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Synthesis and characterization of β-pyrrolic functionalized porphyrins as sensitizers for dye-sensitized solar cells

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ABSTRACT

New β -pyrrolic functionalized porphyrins with donor- π -acceptor character were synthesized and characterized as dye sensitizers for dye-sensitized solar cells. Two types of π -conjugated spacers, namely benzene and thiophene rings, with cyanoacrylic acid as an acceptor were linked to the porphyrin ring at the β -pyrrolic position. These porphyrins showed high thermal and electrochemical stability. As sensitizers, the porphyrin dye bearing a thiophene ring as the π -conjugated spacer gave better cell performance with a short-circuit photocurrent density (J_{sc}) of 4.57 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.59 V, and a fill factor (ff) of 0.59, corresponding to an overall conversion efficiency (η) of 1.94%.

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Dye-sensitized solar cells (DSSCs) have attracted considerable and sustained attention as they offer the possibility of low-cost conversion of photoenergy.¹ To date, DSSCs with a validated efficiency record of >11% have been obtained with Ru complex dyes.² More recently, a DSSC submodule of 17 cm² consisting of eight parallel cells with conversion efficiency of >9.9% was fabricated by Sony.³ Though there is still room for improvement of the efficiency of Ru-based DSSCs, Ru dyes are nevertheless costly, hard to obtain, and normally have moderate absorption intensity.^{2,4} Significant effort is being dedicated to develop new and efficient dyes being suitable for their modest cost, ease of synthesis and modification, large molar extinction coefficients, and long-term stability.⁵ Organic dyes with donor- π -acceptor $(D-\pi-A)$ character meet all these criteria. Remarkable progress has been made in the pursuit of organic dyes as sensitizers for DSSCs⁶ and efficiencies exceeding 11% have been achieved.⁷ Most of the efficient dyes have a cyanoacrylic acid unit as acceptor and anchoring groups.⁶

Among these dyes, porphyrin has attracted a great deal of attention because of its natural role in photosynthesis, its intense absorption in the visible region, its high stability and the relative ease with which functional groups can be attached to its framework.⁸ Furthermore, its inherent LUMO level is situated above the conduction band of TiO₂, and its HOMO level is below the redox couple of the electrolyte solution required for charge separation at the semiconductor-dye-electrolyte surface, which makes it a good donor moiety.⁹ A large number of porphyrins have been developed as sensitizers for DSSCs such as carboxyphenyl metalloporphyrins,¹⁰ thiophene-, olefin-, and acetylene-linked porphyrins,¹¹ quinoxaline-fused porphyrins,¹² a Zn–Zn porphyrin dimer,¹³ oligo(phenylethynyl)-linked porphyrins,¹⁴ and bacteriochlorin.¹⁵

From the Goutermann orbital model of porphyrin (Fig. 1), in the ground state, the HOMOs (a_{1u} or a_{2u}) have the orbital density mostly on the porphyrin *meso*-positions and the nitrogens with a small amount of electron density on the β -pyrrolic positions. In the excited state, the electrons go into the LUMO orbitals (E_g) which have electron density on the β -pyrrolic and *meso*-positions. This means that a porphyrin functionalized at the β -pyrrolic positions would be expected to show strong excited state communication. Therefore, incorporation of π -conjugated spacers with cyanoacrylic acid as an acceptor at the β -pyrrolic position of porphyrin would potentially offer strong excited state electron transfer from the porphyrin dye to TiO₂, consequently resulting in a highly efficient dye for DSSCs.

In this work, we present the synthesis and characterization of new functionalized porphyrins bearing two types of π -conjugated spacers, namely benzene and thiophene rings, with cyanoacrylic



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Figure 1. The Gouterman orbital models for the HOMO and LUMO orbitals of porphyrin.

acid as an acceptor unit linked to the porphyrin ring at the β -pyrrolic position. An investigation of the physical and photophysical properties, and their applications as sensitizers in DSSCs are also reported.

