1136 *Journal of the Chinese Chemical Society*, **2010**, *57*, 1136-1140

Invited Paper

Preparation and Photovoltaic Characterization of Free-Base and Metallo Carboxyphenylethynyl Porphyrins for Dye-Sensitized Solar Cells

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Free-base, manganese, iron, cobalt, nickel, copper and zinc 5-(4-carboxy-phenylethynyl)-10,20-biphenylporphines are synthesized to study the impact of central metal ions to the photovoltaic performance of the solar cells.

Keywords: Porphyrin; Dye-sensitized solar cell; Central metal effect.

INTRODUCTION

Dye-sensitized solar cells (DSSC) have drawn much attention in recent decades.[1,2] The strategy is to adsorb suitable photosensitizers onto high-surface-area nanocrystalline TiO_2 films for light harvesting. Ru(II) complexes, such as N3, N719 and C101 dyes, are the most efficient photosensitizers to-date with overall efficiencies (η) greater than 11%.[3,4] On the other hand, porphyrins have also been considered for DSSC applications because of their vital roles in photosynthetic reaction.[2b,5-9] Many factors affect the usefulness of a porphyrin for DSSC and it has been demonstrated that a fully conjugated system with an edgewise adsorption mode improves the charge transfer processes and the surface area coverage, resulting in an enhanced overall efficiency.[2b] By this strategy, the most efficient porphyrin-sensitized solar cell has been reported to have achieved an overall efficiency of 7.1%.[5a]

We have previously reported studies of a series of zinc porphyrins bearing linear, length-controlled phenylethynyl anchoring groups (denoted as PE1 to PE4).[9a,b] In those reports, we have established that (1) these fully conjugated, *meso*-substituted porphyrins adsorb onto TiO_2 surfaces in an edgewise fashion and (2) PE1 outperforms other dyes in the series. In this work, we aim to investigate the central metal effect of PE1 porphyrin by studying the properties of free-base, manganese, iron, cobalt, nickel, copper and zinc 5-(4-carboxy-phenylethynyl)-10,20-biphenylporphines (denoted as H_2PE1, MnPE1, FePE1, CoPE1, NiPE1, CuPE1, and ZnPE1, respectively). Fig. 1 depicts the molecular structures of these new porphyrins. It is known that the central metals greatly affect the redox and electron transfer properties of porphyrins.[10,11] To the best of our knowledge, there has been only one report in the literature that addressed the central metal effects of porphyrin-sensitized solar cells:[2b] Officer and co-workers found that Zn porphyrin performs better than the Cu and free-base analogues. Hence, it is curious to know the impact of other central metals to the photovoltaic performances of the porphyrin-sensitized solar cells as reported herein.

EXPERIMENTAL

Materials

Air-sensitive solids were handled in an MBraun

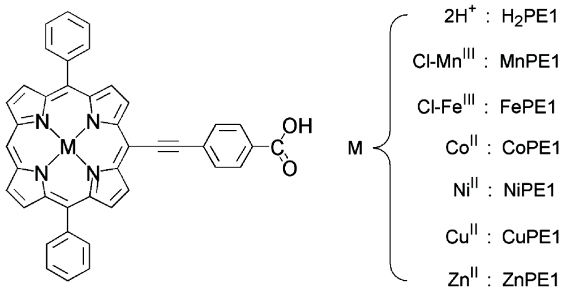

Fig. 1. Molecular structures of porphyrin photo-sensitizers studied in this work.

Special Issue for the 2009 International Symposium of Dye-Sensitized Solar Cells

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Uni-lab glove box. A vacuum line and standard Schlenk techniques were employed to process air-sensitive solutions. Solvents used in the synthesis (ACS Grade) were obtained from Mallinckrodt Baker, Inc. (CH_2Cl_2, $CHCl_3$ and ethyl acetate; Kentucky, U.S.A.), Haltermann (hexanes; Hamburg, Germany), and Merck (THF; Darmstadt, Germany). These solvents were used as received unless otherwise stated. Other chemicals were ordered from Acros Organics (New Jersey, U.S.A.). Tetrahydrofuran (THF), DMF and tetrabutylammonium perchlorate (TBAP) were were purified according to the literature methods.[12] For certain cyclic voltammetry experiments, the THF were purified and dried by an Asiawong SD-500 Solvent Purification System (Taipei, Taiwan). Around 10 ppm of H_2O were found in the THF purified by the system. All NMR solvents were used as received. $Pd(PPh_3)_4$ catalyst was purchased from Strem Chemical Inc (MA, U.S.A.). Chromatographic purification was performed with Silica Gel 60 (230-400 mesh, Merck).

