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Pyridyl vs bipyridyl anchoring groups of porphyrin sensitizers for dye sensitized solar cells

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keywords: Porphyrin, anchoring groups, pyridine, bipyridine, DSSC

ABSTRACT: The synthesis of two porphyrins with donor- π -acceptor (D- π -A) molecular architecture is described, namely Znpor-py (**3a**) and Znpor-bpy (**3b**), which consist of a 4-*tert*-butyl-phenyl group as donor and either a pyridine or a bipyridine group as acceptor at opposite positions of the porphyrin macrocycle. Photophysical and electrochemical properties of the two compounds, as well as theoretical DFT calculation results suggest that the two porphyrins have the potential to act as sensitizers in dye-sensitized solar cells (DSSCs). Both dyes contain *N*(pyridyl) atoms able to act as anchors onto the acid sites of TiO₂. Znpor-py (**3a**) sensitized solar cell was found to exhibit power conversion efficiency (PCE) of 3.57%, while the corresponding Znpor-bpy (**3b**)-functionalized solar cell showed a higher PCE of 5.08%. The enhanced short circuit current J_{sc} and open circuit voltage V_{oc} parameters are the main factors responsible for the improved photovoltaic performance of the latter solar cell. These are attributed to its faster charge injection into the TiO₂ photoanode and its reduced charge recombination at the electrode/electrolyte interface, which result from the stronger binding and coordination geometry of the bipyridine anchoring group on TiO₂. Electrochemical impedance spectra (EIS) of the two solar cells further support these assumptions, revealing a higher charge recombination resistance R_{rec} and a longer electron lifetime τ_e for the Znpor-bpy (**3b**) sensitized solar cell.

INTRODUCTION

Dye sensitized solar cells (DSSCs), since their first report in 1991,¹ have attracted considerable research interest, owing to their potential use in solar-into-electrical energy conversion devices that exhibit high power conversion efficiencies (PCE), and low cost of fabrication.²⁻⁷ Photosensitizers are key components of DSSCs, which are responsible for absorbing photons and injecting electrons, upon their excitation, into the TiO₂ conduction band at the anode electrode of the devices.⁸⁻¹⁰ Thus, the development of new efficient sensitizers has become a very attractive and challenging field of today's research. Among the most efficient DSSC sensitizers are ruthenium-polypyridyl complexes, which have allowed the fabrication of DSSCs with PCE values of 11%.¹¹⁻¹³ However, the limited resources and the high cost of ruthenium metal substantially hinder their practical application.

Over the last decade, many efforts have been devoted to the design of new, low-cost, noble metal-free DSSC sensitizers.^{2, 14, 15} The basic design strategy for efficient dyes of this type is the synthesis of molecules with a donor- π -acceptor (D- π -A) or "push-pull" molecular architecture, which, in some cases, resulted in PCE values of 10%.¹⁶⁻¹⁹ Porphyrins constitute a particular type of noble metal-free dyes considered to be a very promising class of DSSC sensitizers.²⁰⁻³⁰ This is due to their unique properties, which include efficient solar energy absorption in the visible region of electromagnetic spectrum with high molar extinction coefficients, suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, and ability to control their physicochemical properties through appropriate synthetic modification. Indeed, porphyrin based sensitizers with "push-pull" molecular architectures have resulted in DSSCs that exhibit higher than 10%PCE values,³¹⁻³⁷ with the most efficient porphyrin dyes reaching the impressive PCE values of 12-13%.³⁸⁻⁴⁰

In most of these noble metal-free D- π -A sensitizers, carboxylic acids and cyanoacrylic acid have commonly been used as acceptor and anchoring groups for the attachment of the dye onto the TiO₂ surface of the anode electrode. Among them, cyanoacrylic acid has been proved to be the most effective, since it red shifts and broadens the absorption spectra of the corresponding dyes resulting in enhanced electron injection efficiencies. However, the use of cyanoacrylic acid as binding unit also results in fast degradation of the dyes on the TiO₂ surface, affecting the device long-term stability.⁴¹ Moreover, it can undergo *trans*-to-*cis*-photo isomerization, a process that competes with electron injection and has a harmful effect on the cell performance.⁴² Recently, a tropolone group has been employed for the first time as an anchoring group for dye-sensitized solar cells, enhancing the binding ability with respect to its carboxylic analogue porphyrin.⁴³

