Synthesis and Characterization of Peripherally Ferrocene-modified Zinc Phthalocyanine for Dye-sensitized Solar Cell

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Synthesis and structural characterization of peripherally ferrocene-substituted zinc phthalocyanine (*ZnPc-Fc*) were carried out for efficient far-red/near-IR performance in dye-sensitized nanostructured TiO_2 solar cells. Incorporating ferrocene into phthalocyanine strongly improved the dye solubility in polar organic solvents, and reduced surface aggregation due to the steric effect of bulky ferrocene substituents. The involvement of electron transfer reaction pathways between ferrocene and phthalocyanine in *ZnPc-Fc* was evidenced by completely quenched fluorescence from S1 state (< 0.08% *vs ZnPc*). Strong absorption bands at 542 and 682 nm were observed in the transient absorption spectroscopy of *ZnPc-Fc* in DMSO, which was excited at a 670 nm laser pulse with a 15 ps full width at half maximum. Also, the excited state absorption signals at 450 - 600 and 750 - 850 nm appeared from the formation of charge separated state of phthalocyanine's anion. The lifetime of the charge separate state in *ZnPc-Fc* was determined to be 170 ± 8 ps, which was almost 17 times shorter than that of the *ZnPc*.

Key Words : NIR dye, Ferrocene-modified zinc phthalocyanine, Dye-sensitized solar cell

Introduction

In recent years, dye-sensitized solar cells (DSC) are attracting widespread academic and commercial attention for the conversion of sunlight into electricity because of their low cost and high efficiency.[1] The DSC is a photovoltaic device composed of a photoanode based on mesoporous TiO_2 film covered by monolayer of dye sensitizers, electrolyte (typically I^-/I^{3-}), and Pt counter electrode. Dye sensitizers, which absorb photons and convert them to electric charges, are one of the key components in the photovoltaic cells for high power conversion efficiencies. The most successful charge-transfer sensitizers employed in these cells are polypyridylruthenium complexes, which yield solar-to-electric power conversion efficiencies of 10 - 11% with simulated sunlight.[2] However, the main drawback of the polypyridylruthenium complexes is their lack of absorption in the red region of the visible solar spectrum. A good candidate dye for enhancing the response in the above mentioned spectrum region is phthalocyanines (Pc) which possess not only intensive absorption in the far-red/near-IR region, but also excellent chemical, light, and thermal stability.[3] More importantly, the phthalocyanine dyes also have the appropriate redox properties for sensitization of large band-gap semiconductors, e.g., TiO_2, making them attractive for DSC applications.[4,5] Many groups have tested Pc as sensitizers for DSC, however, resulting in low power conversion efficiencies. The low efficiency of cells using Pc is mainly ascribed to the aggregation of dye on the TiO_2 surface, lack of directionality in the excited state, and easy electron recombination between injected electron in TiO_2 conduction band and oxidized dye.[6,7] One approach to overcome the electron recombination problem suggested by Sundström,[6] was the modification of Pc with an redox-active substituent, which could contribute to blocking back-electron transfer from the TiO_2 conduction band to the oxidized sensitizer. However, in the case of a modified zinc phthalocyanine with tyrosine

substituent, the electron transfer from tyrosine to the oxidized phthalocyanine was found to be not a possible route to block back-electron transfer from the TiO_2 conduction band to the oxidized sensitizer due to the thermodynamic impossibility, originating from the more positive oxidation potential of tyrosine than that of the macrocycle.[6]

Therefore, we designed and synthesized peripherally ferrocene-substituted zinc phthalocyanine (*ZnPc-Fc*, see molecular structure in Scheme 1) as far-red/near-IR sensitizer for DSC, with referencing the literature value for the oxidation potential of the ferrocene that was slightly lower than that of the *ZnPc* macrocycle.[7,8] A potential function of incorporating the redox-active ferrocene groups into phthalocyanine is to transfer an electron from ferrocene to the oxidized *ZnPc*, thereby preventing back-electron transfer. The oxidation potential of *ZnPc-Fc* was determined by differential pulse voltammetry. Intramole-
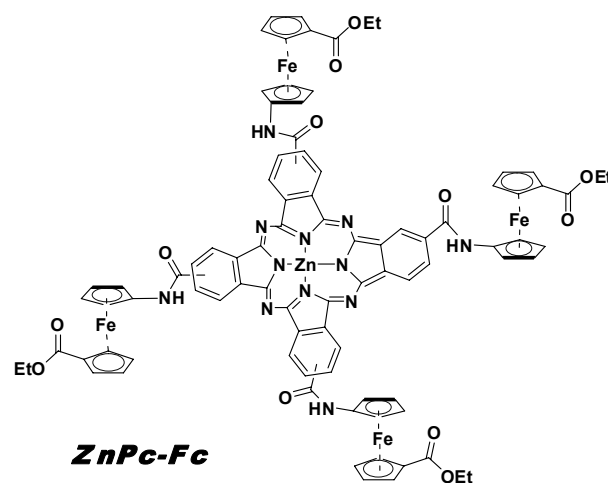
Scheme 1. Molecular structure of *ZnPc-Fc*.

cular electron transfer dynamics of *ZnPc-Fc* diluted in DMSO solution were investigated using femto-second time resolved transient absorption spectroscopy. The performance of a sandwich solar cell based on *ZnPc-Fc*-coated nanostructured TiO$_2$ electrodes was compared with those based on N719-TiO$_2$ electrodes.