Scheme 1 outlines the synthesis of the designed β-pyrrolic functionalized porphyrin dyes. We began with selective bromination of 5,10,15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin (1)¹⁶ at the β -pyrrolic position with NBS in a mixed solvent of CHCl₃/AcOH to give 1-bromo-1,5,15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin (2) in a moderate 45% yield. To facilitate the metal-catalyzed coupling reaction the bromo porphyrin 2 was first chelated with zinc by heating a solution of 2 in $CH_2Cl_2/MeOH$ with $Zn(OAc)_2 \cdot 2H_2O$ to give zinc 1-bromo-5,10,15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin (**3**) in quantitative yield. Cross-coupling of **3** with either 4-formylphenylboronic acid or 5-formyl-2-thiopheneboronic acid catalyzed by Pd(PPh₃)₄/Na₂CO₃ (aq) in THF gave the corresponding aldehydes 4 and 5 in yields of 65% and 59%, respectively. Final Knoevenagel condensation of these aldehydes with cyanoacrylic acid in the presence of a catalytic amount of piperidine in CHCl₃ at reflux afforded (*E*)-3-[4-{5,10,15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin-1-yl}phenyl]-2-cyanoacrylic acid (**6**) and (*E*)-3-[5-{5,10, 15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin-1-yl}thiophen-2 -yl]-2-cyanoacrylic acid (7) as dark red solids in fairly good yields of 86% and 72%, respectively. The structures of all the dye molecules were characterized unambiguously by ¹H NMR and ¹³C NMR spectroscopy as well as by high-resolution mass spectrometry.¹⁷ These compounds show good solubility in organic solvents allowing dye adsorption on TiO₂ film, and thus fabrication of DSSCs could be performed.

To gain insight into the geometrical and electronic properties of these functional porphyrins, quantum chemistry calculations were performed using the PCM-TD-B3LYP/6-31+G(d)//B3LYP/6-31G(d) method.¹⁸ The calculated molecular structures, in the ground-state of dyes 6 and 7, revealed that the plane of the 3',5'-di-tert-butylphenyl ring was aligned nearly orthogonal to the porphyrin plane due to steric interactions between the β -pyrrolic and aryl ring protons. The resulting bulky structures of both dyes could help to prevent effectively the close $\pi - \pi$ aggregation between the dye molecules. It is known that a major factor for low conversion efficiencies of many organic dyes in DSSCs is the occurrence of dye aggregation on the TiO₂ surface.¹⁹ The benzene π -conjugated spacer in 6 (dihedral angle = 65.39°) adopted a less planar conformation than that of the thiophene π -conjugated spacer in **7** (dihedral angle = 39.97°). This suggests that the excited π -electrons from the porphyrin donor moiety can delocalize effectively to the acrylic acid acceptor in 7. which subsequently transfer to the conduction band of TiO₂. The electron distributions of the HOMO and LUMO levels of 6 and 7 are shown in Figure 2. To create an efficient charge-transfer transition, the HOMO must be localized on the donor unit, and the LUMO on the acceptor unit.²⁰ In the HOMOs, electrons are delocalized over the porphyrin moiety, while in the LUMOs, the excited electrons are delocalized across the π -conjugated spacers and cyanoacrylic acid, indicating donor- π -acceptor character in both dyes. The results suggest that the HOMO \rightarrow LU-MO transition can be considered as an intramolecular chargetransfer (ICT) transition.

In a CH₂Cl₂ solution, the absorption spectra of both dyes 6 and 7 showed characteristic absorptions due to the porphyrin, which consist of two sets of bands, namely an intense B band (the Soret band) in the range of 400-430 nm and weaker Q bands in the range of 550-650 nm (Fig. 3a). These characteristic absorption spectra arise due to the configurational interaction of two porphyrin π - π * electronic transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow E_g(\pi^*)$. The constructive interaction corresponds to a strong allowed transition giving rise to the Soret band, whereas the destructive interaction corresponds to a weak disallowed transition giving rise to the O bands at longer wavelength. In most porphyrins, in response to the absorption of light, rapid population of the lowest energy excited singlet state occurs due to fast nonradiative transitions. The absorption spectra of 6 and 7 adsorbed on TiO₂ films showed broader absorption peaks than those in solution. Such a phenomenon is commonly observed in the spectral response of other organic dyes, which may



Scheme 1. Synthesis of β-pyrrolic functionalized porphyrins 6 and 7.