Other electron accepting units that have been recently examined as anchoring groups in DSSC sensitizers⁴⁴ include pyridine⁴⁵⁻⁴⁸ and pyridinium groups.⁴⁹ The coordinate bond of the N-atom of the pyridyl group to the Lewis acid sites of TiO₂ provides good electron communication between them, leading to very efficient electron injection. In 2013, Wang and coworkers first reported DSSCs sensitized by D- π -A porphyrin dyes with pyridyl anchoring groups, which resulted in PCE values of ~4.0%.⁵⁰ Furthermore, Sun and coworkers employed *N*-(carboxymethyl) pyridinium as electron-withdrawing anchoring group for a series of hemicyanine dyes, which showed PCE values higher than their cyanoacrylic acid counterparts (~7.0%). Moreover, Grätzel and coworkers have employed porphyrin sensitizers bearing pyridyl anchoring groups resulting in DSSCs with PCE values of 8.5% and impressing long-term stability.⁵¹

Our research group has also reported the use of simple porphyrin sensitizers with pyridyl anchoring groups for the fabrication of DSSCs, which reached a maximum PCE value of 3.9%.⁵² In a more recent report, we synthesized two tetra-aryl substituted, “spider-shaped”

zinc-metallated porphyrins, bearing four oligo (*p*-phenylenevinylene) pyridyl groups with long dodecyloxy chains on the phenyl groups, as sensitizers for the fabrication of DSSCs achieving a maximum PCE of 5.12%.⁵³ Continuing our efforts towards this direction, we describe herein the synthesis, and optical, electrochemical, and photovoltaic properties of two simple “push-pull” porphyrins bearing pyridyl (py) and bipyridyl (bpy) acceptor-anchoring groups, namely the compounds Znpor-py (**3a**) and Znpor-bpy (**3b**)(Scheme 1). Moreover, we compare the effect of pyridyl and bipyridyl anchoring groups on the photovoltaic performance of the corresponding DSSCs.

EXPERIMENTAL SECTION

Materials and techniques: All manipulations were carried out using standard Schlenk techniques under nitrogen atmosphere. Pyridine-4-carbaldehyde, 4-*tert*-butyl-benzaldehyde, BF₃·OEt₂, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), Et₃N, Zn(CH₃COO)₂·2H₂O, N-bromo succinamide (NBS) and other chemicals and solvents were purchased from usual commercial sources and used as received, unless otherwise stated. Dipyrromethane⁵⁴ and bipyridine-4-carbaldehyde^{55, 56} were prepared according to literature procedures.

5-(4-*tert*-butyl-phenyl)-15-(4-pyridyl)-porphyrin(1a): To a degassed CH₂Cl₂/MeOH mixture (90/10 v/v, 600 mL) dipyrromethane (0.74 g, 5.06 mmol), pyridine-4-carbaldehyde (0.24 mL, 2.53 mmol) and 4-*tert*-butyl-benzaldehyde (0.42 mL, 2.53 mmol) were successively added under nitrogen in the dark. After 20-min nitrogen bubbling, BF₃·OEt₂ (1.74 mL, 14.1 mmol) was slowly added in three portions, and the mixture was stirred for 2 days. Then DDQ (1.724 g, 7.59 mmol) was added and the mixture was further stirred for 20 h before addition of Et₃N (2.1 mL). After 30 min of stirring, the mixture was filtered through silica pad and the filtrate was evaporated to dryness. The crude product was subjected to silica gel column chromatography using CH₂Cl₂ as eluent, from which collecting the second