Result and Discussion

Synthesis. The designed zinc(II)-tetra-(x'-ethyl ester-ferrocenyl)-phthalocyane (*ZnPc-Fc*) was synthesized from condensation of 4-carboxy(*N*-(x'-ethyl ester-ferrocene))phthalonitrile (**8**) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and Zn(OAc)$_2$ (40% yield based on phthalonitrile) based on modified Sundström's preparation method,[6] as outlined in Scheme 2.

The structure of *ZnPc-Fc* was identified by the combination of NMR and MALDI-TOF mass spectrometry. All the peaks of *ZnPc-Fc* could be precisely assigned in the ^{1}H *NMR* spectrum (Figure 1a) despite being muliplets and/or broad after the macrocyclization, due to the existence of statistical isomers and possible aggregation. In addition, the MALDI-TOF mass spectrum of purified *ZnPc-Fc* (Figure 1b) revealed a peak for the molecular ion at *m/z* = 1773.45 [M+H]$^+$, which correctly represents its formular molecular weight.

In general, zinc phthalocyanine (*ZnPc*) is known to show poor solubility in organic solvents, and strong tendency to aggregate due to its planar conjugated structure. However, *ZnPc-Fc* was moderately dispersed in polar solvents such as DMSO, DMF, benzonitril, THF *etc.*, resulting in optically clear solution.

Figure 2 shows absorption spectra of *ZnPc-Fc* in solution and on TiO$_2$ nanoparticle film. First, absorption spectra of *ZnPc-Fc* (5 µM) are compared for the solvents with different polarities (Figure 2a). The absorbance of *ZnPc-Fc* in a polar solvent, i.e. benzonitrile and DMSO showed clearly resolved band structure in the Soret (352 nm) and the Q-band region (688 nm), indicating that the dyes are mainly dispersed in a monomeric state. However, a new absorption band (not clearly defined) near 645 nm appeared in a less polar solvent THF, and it became clearly distinctive in CHCl$_3$. The blue-shifted peak can be assigned to the characteristic Q-band of the face-to-face *ZnPc-Fc* dimer or higher order aggregate (H-aggregate).[9,10] The aggregation of the phthalocyanine molecules shows up in the shape, and the location of the so-called Q-band, originating from the π-π* transitions. Aggregation is more important in solvents with a lower dielectric constant, in which the screening of the Pc-Pc interaction is minimized.[11]

The carboxylate group of *ZnPc-Fc* dyes was linked to the TiO$_2$ nanoparticels pretreated with a Lewis base ((CH$_3$)$_3$-COLi).[12] Dye adsorption onto TiO$_2$ electrode was carried out from benzonitrile solution in order to minimize the aggregate formation which tends to highly decrease the performance of device. The spectrum of the *ZnPc-Fc* adsorbed onto TiO$_2$ electrode (Figure 2b) shows distinctive appearance of the aggregate Q-band at 648 nm with the monomer Q-band at 695 nm that was found to be red-shifted by 7 nm in comparison with that of the dye in benzonitrile solution, revealing a strong interaction between the dye and the semiconductor surface.[4] The extend of the dye aggregation was estimated based on the ratio of the dye absorbances at the aggregate (A_a) and monomer (A_m) maxima. The ratio (A_a/A_m) of the *ZnPc-Fc*/TiO$_2$ film was cal-
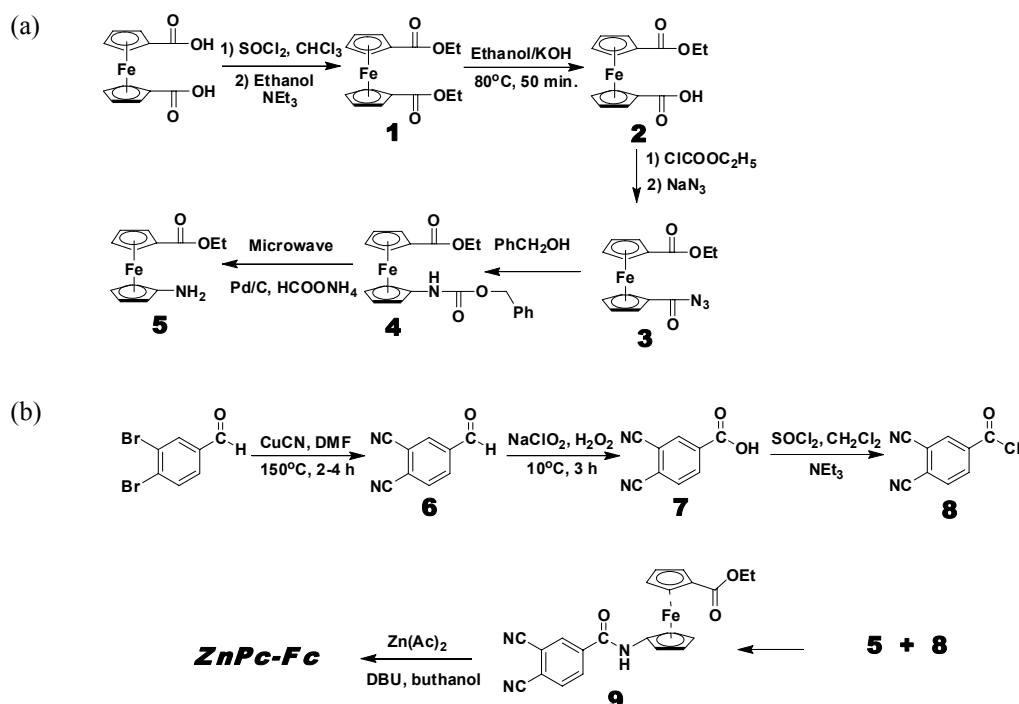
Scheme 2. Detailed synthetic route to ethyl 1'-aminoferrocene-1-carboxylate (a) and *ZnPc-Fc* dye (b).
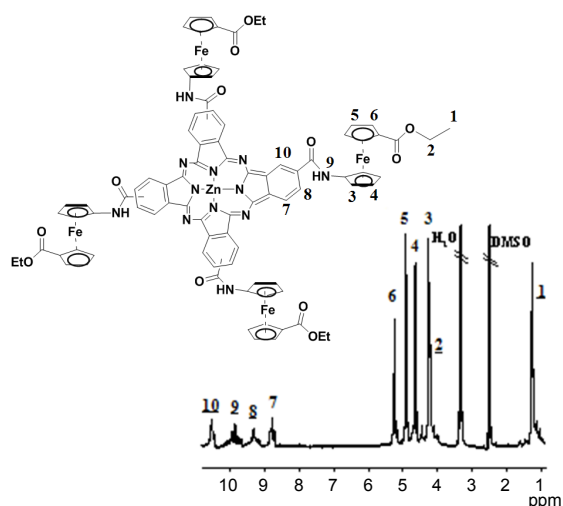
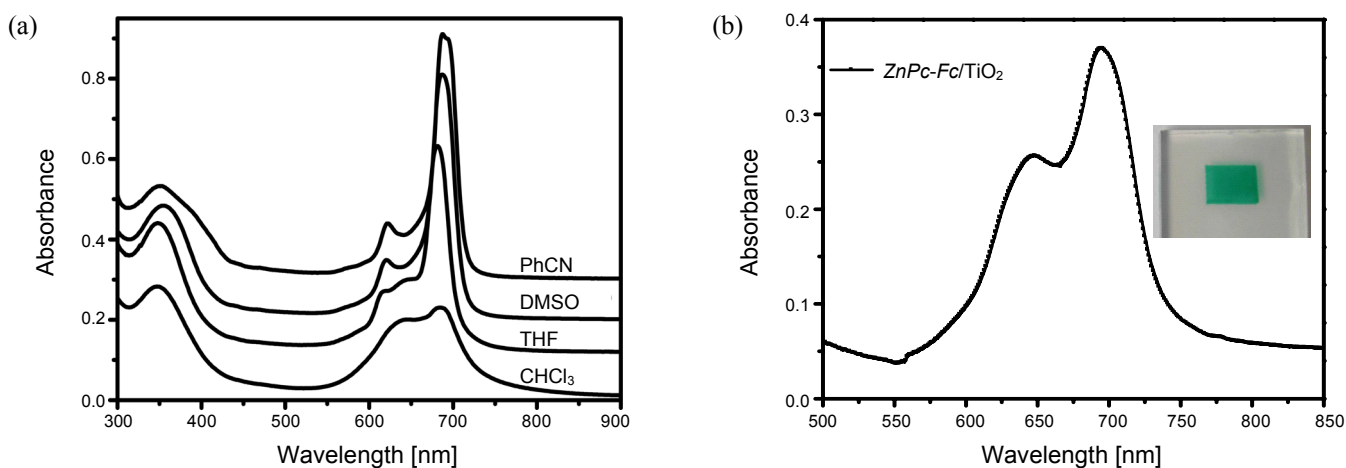**Figure 1.** ^{1}H NMR and MALDI-TOF Mass spectra of *ZnPc-Fc*.