Figure 2. HOMO and LUMO orbitals of 6 and 7 calculated using the PCM-TD-B3LYP/6-31+G(d)//B3LYP/6-31G(d) method.



Figure 3. (a) Absorption spectra of 6 and 7 in CH₂Cl₂ and adsorbed on TiO₂ films. (b) CV curves of 6 and 7 measured in CH₂Cl₂ at a scan rate of 50 mV/s.

Table 1 Device characteristics of DSSCs fabricated with 6 and 7 as dye sensitizers

Dye	Abs (nm) ^a	$E_{1/2}$ versus Ag/Ag ⁺ (V) ^b	HOMO (eV) ^c	LUMO (eV) ^c	$E_{g} (eV)^{c}$	IPCE _{max} (%)	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}\left({\rm V}\right)$	ff	η (%)
6	428, 555, 594	-1.69, -1.43, 0.72, 1.00, 1.37	-5.08	-3.21	1.87	34	2.62	0.59	0.57	1.13
7	428, 557, 597	-1.65, -1.38, 0.74, 1.02	-5.10	-3.10	2.00	70	4.57	0.59	0.59	1.94

^a Measured in CH₂Cl₂.

^b Measured by CV using a glassy carbon working electrode, a Pt counter electrode and an Ag/Ag^{*} reference electrode with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte in CH₂Cl₂.

^c Calculated by HOMO = $-(4.44 + E_{onset}^{ox})$; LUMO = $-(4.44 + E_{onset}^{re})$; E_g = HOMO-LUMO.

be ascribed to the interaction of the anchoring groups of the dyes with the surface of TiO_2 .²¹ The wide absorption spectrum is an advantageous spectral property for light-harvesting of the solar spectrum.

A cyclic voltammetry (CV) study on **6** and **7** revealed quasireversible oxidation and reduction waves (Fig. 3b). The first and second oxidation potentials (0.70–0.72 and 1.00–1.02 V) of **6** and **7** are nearly the same, and they are assigned to removal of electrons from the porphyrin ring resulting in porphyrin radical cations and dications, respectively. The first reduction wave of **6** and **7** is assigned to the reduction of the porphyrin to form an anion radical, while the second reduction wave is assigned to the reduction of the cyanoacrylic acid moiety. Multiple CV scans of both **6** and **7** displayed unchanged CV curves indicating electrochemically stable molecules. The HOMO and LUMO levels of **6** and **7** were calculated to be -5.08 and -3.21 eV, and -5.10 and -3.10 eV, respectively (Table 1). From these CV results, it was found that substitution at the β -pyrrolic position of the porphyrin ring with either phenyl cyanoacrylic acid or thiophen-2-yl cyanoacrylic acid had a major effect on the excited state (reduction) of the porphyrin ring, while



Figure 4. (a) IPCE spectra and (b) I-V characteristics of the fabricated DSSCs.

a weak effect was found in the ground state (oxidation). This is in agreement with the Gouterman orbital models (Fig. 1) and the quantum chemical calculations (Fig. 2). Thermogravimetric analysis (TGA) revealed that **6** and **7** were thermally stable with a 5% weight loss (T_{5d}) at a temperature well over 500 °C.