red band isolated the desired asymmetric trans-AB porphyrin. After evaporation of the solvent, the product was further purified by a short alumina column chromatography with CH_2Cl_2 as eluent. The solvent was removed and, after washing with *n*-hexane (50 mL), porphyrin **1a** was isolated as red-brown powder (0.18 g, 13%). mp >300 °C. ^1H NMR (300 MHz, CDCl_3 + 1% Et_3N): δ 10.34 (s, 2H), 9.42 (m, 4H), 9.16 (d, J = 4.6 Hz, 2H), 9.07 (d, J = 5.4 Hz, 2H), 9.03 (d, J = 4.5 Hz, 2H), 8.21 (m, 4H), 7.83 (d, J = 8.2 Hz, 2H), 1.64 (s, 9H), -3.14 (s, 2H). ^{13}C NMR could not be obtained due to solubility problems. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{35}\text{H}_{30}\text{N}_5$, 520.2501 $[\text{M} + \text{H}]^+$: found 520.2509. UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ (ϵ , $10^3\text{M}^{-1}\text{cm}^{-1}$) = 407 (341.6), 502 (15.4), 537 (5.8), 574 (5.2), 623 (2.0). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3278, 2950, 1589, 1535, 1461, 1405, 1240, 1143, 1062, 1049, 971, 956, 848, 782, 736, 688. Anal. Calcd for $\text{C}_{35}\text{H}_{29}\text{N}_5$: C, 80.90; H, 5.63; N, 13.48. Found: C, 80.99; H, 5.57; N, 13.56.

5-(4-*tert*-butyl-phenyl)-15-(4-pyridyl)-porphyrin zinc (2a): Free-baseporphyrin **1a** (0.168 g, 0.32 mmol) was placed in a 250 mL round-bottom flask and 100 mL of CH_2Cl_2 was added. The mixture was treated with a MeOH (10 mL) solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.354 g, 1.6 mmol) and stirred at 40°C for 24h. After solvent evaporation, the residue was extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (3×50 mL) and then THF (60 mL) was added in the organic phase in order to ensure porphyrin's solubility. The red solution was dried over anhydrous Na_2SO_4 and the solvent was removed in a rotary evaporator. Metallated porphyrin **2a** was collected as dark purple solid (0.180 g, 95%). mp >300 °C. NMR data could not be obtained due to poor solubility. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{35}\text{H}_{28}\text{N}_5\text{Zn}$, 582.1636 $[\text{M} + \text{H}]^+$: found 582.1629. UV-vis ($\text{CH}_2\text{Cl}_2/\text{THF}$: 1/1): $\lambda_{\text{max}}/\text{nm}$ (ϵ , $10^3\text{M}^{-1}\text{cm}^{-1}$) = 412 (399.4), 543 (15.2), 580 (2.8). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 2952, 1600, 1517, 1392, 1355, 1282, 1213, 1145, 1056, 985, 848, 773, 721, 700, 659. Anal. Calcd for $\text{C}_{35}\text{H}_{27}\text{N}_5\text{Zn}$: C, 72.11; H, 4.67; N, 12.01. Found: C, 72.22; H, 4.78; N, 11.72.

5-(4-*tert*-butyl-phenyl)-10-bromo-15-(4-pyridyl)-20-bromo-porphyrin zinc (3a): To a solution of zinc-metallated porphyrin **2a** (0.170 g, 0.29 mmol) in CH₂Cl₂/THF (1/1 v/v, 110 mL), a solution of NBS (0.104 g, 0.58 mmol) in CH₂Cl₂ (20 mL) was slowly added at 0°C. The mixture was stirred for 25 min, while checking the reaction progress with TLC, and then acetone (10 mL) was added to quench the reaction. After removing half of the solvent volume under reduced pressure, di-brominated porphyrin **3a** was isolated by filtration as purple, microcrystalline solid (0.131 g, 61%). mp >300 °C. ¹H NMR (THF-*d*₈, 500 MHz): δ 9.69 (d, *J* = 4.7 Hz, 2H), 9.66 (d, *J* = 4.7 Hz, 2H), 8.90 (d, *J* = 4.7 Hz, 2H), 8.81 (d, *J* = 4.7 Hz, 2H), 8.78 (d, *J* = 5.0 Hz, 2H), 8.09 (m, 4H), 7.84 (d, *J* = 8.2 Hz, 2H), 1.64 (s, 9H). ¹³C NMR (THF-*d*₈, 125 MHz): δ 151.8, 151.5, 151.2, 151.0, 150.8, 150.4, 148.4, 140.4, 135.2, 134.2, 133.8, 133.3, 133.0, 130.2, 124.2, 123.7, 119.0, 105.3, 35.4, 31.8. HRMS (MALDI-TOF): *m/z* calcd for C₃₅H₂₆Br₂N₅Zn, 737.9846 [M + H]⁺: found 737.9855. UV-vis (THF): λ_{max}/nm (ε, 10³ M⁻¹ cm⁻¹) = 4.28 (378.4), 564 (16.0), 605 (8.9). IR ν_{max}/cm⁻¹: 2944, 1602, 1523, 1452, 1409, 1324, 1282, 1259, 1199, 1070, 11020, 993, 784, 727, 698. Anal. Calcd for C₃₅H₂₅Br₂N₅Zn: C, 56.75; H, 3.40; N, 9.45. Found: C, 56.86; H, 3.32; N, 9.38.