Figure 2. Absorption spectra of *ZnPc-Fc* in different solvents (a) and on the TiO$_2$ surface (b). The picture in inlet is image of *ZnPc-Fc*- TiO$_2$ film.

culated to 0.65, which is relatively low in comparison with the values of the glycine- and tyrocine-substituted zinc phthalocyanine dyes reported earlier, i.e., *ZnPcGly*-TiO$_2$ (A_a/A_m = 1.01) and *ZnPcTyr*-TiO$_2$ (A_a/A_m = 0.80),[6] indicating that the aggregate formation was to some extend avoided due to steric effect of the bulky ferrocene groups in *ZnPc-Fc*. Note that the *ZnPc-Fc*-TiO$_2$ film colored green after multiple washing steps with organic solvent (inlet picture in Figure 2b).

Differential pulse voltametry. *ZnPc-Fc* is dispersed in dried benzonitrile to a concentration of 0.5 mM. The oxidation potential was determined from peak potentials (Ep) by differential pulse voltammetry (DPV). The DPV were recorded at an ITO electrode with respect to Ag/AgCl reference electrode in the benzonitrile solvent containing 0.1 M of tetrabutylammonium perchlorate, as shown in Figure 3. The oxidation potentials are 0.52 V *vs* Ag/AgCl (0.48 V *vs* SCE) and 0.88 V vs Ag/AgCl (0.84 V *vs* SCE), respectively. The peak I at 0.52 V *vs* Ag/AgCl is assigned to oxidations of ferrocene and macrocycle of *ZnPc-Fc* on the basis of a reported oxidation potential of 0.5 V *vs* Ag/AgCl for ferrocene derivatives in acetonitrile[8] and 0.47 ~ 0.55 V *vs* Ag/AgCl for zinc phthalocyanine derivatives.[13,14] The peak II (0.88 V *vs* Ag/AgCl) can be assigned to one-electron process
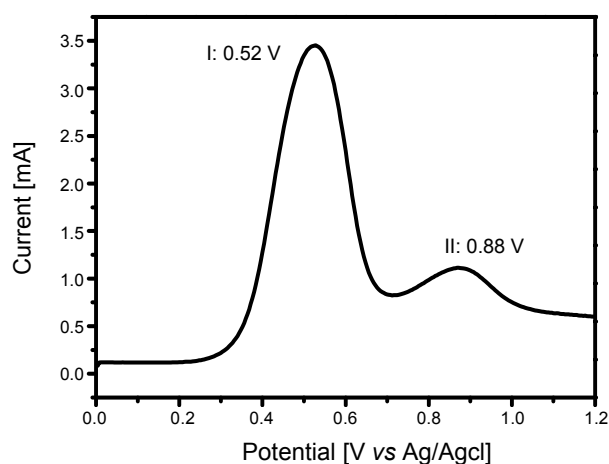