The photovoltaic properties of 6 and 7 as sensitizers for dye-sensitized nanocrystalline anatase TiO₂ solar cells (DSSCs) were investigated. Cells with an effective area of 0.25 cm² $(0.5 \times 0.5 \text{ cm})$ were fabricated with an 11 μ m (9.5 μ m transparent + 1.5 µm scattering) thick TiO₂ working electrode, a platinum (Pt) counter electrode, and an electrolyte composed of 0.03 M $I_2/$ 0.6 M Lil/0.1 M guanidinium thiocyanate/0.5 M tert-butylpyridine in a 15/85 (v/v) mixture of benzonitrile/acetonitrile. For the determination of the photovoltaic performance, five cells were prepared and measured under standard conditions. The corresponding current density-voltage (J-V) characteristics and the incident monochromatic photon-to-current conversion efficiency (IPCE) plots are shown in Figure 4, respectively, and the resulting photovoltaic parameters (average values) are summarized in Table 1. The IPCE spectra of sensitizers 6 and 7 plotted as a function of excitation wavelength were coincident with their absorption spectra. The IPCE spectrum of porphyrin 7 showed a high maximum value of 70%, which was higher than the IPCE value of 6 (34%). Under standard AM 1.5G 100 mW cm⁻² illumination, the porphyrin **7**-based solar cell gave a short-circuit photocurrent density (I_{sc}) of 4.57 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.59 V, and a fill factor (ff) of 0.59, corresponding to an overall conversion efficiency (η) of 1.94%, while the porphyrin **6**-based cell showed a lower I_{sc} of 2.62 mA cm⁻² resulting in a lower conversion efficiency, (η) of 1.13%. The better solar cell performance (high IPCE, η and J_{sc}) of 7 could be rationalized by the more efficient electron transfer from the porphyrin donor through the π -conjugated spacer (thiophene ring) to the acrylic acceptor in 7 than that in 6, as indicated by the quantum chemical calculations.

In summary, we have designed and synthesized β -pyrrolic functionalized porphyrins as sensitizers for dye-sensitized solar cells. For comparison, two types of π -conjugated spacers, namely benzene and thiophene rings, with cyanoacrylic acid as an acceptor were linked to the porphyrin ring at the β -pyrrolic position. These porphyrins showed donor– π –acceptor character, and high thermal and electrochemical stability. DSSCs fabricated using these porphyrins as sensitizers exhibited efficiencies ranging from 1.13–1.94% under AM 1.5G illumination. The porphyrin dye bearing a thiophene ring as the π -conjugated spacer gave a better cell performance among both dyes with a maximum IPCE value of 70%, a J_{sc} value of 4.57 mA cm⁻², a V_{oc} value of 0.59, a ff value of 0.59, and overall conversion efficiency (η) of 1.94%. This work suggests that a dye sensitizer based on porphyrin as a donor moiety is a promising candidate for DSSCs. The degree of electron transfer

from the porphyrin to the acceptor, and the efficiency of porphyrin-based solar cells are dependent upon the degree of co-planarity between the porphyrin ring and the linker. Further structural modification of porphyrin **7** to widen the absorption spectrum and increase the molar extinction coefficient would be anticipated to give even better cell performance.

Acknowledgements

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- 17. *Characterization data for* **3**: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.15 (s, 1H), 8.99 (m, 6H), 8.12 (s, 4H), 8.08 (d, 2H, *J* = 1.5 Hz), 7.95 (d, 2H, *J* = 1.5 Hz), 7.82 (s, 4H), 1.55 (s, 72H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 151.30, 150.87, 150.73, 150.68, 150.35, 148.69, 148.53, 147.87, 143.04, 141.83, 140.61, 136.91, 132.88, 132.40, 132.35, 132.27, 131.70, 129.61, 129.42, 129.20, 129.07, 122.88, 122.29, 121.97, 121.23, 121.12, 121.05,120.98, 120.79, 119.23, 35.05, 31.77 ppm; HRMS *m/z* calcd for C₇₆H₉₁BrN₄Zn, 1202.5719; found, 1203.5797 [M+H] and 1225.5616 [M+Na].