5-(4-*tert*-butyl-phenyl)-15-(4-bipyridyl)-porphyrin (1b): To a degassed CH₂Cl₂/MeOH mixture (90/10 v/v, 200 mL), dipyrromethane (0.29 g, 2.00 mmol), bipyridine-4-carbaldehyde (0.18 g, 1.0 mmol) and *tert*-butyl-benzaldehyde (0.17 mL, 1.0 mmol) were successively added under nitrogen in the dark. After 20-min nitrogen bubbling, BF₃·OEt₂ (1.48 mL, 12.0 mmol) was slowly added in three portions, and the mixture was stirred for 4 days. Then DDQ (0.68 g, 3.0 mmol) was added and the mixture was further stirred for 1 h before addition of Et₃N (1.68 mL). After 90 min of stirring, the mixture was filtered through silica pad and the filtrate was evaporated to dryness. The crude product was subjected to silica gel column chromatography, using initially CH₂Cl₂ and then CH₂Cl₂/MeOH (9:1) as eluent, from which collecting the second red band isolated the desired asymmetric *trans*-AB

porphyrin. After evaporation of the solvent, the product was further purified by alumina column chromatography with THF/Hex (3:7) as eluent. The solvent was removed and, after washing with *n*-hexane (40 mL), porphyrin **1b** was isolated as red-brown powder (0.055 g, 9%). mp >300 °C. ¹H NMR (CDCl₃, 500 MHz): δ 10.33 (s, 2H), 9.41 (d, *J* = 4.6 Hz, 2H), 9.40 (d, *J* = 4.6 Hz, 2H), 9.39 (m, 1H), 9.16 (d, *J* = 4.6 Hz, 2H), 9.14 (dd, *J*₁ = 4.8 Hz, *J*₂ = 0.8 Hz, 1H), 9.10 (d, *J* = 4.6 Hz, 2H), 8.77 (d, *J* = 8.1 Hz, 1H), 8.69 (m, 1H), 8.23 (m, 3H), 7.98 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.39 (ddd, *J*₁ = 7.6 Hz, *J*₂ = 4.6 Hz, *J*₃ = 1.2 Hz, 1H), 1.65 (s, 9H), -3.11 (s, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 156.1, 154.8, 151.2, 150.8, 149.6, 147.7, 147.5, 146.3, 145.5, 145.3, 138.3, 137.4, 134.9, 132.4, 131.8, 131.7, 130.4, 130.0, 127.2, 124.2, 124.1, 122.0, 120.4, 115.4, 105.7, 35.1, 31.9. HRMS (MALDI-TOF): *m/z* calcd for C₄₀H₃₃N₆, 597.2767 [M + H]⁺; found 597.2778. UV-vis (THF): λ_{max}/nm (ε, 10³ M⁻¹ cm⁻¹) = 406 (320.2), 501 (15.1), 534 (6.3), 574 (5.0), 630 (2.1). IR ν_{max}/cm⁻¹: 3266, 2952, 1581, 1537, 1457, 1384, 1270, 1241, 1189, 1145, 1093, 1062, 1051, 987, 956, 854, 781, 740, 690, 568. Anal. Calcd for C₄₀H₃₂N₆: C, 80.51; H, 5.41; N, 14.08. Found: C, 80.61; H, 5.52; N, 14.19.