Figure 3. Differential pulse voltammogram of *ZnPc-Fc* in benzonitrile.

for the second oxidation of *ZnPc-Fc* generating the dication on the basis of a reported oxidation potential of 0.74 V *vs* Ag/AgCl for the macrocycle of tyrocine-modified *ZnPc* in acetonitrile/DMSO (7/1)[6] with taking it into consideration that
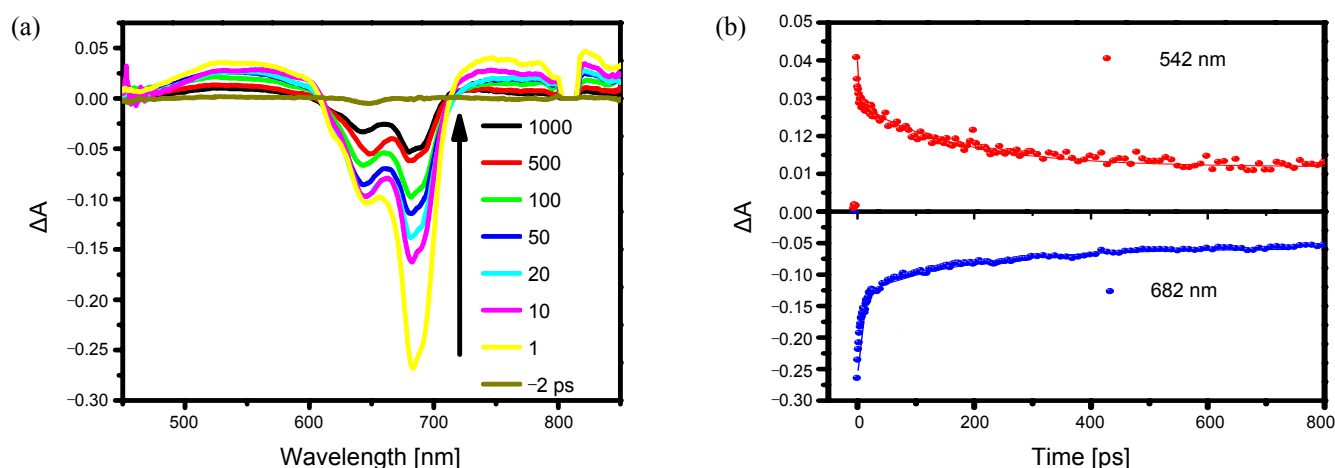
(a)

(b)

Figure 4. (a) Transient absorption spectra of *ZnPc-Fc* in DMSO solution by excitation at 650 nm. (b) Decay profile probed at 542 and 682 nm.
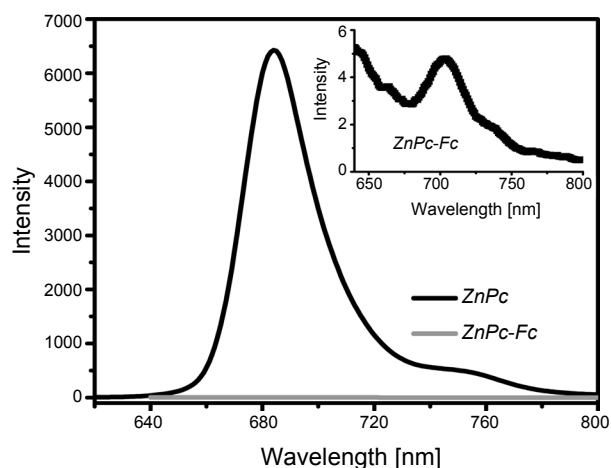

Figure 5. Fluorescence spectra of *ZnPc* and *ZnPc-Fc* in benzonitrile.
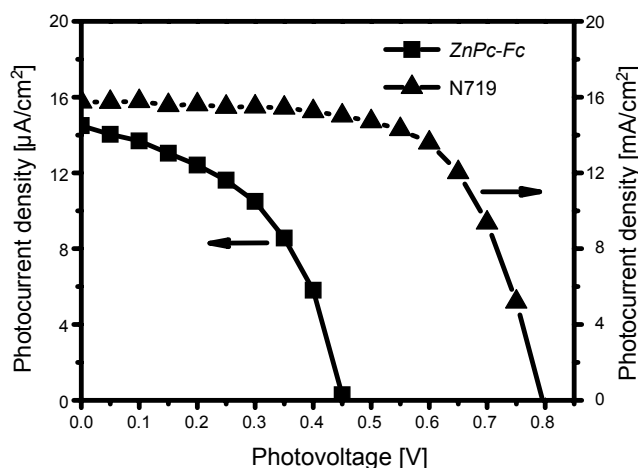

Figure 6. Photocurrent action spectrum of *ZnPc-Fc* sensitized solar cells using liquid iodide electrolytes including 0.6 M 1-butyl-3-methy-limidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate and 0.28 M *tert*-butylpyridine in a 15:85 (v/v) mixture of valeronitrile and acetonitrile.

the oxidation potential shifts in more positive direction owing to the electrowithdrawing effect of the ferrocene group.[14] The assignment was also supported by relative DPV peak heights and areas, indicating that oxidation I seems to involve more electrons than that of oxidation II.