Characterization data for **4**: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.99 (s, 1H), 9.09 (d, 2H, *J* = 3.6 Hz), 9.07 (s, 2H), 9.02 (d, 1H, *J* = 4.5 Hz), 8.99 (s, 1H), 8.87 (d, 1H, *J* = 4.8 Hz), 8.21 (d, 2H, *J* = 1.5 Hz), 8.18 (d, 2H, *J* = 1.5 Hz), 8.15 (d, 2H, *J* = 1.5 Hz), 7.90 (d, 2H, *J* = 1.5 Hz), 7.85-7.83 (m, 3H), 7.72 (d, 2H, *J* = 8.1 Hz), 7.67 (d, 2H, *J* = 8.1 Hz), 7.40 (s, 1H), 1.54 (s, 54H), 1.40 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 191.97, 151.49, 150.87, 150.73, 150.67, 150.54, 148.64, 148.60, 147.78, 146.61, 146.03, 145.40, 141.88, 141.77, 141.05, 135.87, 133.46, 132.83, 132.44, 132.37, 132.28, 131.79, 130.96, 130.48, 129.86, 129.59, 129.50, 128.59, 126.65, 123.19, 122.74, 122.37, 122.12, 121.30, 120.87, 35.07, 34.75, 31.67, ppm; HRMS *m/z* calcd for C₈₃H₉₆N₄OZn, 1228.6876; found, 1229.6954 [M+H] and 1251.6773 [M+Na]. Characterization data for **5**: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.83 (s,

Characterization data for **5**: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.83 (s, 1H), 9.06–9.02 (m, 3H), 8.96 (d, 2H, *J* = 4.7 Hz), 8.40 (d, 2H, *J* = 4.7 Hz), 8.13 (d, 2H, *J* = 1.5 Hz), 7.81 (d, 3H, *J* = 1.5 Hz), 7.81 (d, 3H, *J* = 1.6 Hz), 7.81 (d, 3H, *J* = 1.6 Hz), 7.53 (s, 1H), 7.39 (d, 1H, *J* = 3.8 Hz), 6.80 (d, 1H, *J* = 3.8 Hz), 1.53 (s, 54H), 1.41 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 182.74, 151.65, 151.46, 151.03, 150.96, 150.88, 150.41, 148.65, 148.04, 147.15, 145.51, 142.12, 141.66, 141.60, 141.17, 137.59, 136.63, 136.16, 133.13, 132.52, 131.87, 130.18, 129.86, 129.72, 129.59, 129.53, 35.07, 34.82, 31.77, 31.64 ppm; HRMS *m/z* calcd for C₈₁H₉₄N₄OSZn, 1234.6440; found, 1235.6518 [M+H] and 1257.6338 [M+Na].

Characterization data for **6**: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.89–8.75 (m, 8H), 8.09–8.06 (m, 6H), 7.85–7.69 (m, 8H), 7.51 (d, 2H, J = 7.2 Hz), 7.37 (s,1H), 1.51 (s, 54H), 1.35 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 169.13, 151.24, 150.41, 150.30, 150.25, 150.21, 150.14, 148.28, 148.23, 148.19, 147.57, 145.93, 145.40, 144.32, 142.44, 142.39, 142.35, 141.6, 135.95, 132.63, 131.94, 131.40, 130.77, 129.94, 129.67, 129.57, 129.41, 122.81, 122.03, 121.63, 120.91, 120.46, 118.68, 34.97, 34.73, 31.76, 31.69 ppm; HRMS *m*/*z* calcd for C86H97N5O2Zn, 1295.6934; found, 1295.6831 [M⁺] and 1318.6954 [M+Na]. Characterization data for 7: mp >250 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.13–8.84 (m, 8H), 8.44 (s, 1H), 8.13 (d, 6H, J = 6.6 Hz), 7.95 (s, 2H), 7.83 (s, 2H), 7.74 (s, 1H), 7.54 (d, 2H, J = 21.0 Hz), 6.79 (s, 1H), 1.55 (s, 54H), 1.43 (s, 18H) ppm; ¹³C NMR (75 MHz, CDCl₃) & 169.41, 151.51, 150.96, 150.94, 150.90, 150.84, 150.64, 150.42, 148.62, 148.58, 148.09, 147.29, 145.75, 141.73, 141.53, 141.18, 137.64, 136.91, 136.58, 135.05, 133.22, 132.45, 131.80, 130.03, 129.59, 123.09, 122.68, 122.65, 122.36, 121.87, 120.85, 118.28, 123.09, 122.68, 122.65, 122.36, 121.87, 120.85, 118.28, 35.07, 34.80, 31.79, 31.77 ppm; HRMS m/z calcd for C₈₄H₉₅N₅O₂SZn, 1301.6498; found, 1302.6576 [M+H] and 1324.6396 [M+Na].

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