5-(4-*tert*-butyl-phenyl)-15-(4-bipyridyl)-porphyrin zinc (2b): Free-base porphyrin **1b** (0.030 g, 0.05 mmol) was placed in a 100 mL round-bottom flask and 20 mL of CH₂Cl₂/THF (1:2) was added. The mixture was treated with a MeOH (10 mL) solution of Zn(CH₃COO)₂·2H₂O (0.110 g, 0.5 mmol) and stirred at 50°C for 8h and then at room temperature for 12 h. After solvent evaporation, the residue was extracted with CH₂Cl₂/H₂O (3×50 mL) and then THF (60 mL) was added in the organic phase in order to ensure porphyrin's solubility. The red solution was dried over anhydrous Na₂SO₄ and the solvent was removed in a rotary evaporator. Metallated porphyrin **2b** was collected as a dark purple solid (0.027 g, 93%). mp >300 °C. ¹H NMR (CDCl₃, 500 MHz): δ 10.23 (s, 2H), 9.38 (t, *J* = 4.3 Hz, 4H), 9.29 (s, 1H), 9.18 (d, *J* = 4.3 Hz, 2H), 9.08 (d, *J* = 4.3 Hz, 2H), 9.06 (d, *J* = 4.5

Hz, 1H), 8.68 (d, $J = 8.0$ Hz, 1H), 8.63 (d, $J = 3.5$ Hz, 1H), 8.18 (m, 3H), 7.95 (t, $J = 7.5$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.36 (m, 1H), 1.66 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 156.3, 154.4, 152.4, 150.50, 150.47, 149.7, 149.5, 149.1, 147.6, 139.6, 137.3, 134.7, 134.6, 133.1, 132.3, 131.8, 129.8, 127.1, 124.1, 123.8, 121.9, 121.1, 116.4, 106.5, 35.1, 31.9. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{40}\text{H}_{31}\text{N}_6\text{Zn}$, 659.1902 $[\text{M} + \text{H}]^+$: found 659.1911. UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ (ϵ , $10^3\text{M}^{-1}\text{cm}^{-1}$) = 413 (348.7), 543 (15.1), 580 (8.4). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 2952, 1585, 1540, 1457, 1390, 1259, 1189, 1147, 1105, 1056, 987, 902, 848, 777, 723, 700, 572. Anal. Calcd for $\text{C}_{40}\text{H}_{30}\text{N}_6\text{Zn}$: C, 72.78; H, 4.58; N, 12.73. Found: C, 72.86; H, 4.49; N, 12.61.

5-(4-*tert*-butyl-phenyl)-10-bromo-15-(4-bipyridyl)-20-bromo-porphyrin zinc (3b): To a solution of zinc-metallated porphyrin **2b** (0.027 g, 0.04 mmol) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (1/2 v/v, 40 mL), a solution of NBS (0.0153 g, 0.08mmol) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (1/2 v/v, 10 mL) was slowly added at 0°C . The mixture was stirred for 60 min, while checking the reaction progress with TLC, and then acetone (10 mL) was added to quench the reaction. After removing half of the solvent volume under reduced pressure, di-brominated porphyrin **3b** was isolated by filtration as purple, microcrystalline solid (0.021 g, 64%). mp $>300^\circ\text{C}$. ^1H NMR ($\text{THF}-d_8$, 500 MHz): δ 9.70 (d, $J = 4.7$ Hz, 2H), 9.67 (d, $J = 4.7$ Hz, 2H), 9.37 (m, 1H), 9.06 (d, $J = 4.6$ Hz, 1H), 8.95 (d, $J = 4.7$ Hz, 2H), 8.91 (d, $J = 4.7$ Hz, 2H), 8.87 (d, $J = 8.0$ Hz, 1H), 8.60 (d, $J = 3.8$ Hz, 1H), 8.15 (d, $J = 3.2$ Hz, 1H), 8.11 (d, $J = 8.3$ Hz, 2H), 7.99 (dt, $J_1 = 7.9$ Hz, $J_2 = 1.8$ Hz, 1H), 7.85 (d, $J = 8.3$ Hz, 2H), 7.38 (m, 1H), 1.65 (s, 9H). ^{13}C NMR ($\text{THF}-d_8$, 75 MHz): δ 156.9, 155.2, 152.2, 151.7, 151.2, 151.0, 150.9, 150.6, 149.9, 148.1, 140.4, 137.5, 135.3, 135.2, 134.1, 133.9, 133.3, 130.4, 127.0, 124.6, 124.2, 123.6, 121.9, 119.6, 105.3, 35.4, 31.8. HRMS (MALDI-TOF): m/z calcd for $\text{C}_{40}\text{H}_{29}\text{Br}_2\text{N}_6\text{Zn}$, 815.0112 $[\text{M} + \text{H}]^+$: found 815.0123. UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ (ϵ , $10^3\text{M}^{-1}\text{cm}^{-1}$) = 430 (361.6), 565 (15.7), 605 (8.8). IR $\nu_{\text{max}}/\text{cm}^{-1}$: 2946, 1581, 1540, 1454, 1386, 1319, 1282, 1108, 1074, 1022, 997, 908, 865, 808, 788, 730,