Transient absorption changes. To directly probe the electron transfer reactions, transient absorption spectroscopy was applied to *ZnPc-Fc* in DMSO. *ZnPc-Fc* in DMSO was found to exist predominantly in the monomeric form (Also see Figure 2a). Figure 4a shows the transient absorption spectra of *ZnPc-Fc* that was excited at a 670 nm laser pulse with a 15 ps full width at half maximum (fwhm). Electron transfer was detected to be faster than the instrumental response function (<300 fs). The spectra of *ZnPc-Fc* are characterized by a strong absorption band at 542 and 682 nm. Note that the excited state absorption signals at 450 - 600 and 750 - 850 nm appeared from the formation of charge separated (CS) state of phthalocyanine's anion.[15,16] The transient signal probed at 542 nm (Figure 4b) features a quick rise, limited to the laser pulse (<300 fs) and a double exponential decay. The fast decay ($\tau_1 < 1$ ps) at 542 nm was due to the decreasing S_1 state or vibrational relaxation process.[16] The lifetime of the charge separate state was determined to be 170 ± 8 ps (τ_2).

The bleach recovery signals at 682 nm ($\tau_1 < 2.5$ ps, $\tau_2 = 177 \pm 10$ ps) were also found in a similar time scale of the excited state absorption. The observed fast excited-state decay (<170 ps) hasn't been clearly understood yet, and is now under further investigation.

The fluorescence spectra of *ZnPc-Fc* (5 μM) and *ZnPc* (5 μM) in benzonitrile were collected using excitation light ($\lambda_{ex} = 600$ nm), and shown in Figure 5. The fluorescence of the *ZnPc-Fc* was found to be completely quenched (<0.08%). The result of fluorescence quenching suggests the involvement of electron transfer reaction pathways from the S1 state. The observation is in a good agreement with that from a porphyrin-ferrocene dyad.[16]

Photovoltaic studies. Figure 6 shows the photocurrent-photovoltage characteristics of sandwich solar cells based on the dye-sensitized TiO$_2$ electrodes illuminated by a sun simulator in comparison with those of N719 dye-sensitized reference cell. The short-circuit photocurrent (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall conversion efficiency (η) for each

Table 1. Detailed photovoltaic parameters of cells made with *ZnPc-Fc* and N719 dye

Dye	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η/%
N719	15.75	0.80	0.65	8.14
ZnPc-Fc	14×10^{-3}	0.45	0.48	0.003

system are also summarized in Table 1. A low overall photon conversion efficiency (η = 0.003%) was obtained from the *ZnPc-Fc*-sensitized solar cell compared to the N719 dye-sensitized system (η = 8.14%) under 1 sun condition. The low overall conversion efficiency of the *ZnPc-Fc*-sensitized solar cell was mainly ascribed to extremely low photocurrent.

Conclusions and Perspectives

The synthesis of a modified zinc phthalocyanine dye with ferrocene (*ZnPc-Fc*) was described. It was found that *ZnPc-Fc* was good soluble in polar organic solvents, such as benzonitrile, DMSO, DMF, and mainly dispersed in a monomeric state. The improvement of the solubility in organic solvents compared to other *ZnPc* derivatives reported earlier[17] could be ascribed to the steric effect of the bulky ferrocene substituents. However, the surface aggregation of *ZnPc-Fc* dyes adsorbed on TiO$_2$ was not significantly avoided.

As mentioned in the Introduction, incorporating the redox-active ferrocene groups into phthalocyanine has the potential function of blocking back-electron transfer from the conduction band of TiO$_2$ to the oxidized sensitizer by electron transfer from ferrocene to the oxidized *ZnPc*. Due to the oxidation potentials of *ZnPc-Fc* determined in our experiment and the literature values,[7,8] the first oxidation peak of ferrocene is located slightly lower than that of the macrocycle. This would satisfy the thermodynamic condition for electron transfer from ferrocene to oxidized *ZnPc* macrocycle. The existence of the electron transfer pathways between *ZnPc* and ferrocene was confirmed from the completely quenched fluorescence of the *ZnPc-Fc* (<0.08% *vs ZnPc*), which was mainly dispersed mono-molecularly in benzonitrile. However, *ZnPc-Fc*-sensitized solar cells exhibited low overall photon conversion efficiency, which was mainly resulted from ignorable photocurrent. An important reason for poor performance of these solar cells would be counted to the short lifetime of the charge separate state (τ_2 = 170 ± 8 *ps*) besides the strong aggregate formation of dyes on the TiO$_2$ nanoparticles surface, which leads to a considerable decrease in solar cell performance due to quenching processes from energy transfer[18] or charge-transfer reactions[19] between aggregated molecules and/or between molecules in the aggregates and monomers. Optimization of the above designed sensitizer is currently in progress with other redox-active substituents that are asymmetrically incorporated into phthalocyanine macrocycle. We believe that the work would contribute to the new design of the efficient sensitizers for the dye-sensitized solar cell.

Experimental Section

Materials. Solvents were distilled before use. Transparent TiO$_2$, light scattering TiO$_2$, and Pt catalyst pastes were purchased from Solaronix (Switzerland). Fluorine doped SnO$_2$ glass (TEC-15, 15 Ω/sq) were obtained from JJ TRADING Co. Synthetic route to *ZnPc-Fc* was outlined in Scheme 1.

