determined from half-wave potentials ($E_{1/2}$)($E_{\text{ox}} - E_{\text{red}}$)/2 by cyclic voltammetry or peak potentials by differential pulse voltammetry. The corresponding cyclic and differential pulse voltammograms were presented in Figs. 4-6. The first oxidation potentials ($E_{1/2(\text{ox})}$) correspond to the HOMO level of phthalocyanines. The SPC, TPC and FPC exhibit quasi-reversible oxidation at 0.85, 0.9,

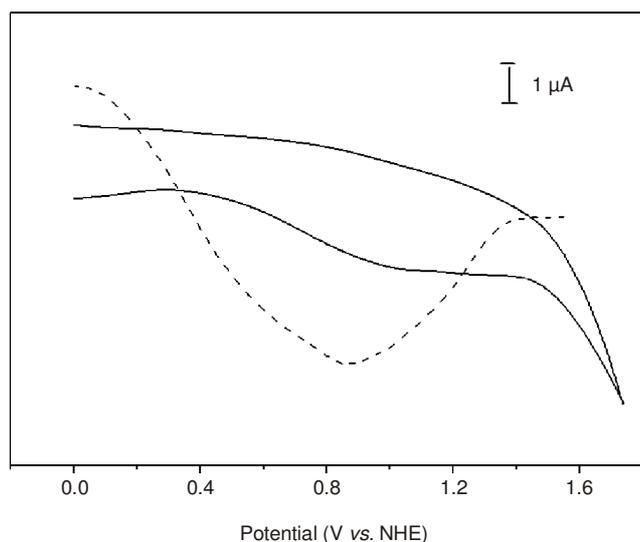


Fig. 4. Cyclic (—) and differential pulse voltammograms (---) of SPC in DMF

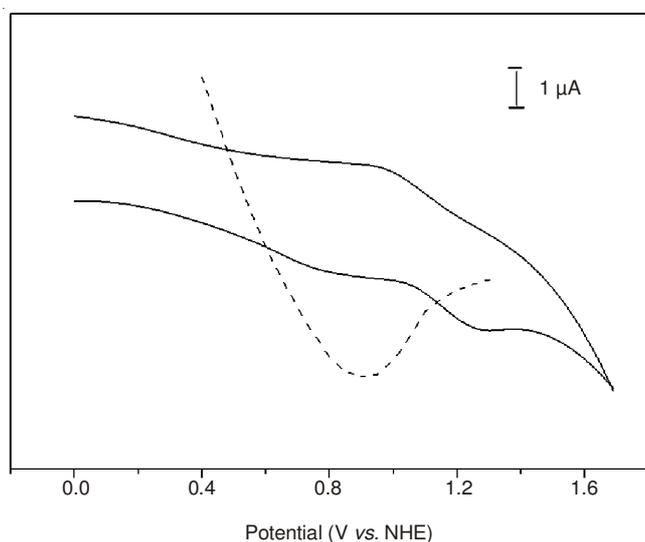


Fig. 5. Cyclic (—) and differential pulse voltammograms (---) of TPC in DMF

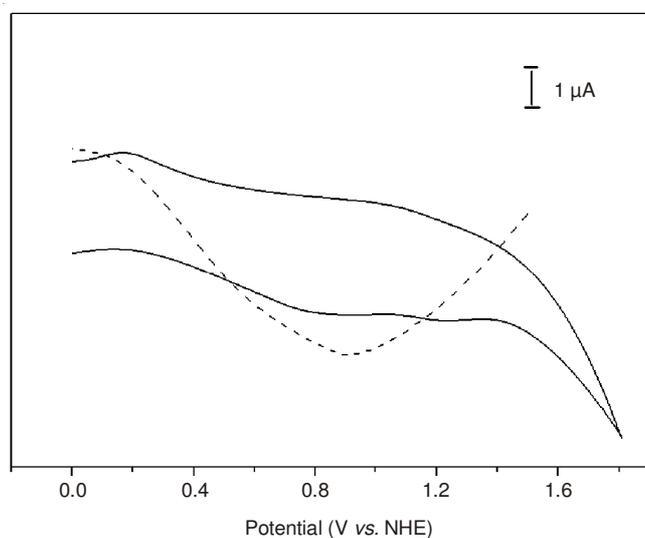


Fig. 6. Cyclic (—) and differential pulse voltammograms (---) of FPC in DMF

0.9 V respectively. With respect to dye-sensitization of wide-band gap semiconductors, *e.g.* TiO₂, the first oxidation potentials of SPC, TPC and FPC and the E₀₋₀ transition energy, the energy levels of the LUMO were deduced to be -0.96 V vs. SCE, -0.9 V vs. SCE and -0.9 V vs. SCE, respectively. The LUMO is calculated according to the following equation.