Instrumentation

Absorption spectra were recorded on an Agilent 8453 UV-Visible spectrophotometry system. NMR data were obtained on a Varian Unity Inova 300WB NMR Spectrometer. Elemental analyses were carried out on an Elementar Vario EL III (NSC Instrumentation Center at National Chung Hsing University). Mass Spectroscopy measurements were performed on either a Liquid Chromatography Tandem Mass Spectrometer (National Science Council Instrumentation Center at National Chiao Tung University) or a JEOL JMS MStation (Academia Sinica).

Synthesis procedure

ZnPE1: The synthsis of ZnPE1 has been published previously.[9a]

H_2PE1: 70 mg of Zn PE1 was demetallated in 100 mL of $CHCl_3$ with 10 equivalent of HCl at room temperature for 1 hour. The reaction were monitored by UV-Visible spectroscopy. Upon completion, the reaction was quenched by 0.5 M $K_2CO_{3(aq)}$ washes, followed by 0.5 M $NH_4Cl_{(aq)}$ washes. The organic layer was collected and dried over Na_2SO4. 92% of H_2PE1 was obtained after chromatographic separation (silica gel, 10% MeOH in CH_2Cl_2) and crystallization (THF/hexanes).

MnPE1:[13] 50 mg of H_2 PE1 was first reacted with 5 eq. of $LiN(SiMe_3)_2$ in 30 mL THF under N_2. After reflux for 3 hours, a de-gassed THF solution of $MnCl_2$ (5 eq.) was introduced to the reaction mixture. The mixture was allowed to reflux for another 1 hour and monitored by UV-Visible spectroscopy. After precipitation from 300 mL of 0.1 M $HCl_{(aq)}$, chromatographic separation (silica gel, 10% MeOH in CH_2Cl_2) and crystallization (THF/hexanes), 30 mg of Cl-Mn(III)PE1 was collected (53% yield).

FePE1:[14] 40 mg of H_2 PE1 and 5 eq. of $FeCl_2$ in 20 mL of DMF under N_2 underwent reflux for 1 hour. After precipitation from 60 mL of 0.5 M $KCl_{(aq)}$, chromatographic separation (silica gel, 7% MeOH in CH_2Cl_2) and evaporation under reduced pressure. The solids were dessolved in 100 mL of THF, followed by drop-wisely adding the THF solution into 300 mL of 0.1 N of $HCl_{(aq)}$ to prevent the formation of μ-oxo-dimer. 27 mg (60%) of Cl-Fe(III)PE1 was obtained after crystallization from THF/hexanes.

CoPE1:[14] 50 mg of H_2PE1 and 16 eq. of $Co(OAc)_2$ in 30 mL of DMF under N_2 were reflux for 40 minutes. After precipitation from 100 mL of 0.1 M $KCl_{(aq)}$, the precipitates were put through chromatographic separation (silica gel, hexanes/THF = 1/4). 24 mg of Co(II)PE1 (44%) was collected after recrystallization from THF/hexanes.

Ni and **CuPE1**:[15] 50 mg of H_2PE1 and 10-20 eq. of $NiCl_2$ or $Cu(OAC)_2$ were reflux under N_2 in 30 mL of DMF for 30-40 minutes. After precipitation from 0.1 M $NH_4Cl_{(aq)}$, chromatographic separation (silica gel, CH_2Cl_2/THF = 1/3 for NiPE1 and hexanes/THF = 1/3 for CuPE1), and crystallization from THF/hexanes. 71% of Ni(II)PE1 and 78% of Cu(II)PE1 were afforded.