Synthesis of 1,1'-diethyl ferrocenedicarboxylate (1). A mixture of thionyl chloride (7.0 mL) and triethylamine (17.1 mL) in 10 mL dichloromethane was drop-wise added to a solution of 1,1'-ferrocene-dicarboxylic acid (9 g, 32.8 mmol) in 35 mL of freshly dried dichloromethane at 0 °C. The solution was first stirred for 2 hrs at 0 °C, and then for 6 hrs at rt, respectively. After the completion of the reaction, solvent was evaporated. The product was extracted with ether for 5 times. Subsequently, the ether was evaporated under vacuum at a low temperature to give 1,1'-ferrocenedicarbonyl chloride. A solution of triethylamine in dry ethanol (14 mL) was added to the acid chloride solution in 30 mL of dry ethanol. The reaction mixture was refluxed for 12 hrs. The product was extracted with ether after the evaporation of the solvent, and then separated by column chromatography (silica gel, dichloromethane/hexane 7/1) as reddish brown oil. Yield: 2g (20.1%). ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3 H, CH$_3$), 4.27 (q, 2 H , CH$_2$), 4.40 (d, 4 H, H-3 H-4 H-3' H-4', Fc), 4.81 (d, 4 H, H-2 H-4 H-2' H-4', Fc). FT-IR (KBr pellet): (cm^{-1}) = 2854, 2929 (CH$_2$), 1706 (C=O ester), 1240 (C-O ester).

Synthesis of 1-ethoxycarbonylferrocene-1'-carboxylic acid (2). A solution of NaOH (0.43 g, 10.7 mmol) in 1.2 mL water was added into 1,1'-diethyl ferrocene-dicarboxylate (1) (3.5 g, 10.7 mmol) in 36 mL ethanol. The reaction mixture was heated at 80 °C for 50 min and extracted with CH$_2$Cl$_2$. The product (2) and the unreacted diester (1) were found in alkali water, and organic layer, respectively. The product (2) was precipitated during acidification of the alkali water layer with concentrated HCl. Yield: 1.5 g (46.7%). ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3 H, CH$_3$), 4.32 (q, 2 H, CH$_2$), 4.47 (d, 4 H, H-3 H-4 H-3' H-4', Fc), 4.87 (m, 4 H, H-2 H-5 H-2' H-5', Fc). IR (KBr pellet): (cm^{-1}) = 2600 ~ 3300 (OH acid), 2854, 2929 (CH$_2$), 1713 (C=O ester), 1670 (C=O acid), 1240 (C-O ester).

Synthesis of ethyl 1'-azidocarbonylferrocene-1-carboxylate (3). 1'-Ethoxycarbonyl-ferrocene-1-carboxylic acid (2) (3 g, 9.93 mmol) was suspended in 2.4 mL water, adding acetone until the solution turned clear. After cooling to 0 °C, triethylamine (1.8 mL, 12 mmol) in 15 mL acetone was added into 2 solution, and then ethyl chloroformate (1.19 mL, 12.5 mmol) in 2.4 mL acetone. The reaction mixture was stirred for 30 min. After that, sodium azide (969 mg, 14.9 mmol) in 3 mL water was added. The mixture was stirred for 1 hour at 0 °C, and poured into excess of ice water. The product was extracted with dichloromethane. The extract was washed with a 5% aqueous solution of sodium bicarbonate and saturated solution of sodium chloride, and dried over sodium sulfate. The solvent was evaporated in vacuum at r.t to dryness to leave red crystals. Yield: 2.43 g (84%). ^{1}H NMR spectrum (CDCl$_3$) δ 1.37 (t, 3 H, CH$_3$), 4.31 (q, 2 H, CH$_2$), 4.44 (m, 2H, H-3, H-4, Fc), 4.50 (m, 2H, H-3', H-4', Fc) 4.83 (d, 2 H, H-2, H-5, Fc), 4.87 (d, H-2', H-5', Fc). IR (KBr pellet): (cm^{-1}) = 2136 (N$_3$), 1712 (C=O ester), 1687 (C=O azide).

Synthesis of 1-ethylcarbonyl-1'-ferrocenecarbamate (4). A solution of 3 (2.43 g, 7.43 mmol) in 40 mL benzyl alcohol was heated in an oil-bath at 100 °C for 30 min. The alcohol was removed in vacuum, and the residual dark oil was purified by

column chromatography using dichloromethane as eluent, giving orange crystals. Yield: 2.14 g (70.7%). ^{1}H NMR spectrum (CDCl$_3$) δ 1.29 (t, 3H, CH$_3$), 4.23 (q, 2H, CH$_2$), 4.01 (m, 2H, H-3', H-4', Fc), 4.36 (m, 2H, H-3, H-4, Fc) 4.49 (d, 2H, H-2', H-5', Fc), 4.78 (d, H-2, H-5, Fc), 5.15 (2H, benzyl), 6.00 (s, 1H, NH) 7.37 (5H, Ph). IR (KBr pellet): (cm^{-1}) = 3426 (N-H), 1731 (C=O COOCH$_2$CH$_3$), 1708 (C=O COOCH$_2$Ph).

Synthesis of ethyl 1'-aminoferrocene-1-carboxyate (5). 200 mg (0.49 mmol) 1-ethylcarbonyl-1'-ferrocenecarbamate (**4**) was dissolved in an Erlenmeyer flask with 15 mL isopropanol. 123.5 mg (1.96 mmol, 8 equiv) HCOONH$_4$ and 100 mg Pd/C 10% (5% in weight with respect to the substrate) were added into the solution of **4**. The flask was irradiated for 1 min at 600 W (unmodified domestic microwave oven), and followed by at least 1 min of rest in an ice bath. The two procedures were repeated 4 times. After the reaction, the product was isolated by the filtration, and dried in vacuum at r.t. Yield: 141 mg, (95%). ^{1}H NMR (Acetone-d_6) δ 1.30 (t, 3 H, CH$_3$), 3.29 (s, 2H, NH$_2$) 4.23 (q, 2 H, CH$_2$), 3.79 (d, 2 H, H-2', H-5', Fc), 3.92(m, 2H, H-3', H-4', Fc), 4.31 (m, 2 H, H-3, H-4, Fc), 4.65 (2H, H-2, H-5, Fc). FT-IR (KBr pellet) (cm^{-1}) = 2854, 2929 (CH$_2$ ester), 1693 (C=O ester), 3310, 3400 (NH$_2$).