$$\text{LUMO} = \text{HOME} - E_{0-0} \quad (2)$$

The energy level of the conduction band edge of TiO₂ is -0.74 V vs. SCE²⁹. This makes electron injection from the excited state of SPC, TPC and FPC into the conduction band of TiO₂ thermodynamically feasible. The HOMO levels of SPC, TPC and FPC are more positive than the energy level of the redox couple I⁻/I₃⁻ (0.2 V vs. SCE) in the electrolyte, indicating more efficient phthalocyanines regeneration by electron transfer from I⁻. Fig. 7 shows the schematic energy diagram of SPC, TPC and FPC dye-sensitized TiO₂ electrodes. SPC, TPC and FPC have negative LUMO levels and positive HOMO levels, satisfying the energy gap rule. This means that, the SPC, TPC and FPC can be employed as sensitizers for dye-sensitized solar cells applications³⁰. SPC has stronger electron injection than TPC and FPC. Data of electrochemistry for SPC, TPC and FPC in DMF are shown in Table-2.

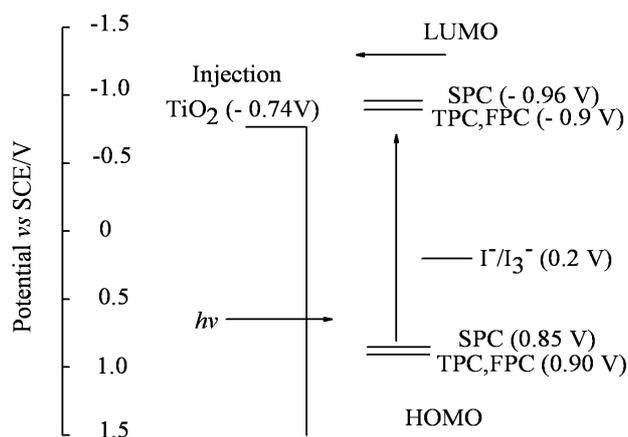


Fig. 7. Energy level diagram for SPC, TPC and FPC

TABLE-2
DATA OF ELECTROCHEMISTRY FOR SPC, TPC
AND FPC IN DMF

Compound	E _{1/2(ox)} (V)	E* (V vs SCE)
SPC	0.85	-0.96
TPC	0.9	-0.9
FPC	0.9	-0.9

Photovoltaic characterization: The solar energy-to-electricity conversion efficiency, η , under white light irradiation can be obtained from the following equation.

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

where I_0 is the photon flux (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.

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

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. Photovoltaic characterization data for SPC, TPC and FPC grafted onto nanocrystalline TiO_2 films is shown in Table-3. We have observed an overall efficiency 1.42, 1.67, 1.64 % under 1 sun irradiation.

TABLE-3
DATA OF PHOTOVOLTAIC CHARACTERIZATION
FOR SPC, TPC AND FPC

DSSC	J_{SC} (mA cm ⁻²)	V_{OC} (V)	ff	η (%)
SPC	1.53	0.48	0.57	1.42
TPC	2.07	0.55	0.59	1.67
FPC	1.89	0.56	0.60	1.64

The low overall conversion efficiency of SPC, TPC and FPC 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 ³¹⁻³³.

Conclusion

The new unsymmetrical zinc phthalocyanines, SPC, TPC and FPC based on 'push-pull' or donor- π -acceptor conjugates concept, were successfully prepared and characterized. The presence of carboxylic acid acted as electron acceptors ('pull') and server to graft onto nanocrystalline TiO_2 . The surface aggregation of SPC, TPC and FPC adsorbed onto TiO_2 was not significantly avoided. The new photosensitizers were tested in dye-sensitized solar cells by using I/I_3^- redox electrolyte, the dye-sensitized solar cells had been fabricated.

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