Characterization data

Charaterization data of ZnPE1 have been published previously.[9a] In addition, the fundamental properties of MnPE1, FePE1 and CoPE1 are consistent with the forms of Cl-Mn(III)PE1, Cl-Fe(III)PE1 and Co(II)PE1.

H_2PE1: ^{1}H-NMR(DMSO-d_6 at 2.50 ppm) 10.53(s, 1H), 9.88(d, J = 4 Hz, 2H), 9.55(d, J 4 Hz, 2H), 8.95(d, J 4 Hz, 2H), 8.89(d, J = 4 Hz, 2H), 8.24(m, 8H), 7.88(m, 6H), -2.77(s, 2H), Elemental Analysis, $C_{41}H_{26}N_4O_2 \cdot 1.5\ H_2O$, calc'd C: 77.71%, H: 4.61%, N: 8.84%; found C: 77.41%, H: 4.88%, N: 8.83%. Mass, MH^+: calc'd 607.2, found 607.2.

MnPE1: Elemental Analysis: $C_{41}H_{24}ClMnN_4O_2 \cdot 1.5\ H_2O$ calc'd: C: 68.20%, H: 3.77%, N: 7.76%; found: C: 68.45%, H: 3.98%, N: 7.82%. Mass, M: calc'd 659.1, found 659.2.

FePE1: Elemental Analysis: $C_{41}H_{24}ClFeN_4O_2 \cdot H_2O$ calc'd: C: 68.97%, H: 3.67%, N: 7.85%; found: C: 68.49%, H: 3.68%, N: 7.32%. Mass, M: calc'd 660.1, found 660.1.

CoPE1: Elemental Analysis: $C_{41}H_{24}CoN_4O_2 \cdot 1.5\ H_2O$ calc'd: C: 71.30%, H: 3.94%, N: 8.11%; found: C: 71.26%,

Table 1. Absorption maxima (in nm) and absorption coefficients (in $cm^{-1}M^{-1}$) of PE1s and the corresponding TPPs

Porphyrins[a]	Soret (log ε)	Q (log ε)	Porphyrins[b]	Soret (log ε)
H_2PE1	430(5.54)	526(4.12), 566(4.37), 604(3.77), 661(3.96)	H_2TPP	418(5.55)
MnPE1	381(4.69), 426(4.65), 481(4.95)	544(3.75), 597(3.97), 641(4.22)	MnTPP	478(4.91)
FePE1	363(4.56), 434(4.97)	519(4.00), 555(3.86), 701(3.62)	FeTPP	416(5.01)
CoPE1	430(5.40)	541(4.15), 577(4.09)	CoTPP	411(5.23)
NiPE1	427(5.36)	538(4.23), 573(4.14)	NiTPP	415(5.27)
CuPE1	431(5.50)	552(4.24), 594(4.20)	CuTPP	415(5.48)
ZnPE1	439(5.65)	568(4.23), 616(4.44)	ZnTPP	419(5.62)

[a] This work, measured in THF. [b] Taken from ref. 16, in $CHCl_3$.

H: 4.02%, N: 8.07%. Mass, M: calc'd 663.1, found 663.2.

NiPE1: ^{1}H-NMR (DMSO-d_6 at 2.50 ppm) 10.16(s, 1H), 9.80(d, $J = 5$Hz, 2H), 9.45(d, $J = 5$Hz, 2H), 8.91(d, $J = 5$Hz, 2H), 8.85(d, $J = 4$Hz, 2H), 8.16(two overlapped doublets, $J = 9$Hz, 4H), 8.04(m, 4H), 7.82(m, 6H), Elemental Analysis: $C_{41}H_{24}NiN_4O_2 \cdot H_2O$ calc'd: C: 72.27%, H: 3.85%, N: 8.22%; found: C: 72.40%, H: 3.82%, N: 7.99%. Mass, M: calc'd 663.1, found 663.2.