670, 574. Anal. Calcd for $C_{40}H_{28}Br_2N_6Zn$: C, 58.74; H, 3.45; N, 10.28. Found: C, 58.63; H, 3.53; N, 10.39.

NMR spectra: 1H NMR spectra were recorded on Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers as solutions in deuterated solvents by using the solvent peak as the internal standard.

Melting point: Buchi M-560 melting point instrument was used to for the determination of the melting points of all newly prepared products.

Mass spectra: High-resolution mass spectra (HRMS) were recorded on a Bruker Ultrafle Xtreme MALDI-TOF/TOF spectrometer.

FTIR spectra: FTIR were recorded on a Perkin Elmer 16PC FTIR spectrometer.

X-ray: Single crystal X-ray crystallographic data were recorded on a STOE IPDS II diffractometer equipped with an image plate detector.

Electrochemistry: Cyclic voltammetry experiments were carried out at room temperature using an Auto Lab PGSTAT20 potentiostat and appropriate routines available in the operating software (GPES, version 4.9). Measurements were carried out in freshly distilled and deoxygenated THF, with a scan rate 100 mV/s, with a solute concentration of 1.0 mM, in the presence of tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte. A three-electrode cell setup was used with a platinum working electrode, a saturated calomel (SCE) reference electrode, and a platinum wire as counter electrode.

Photophysical measurements: UV-vis absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. Emission spectra were recorded on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red sensitive WRE-343 photomultiplier tube (wavelength range 200-850 nm). For the UV-Vis spectra on TiO_2 film, the TiO_2 (~12 μm) was immersed into a dye solution THF/EtOH (2:1 v/v) mixture containing chenodeoxycholic acid (CDCA, 0.4 mM) for 12 h and then washed. Then the dye

loaded TiO₂ film was put on the sample assembly for thin film absorption in the UV-absorption spectrophotometer and recorded the absorption spectra at the interval of 0.5 nm. For the emission measurements on the TiO₂ films, the films were placed diagonally in an appropriate holder. The excitation beam was directed 45° to the film surface and the emitted light was monitored from the front face of the sample

Computational Methods: Density functional theory (DFT) calculations⁵⁷ were performed using the GAUSSIAN 03 program suite.⁵⁸ Geometry optimizations in gas phase and in THF were carried out by employing Becke three parameter exchange in conjunction with Lee-Yang-Parr correlation functional (B3LYP).^{59, 60} For the geometry optimizations, the LANL2DZ basis set was used for Zn atoms and the 6-31G(d) basis sets for lighter atoms. The input geometries were modeled using the ChemCraft software.⁶¹ The optimized minimum-energy structures were verified as stationary points on the potential energy surface by vibrational frequency analysis calculation. Solvent effects were evaluated by using the polarizable continuum model (PCM) implemented on Gaussian 03, in which the cavity is generated via overlapping spheres, previously developed by Tomasi.^{62, 63} Computed structures and molecular orbitals were visualized and analyzed using ChemCraft software.

Cell Fabrication: Electrodes of DSSCs were based on fluorine doped tin oxide (FTO) glass substrates, which were pre-cleaned with deionized water, acetone, and ethanol and then dried in ambient conditions. TiO₂ working electrodes and Pt coated counter electrodes were fabricated as reported earlier.⁶⁴ Dye-sensitized photoanodes were obtained by immersing the TiO₂ electrode into 0.3 mM solutions of porphyrins in a THF/EtOH (2:1 v/v) mixture containing chenodeoxycholic acid (CDCA, 0.4 mM) for 12 h. We have used CDCA to reduce the dye aggregation, as most of the porphyrin dye undergoes dye aggregation when adsorbed on to TiO₂ film. The electrodes were assembled into a sealed sandwiched type cell by heating at 80°C with a thermal adhesive film (25 µm thick surlyn) as spacer between the

electrodes. A drop of electrolyte solution containing 0.05 M I_2 , 0.5 M LiI, 0.5 M 1,2-dimethyl-3-n-propylimidazolium iodide and 0.5 M *tert*-butyl-pyridine (TBP) in a CH_3CN /valeronitrile (85/15 v/v) mixture, was placed space between the electrodes, through a hole predrilled in the counter electrode and then the hole was again sealed with surlyn polymer and cover glass.