Synthesis of 3,4-dicyanobenzaldehyde (6). A mixture of 4.3 g (16.2 mmol) 3,4-dibromobenzaldehyde and copper cyanide (8.70 g, 97.2 mmol) in 70 mL of dry dimethyl formamide was stirred for 4 h at 150 ^{o}C until the completion of the reaction. The dark brown mixture was then cooled to r.t. The residue remained after the removal of the solvent in vacuum was purified by column chromatography (silica gel, dichloromethane) to give white solid. Yield: 1.3 g (53%). ^{1}H NMR (CDCl$_3$) δ 8.57 [s, 1H, C$_1$H (Ph)], 8.33 [d, 1H, C$_5$H (Ph)], 8.43 [d, 1H, C$_6$H (Ph)], 10.21 (s, 1H, aldehyde). IR (KBr pellet): (cm^{-1}) = 2877 (CHO), 2237 (CN), 1710 (C=O aldehyde).

Synthesis of 3,4-dicyanobenzoic acid (7). A solution of 1.19 g (10.4 mmol) NaClO$_2$ (80% purity) in 5 mL water was added drop-wise within a hour into a mixture of 1.15 g (7.4 mmol) 3,4-dicyanobenzaldehyde (**6**) in 10 mL acetonitrile, 0.31 g NaH$_2$PO$_4$ in 5 mL water, and 0.86 mL (7.7 mmol) of 30% H$_2$O$_2$ with strong stirring, whereby the temperature of the reaction mixture was kept at 10 ^{o}C with icy water cooling. Oxygen evolution was monitored from the solution through a bubbler connected to the apparatus until the end of the reaction (about 7 h). A small amount of Na$_2$SO$_3$ (0.07 g) was added to destroy the remained HOCl and H$_2$O$_2$. Acidification with 10% aqueous HCl yielded white solid. Yield: 1.00 g (78%). ^{1}H NMR (CDCl$_3$) δ 8.57 [s, 1 H, C$_1$H (Ph)], 8.26 [d, 1 H, C$_5$H (Ph)], 8.51 [d, 1 H, C$_6$H (Ph)]. IR (KBr pellet): (cm^{-1}) = 2400 ~ 3300 (OH acid), 2237 (CN), 1706 (C=O acid). EA [%]: C, 62.51; H, 2.31; N, 15.87; O, 19.29. Calculated [%]: C$_9$H$_4$N$_2$O$_2$: C, 62.80; H, 2.34; N, 16.27; O, 18.59.

Synthesis of 4-carboxy(*N*-Ferrocene ethyl ester)phthalonitrile (9). 0.774 mg (4.5 mmol) 3,4-dicyanobenzoic acid (**7**) was refluxed with 6 mL thionyl chloride and 10 mL chloroform for 24 h under nitrogen atmosphere until the gas evolution has ceased. The excess of thionyl chloride (**8**) and residue on a water bath were distilled off in vacuum. The crude acid chloride was used for next reaction without further purification. The acid chloride (*ca.* 4.5 mmol) dissolved in 20 mL dry chloroform was added drop-wise into the mixture of 1.13 g (3.73 mmol) ethyl 1'-

aminoferrocene-1-carbamate, 3.73 mL (37.3 mmol) triethylamine, and 20 mL dry chloroform at 0 ^{o}C for 40 min while stirring and cooling with an ice-water bath. The reaction mixture was stirred at the same temperature for an additional 10 min, and then 20 mL water was added. The product was extracted with dichloromethane (20 mL × 3). The organic phase was dried over sodium carbonate and then evaporated. The residue was purified by column chromatography [silica gel, chloroform/methanol (9/1, v/v)] to give red solid. Yield: 1.28 g (75.3%). mp: 63 ^{o}C. ^{1}H NMR (CDCl$_3$) δ 1.22 (t, 3 H, CH$_3$), 4.05 (q, 2 H, CH$_2$), 4.12 (d, 2 H, H-2' H-5', Fc), 4.45 (m, 2 H, H-3' H4', Fc), 4.77 (m, 2H, H-3 H4, Fc), 4.92 (d, 2 H, H-2, H-5, Fc), 9.45 (s, 1H, NH), 8.55 [s, 1H, C$_2$H (Ph)], 8.25 [d, 1H, C5H (Ph)], 8.45 [d, 1H, C$_6$H (Ph)]. IR (KBr pellet): (cm^{-1}) = 3300 (NH), 2237 (CN), 1677 (C=O amide), 1704 (C=O ester).