CuPE1: Elemental Analysis: $C_{41}H_{24}CuN_4O_2 \cdot 1/2$ THF calc'd: C: 73.33%, H: 4.01%, N: 7.96%; found: C: 73.06%, H: 3.84%, N: 8.32%. Mass, M: calc'd 667.1 (^{63}Cu) and 669.1 (^{65}Cu), found 667.0 and 669.0.

Device Fabrication and Characterization

Cell Fabrication and photovoltaic performance measurements are the same as those published in our previous report.[9a]

RESULTS AND DISCUSSION

Absorption Spectra

Fig. 2 depicts UV-Visible spectra of (a) H_2, Co, Ni, Cu, Zn, (b) Mn and FePE1 in THF. Table 1 lists the absorption maxima and absorption coefficients of PE1 porphyrins, along with the reported B band data of free-base and metallo tetraphenylporphines (TPPs) for comparison.[16] First of all, typical porphyrin absorption spectra are observed for PE1s: strong Soret bands in the higher energy region and weaker Q bands in the lower energy region. Secondly, the trend of PE1s' absorption bands are consistent with that of the TPP analogues.[16] For example, the B band wavelengths red-shift from H_2, Co, Ni, Cu to ZnPE1 and the absorption coefficients decrease from Zn, H_2, Cu, Co to NiPE1. Similar patterns are observed for the TPP counterparts with only slight deviation. Thirdly, Q bands of H_2PE1 are divided into four groups due to its lower symmetry.[17] Forthly, MnPE1's split Soret bands are the characteristics of a Mn(III) porphyrin and are not present in Mn(II) or Mn(IV) porphyrins.[18] Finally, the absorption spectrum of FePE1 is consistent with that of a monomeric Fe(III) porphyrin,[19] not that of a μ-oxo-dimer.[20]

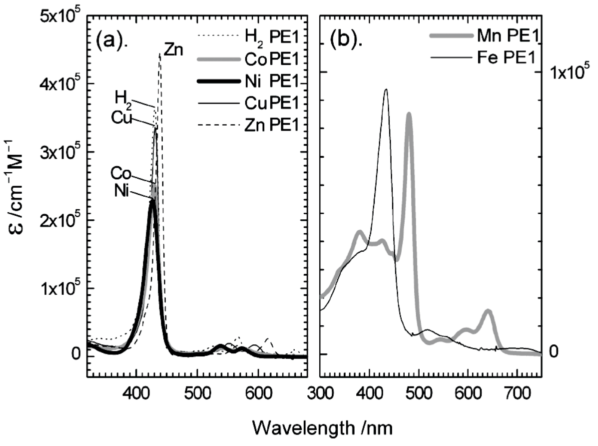

Fig. 2. Absorption spectra of (a) H_2, Co, Ni, Cu, Zn, (b) Mn and FePE1 in THF.

Photovoltaic Measurements

It is known that the central metals greatly affect the redox and electron transfer properties of porphyrins.[10,11] Therefore, the performances of the PE1-sensitized solar cells may also be affected. Table 2 collects the averaged photovoltaic parameters of PE1-sensitized solar cells. The current-voltage (*I-V*) curves of N3 and PE1 porphyrins are compared in Fig. 3. For each sensitizer, only the *I-V* curve of the best power conversion efficiency is shown in the figure.

The average overall efficiencies of PE1 porphyrins vary greatly, and the order is: ZnPE1 (3.6 ± 0.1%) > H_2PE1 (2.6 ± 0.0%) > CuPE1 (0.4 ± 0.1%) > NiPE1 (0.1 ± 0.0%) > CoPE1 (0.0 ± 0.0%), FePE1 (0.0%), and MnPE1 (0.0%). It is clear that ZnPE1 outperforms other metallo-PE1 porphyrins with an open-shell central metal ion. Therefore, it is

Table 2. Photovoltaic parameters of PE1-sensitized solar cells[a]