Synthesis of Zinc(II)-tetra(x'-ethylester-ferrocenyl)-phthalocyanie (*ZnPc-Fc*, 9). The mixture of **8** (1.27 g, 2.98 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.681 g, 4.47 mmol), zinc acetate dihydrate (0.164 g, 0.745 mmol), and butanol (20 mL) was refluxed for 1 h. After cooling to rt, 45 mL hexane was added drop-wise, and the reaction mixture was stirred for 2 h. The precipitate was collected, washed with diethyl ether, and then dried. The crude product was purified by column chromatography [silica gel, chloroform/methanol (9/1, v/v)] to give dark green solid. Yield: 500 mg (40%). ^{1}H NMR (DMSO-d_6) δ 1.26 (t, 12 H, CH$_3$), 4.10 (q, 8H, CH$_2$), 4.19 (d, 8H, H-2' H-5', Fc), 4.62 (m, 8H, H-3' H4', Fc), 4.90 (m, 8H, H-3 H4, Fc), 5.21 (d, 8H, H-2 H-5, Fc), 8.77 (s, 1H, NH), 10.51 [s, 1H, C$_2$H (Ph)], 9.35 [d, 1H, C$_5$H (Ph)], 9.84 [d, 1H, C$_6$H (Ph)]. IR (KBr pellet): (cm^{-1}) = 3400 (NH), 2237 (CN), 1680 (C=O amide), 1708 (C=O ester). UV-vis absorption spectrum (DMSO): 687 nm (ε =1.16 × 10^5 mol^{-1} cm^{-1}). MALDI TOF Mass (C$_{88}$H$_{68}$N$_{12}$O$_{12}$Fe$_4$Zn): [M+ H$^+$] 1773.45, [M] = 1772.45.

Electrochemical measurement. The electrochemical experiments were performed at r.t in a conventional three electrode cell with separate compartments for counter and reference electrodes. The ITO (indium tin oxide) glass was employed as the working electrode, a non-aqueous Ag/AgCl electrode as the reference at a potential, and a platinum wire as the counter electrode, respectively. The ITO glass was washed with pirana solution (H$_2$SO$_4$/H$_2$O$_2$ = 3/7), deionized water, and acetone, and then dried with nitrogen blow before each measurement. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dried benzonitrile. The concentration of the dye in the electrolyte was 0.5 mM. The differential pulse voltammogram (DPV) of the dye was recorded using compactstat (IVIUM TECHNOLOGIES). Scans are initiated from 0 V to 1.2 V versus Ag/AgCl in positive direction at a rate of 50 mV/s. The modulation time is 50 ms, interval time 100 ms, step potential 5 mV, and modulation amplitude 25 mV. The solutions were purged with nitrogen, and stirred for over 15 min prior to the measurements.

Fabrication of *ZnP-cFc* sensitized solar cells. Transparent TiO$_2$ paste was coated onto a FTO glass using the doctor-blade method to get an appropriate thickness (~10 μm) for the working electrode. After drying the films at 125 ^{o}C, light scattering paste were deposited on the top in 4 - 5 μm thickness in the same way. Subsequently, the TiO$_2$ pastes coated FTO glass was gradually heated under an air flow at 325 ^{o}C for 5 min, at 375 ^{o}C for 5 min,

and at 450 °C for 15min, and at 500 °C for 15 min.

ZnPc-Fc adsorbed TiO$_2$ films were prepared in an oxygen-free glove box at 25 °C on the basis of the Sten-Eric Lindquist methods.[7] Briefly, the prepared TiO$_2$ film was immersed in a solution of lithium *tert*-butoxide ((CH$_3$)$_3$COLi) in hexane (1.0 M) for 24 h. The base-treated film was washed with hexane thoroughly, and then immersed into a benzonitrile solution of *ZnPc-Fc* (0.1 mM) for 24 h at 50 °C, followed by a wash with benzonitrile and ethanol. The *ZnPc-Fc* sensitized TiO$_2$ electrode was assembled with a thermally platinized FTO electrode. The electrodes were separated by a 30-μm-thick Bynel (DuPont) hotmelt gasket, and sealed by heating. The internal space was filled with a liquid electrolyte (0.6 M 1-butyl-3-methylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M *tert*-butylpyridine in a 15:85 (v/v) mixture of valeronitrile and acetonitrile). The electrolyte-injecting hole on the counter electrode glass substrate, made with a sand-blasting drill, was sealed with a Bynel sheet and a thin glass cover by heating.

Photovoltaic characterization. The *ZnPc-Fc* sensitized solar cells were exposed to simulated AM 1.5 solar lights at 1 sun light intensity (100 mW/cm^2) using an Oriel 300 W xenon lamp, and appropriate filters. Photocurrents and photovoltages were measured using a Keithley 2400 source meter connected to a personal computer.

The active electrode area was typically 0.20 cm^2. The fill factor (FF) was defined by

$$FF = \frac{J_{ph(max)} \times V_{ph(max)}}{J_{sc} \times V_{oc}}$$

where $J_{ph(max)}$, $V_{ph(max)}$, J_{sc} and V_{oc} are the photocurrent, photovoltage for maximal power output, the short-circuit photocurrent, and open-circuit photovoltage, respectively. The overall conversion efficiency (η) is defined as the following equation:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

Here P_{in} is the power of incident white light.

Femto-second transient absorption: A dual-beam femto-second time-resolved transient absorption spectrometer with an IR-OPA (infra-red optical parametric amplifier) as pump pulses and white light continuum as probe pulses was employed for transient absorption measurements. The system has also been described in previous reports.[20]

Other methods. UV-vis and fluorescence spectra were recorded using a Perkin-Elmer Lambda 40 spectrophotometer and fluorescence spectrometer (Shimadzu RF-5000), respectively. Nuclear magnetic resonance (NMR) spectra were obtained from a VARIAN UNITYINOVA 400 instrument. Infrared spectra were taken using FT-IR Spectrophotometer (Nicolet).

MALDI-TOF Mass analysis was carried out using a (Voyager DE-STR, Applied Biosystems, Framingham, MA, USA) instrument in a reflector mode, and 3,5-dimethoxy-4-hydroxy-trans-cinnamic acid (sinapinic acid) was used as a matrix in all cases.

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