Dye	J_{SC} /mA cm^{-2}	V_{OC} /V	FF	η (%)
N3	12.68 ± 0.27	0.73 ± 0.01	0.64 ± 0.02	5.85 ± 0.16
ZnPE1	8.60 ± 0.13	0.65 ± 0.02	0.64 ± 0.02	3.58 ± 0.09
CuPE1	1.27 ± 0.09	0.58 ± 0.01	0.58 ± 0.05	0.43 ± 0.07
NiPE1	0.25 ± 0.00	0.44 ± 0.02	0.43 ± 0.05	0.05 ± 0.01
CoPE1	0.02 ± 0.00	0.08 ± 0.02	0.26 ± 0.03	0.00 ± 0.00
FePE1	0.01	0.01	0.11	0.00
MnPE1	0.05	0.01	0.35	0.00
H_2PE1	5.93 ± 0.01	0.62 ± 0.00	0.71 ± 0.01	2.59 ± 0.04

[a] under AM1.5 illumination (power 100 mW cm^{-2}) with an active area of 0.16 cm^2. Three independent measurements were performed for all dyes using the TiO_2 films fabricated with an identical procedure in order to demonstrate the reproducibility of the data.

logical to suggest that the *d-d* transitions of these open-shell central metals have a negative impact to the performance of the solar cells. The extremely low J_{SC} values in the devices made of the open-shell species suggest that the photo-induced reduction of the central metal in those porphyrin sensitizers might be a more efficient process than electron injection into TiO_2. This phenomenon is also consistent with the trend of the observed V_{OC} values which decreased systematically from the central metals of Zn to Cu, Ni, Co, Fe and Mn. As such, for the open-shell metallo-PE1 sensitizers, we expect that the more efficient central metal reduction results in the less efficient electron injection into the conduction band of TiO_2. Finally, the trend observed in this work is relatively consistent with the finding reported by Officer and co-workers on Zn-, Cu- and H_2-1a porphyrins.[2b] In that report, the order of the DSSC performance is Zn-1a > Cu-1a > H_2-1a porphyrins. In our case, however, H_2PE1 performs better than CuPE1, which is consistent with the reduction model for copper ion to be easily reduced while it is not feasible for the free-base porphyrin. Another reason to account for the discrepancy between the two porphyrin systems is attributed to the differences in their structures: porphyrins 1a are pyrrole β-substituted systems whereas PE1s are *meso*-substituted porphyrins.

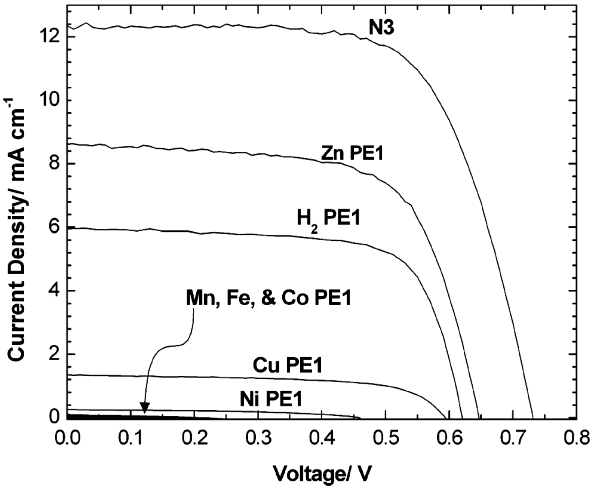

Fig. 3. Current-voltage characteristics of porphyrin-sensitized solar cells under AM 1.5 one-sun irradiation (100 mW cm^{-2}) and an active area of 0.16 cm^2.

CONCLUSION

Free-base and several metallo-PE1 porphyrins are successfully prepared to investigate their spectral and photovoltaic properties. For the photovoltaic performance, ZnPE1 outperforms H_2PE1, CuPE1, NiPE1, CoPE1, FePE1, and MnPE1 with an overall efficiency of 3.6%. The poor performances of CuPE1, NiPE1, CoPE1, FePE1, and MnPE1 might be due to the *d-d* transitions of the open-shell central metal ions, which facilitate reduction of the central metal ions to impede the electron injection into TiO_2.

ACKNOWLEDGEMENT

This work was supported by the National Science Council (CYL: NSC 97-2113-M-260-007-MY2 and NSC 97-2627-M-260-001; EWGD: NSC 98-2113-M-009-014 and NSC 97-3114-M-009-003).

Received November 29, 2009.

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