Photovoltaic measurements: The current-voltage (J - V) characteristics of DSSCs under illumination were measured by a Keithley source meter, and a solar simulator coupled with a 150 W xenon lamp and an AM optical filter to give 100 mW/cm² illumination at the DSSC surface. The active area of the DSSCs was 0.20 cm². Incident photon to current conversion efficiency (IPCE) data were obtained as a function of different wavelengths by using a xenon lamp, a monochromator, and a Keithley source meter under constant illumination intensity at each wavelength. Intensity calibration for IPCE data was performed using a standard silicon photo-diode. Current was measured in short circuit conditions. Electrochemical impedance (EI) spectra, in dark and under illumination, were recorded using an electrochemical workstation (Autolab PGSTAT) with a frequency response analyzer. A frequency range from 10 mHz to 100 kHz and an alternative-current potential of 10 mV were used. A direct-current bias equivalent to the open-circuit voltage of DSSC was applied. Electrochemical impedance spectroscopy (EIS) data were analyzed using Z-View software with an appropriate equivalent circuit

RESULTS AND DISCUSSION

Synthesis and characterization. As shown in Scheme 1, both Znpor-py (**3a**) and Znpor-bpy (**3b**) consist of zinc-metallated porphyrin units which are substituted at opposite 5 and 15 *meso* positions of the macrocyclic rings with a 4-*tert*-butyl-phenyl group and either a pyridyl or a bipyridyl group, while at the other two *meso* positions bromine atoms are present. The pyridyl-containing moieties of both porphyrins have the potential to act as anchoring groups

onto the TiO₂ surface of DSSC electrodes through Lewis acid-base interactions. Considering the 4-*tert*-butyl-phenyl group as electron donating (D) group and the pyridyl-containing moieties as electron accepting (A) groups, both porphyrins can be regarded as dyes with a donor- π -acceptor (D- π -A) molecular architecture.

The initial step of the synthesis of Znpor-py (**3a**) involved the preparation of porphyrin **1a** (Scheme 2). This 5,15-AB-type porphyrin was synthesized by a mixed condensation reaction of dipyrromethane with two different aldehydes,⁶⁵ namely 4-*tert*-butyl-benzaldehyde and 4-pyridyl-aldehyde, which was acid-catalyzed by BF₃·OEt₂, in a CH₂Cl₂/MeOH mixture for 3 days, followed by addition of DDQ. Due to the fact that the pyridyl group of 4-pyridyl-aldehyde has the potential to react with BF₃ and reduce its efficiency to catalyze the condensation, it is necessary to use excess BF₃·OEt₂ and long reaction time. The desired asymmetric product **1a** was chromatographically separated and isolated from the statistical mixture of the three different porphyrins that are formed, using silica gel followed by alumina column chromatography and CH₂Cl₂ as eluent, in 13% yield. Subsequent reaction of **1a** with excess of Zn(CH₃COO)₂·2H₂O in MeOH/CH₂Cl₂, at 40 °C for 24 h, resulted in the preparation of zinc-metallated porphyrin **2a**. Di-brominated porphyrin **3a** was obtained in 61% yield, by reaction of **2a** with two equivalents of NBS in CH₂Cl₂ at 0°C. Compound Znpor-bpy (**3b**) was prepared following an analogous synthetic route as in the case of porphyrin **3a** (Scheme 2). Initially, porphyrin **1b** was synthesized by acid catalyzed mixed condensation reaction of dipyrromethane with 4-*tert*-butyl-benzaldehyde and bipyridyl-4-aldehyde. After metalation reaction with Zn(CH₃COO)₂·2H₂O and bromination reaction with NBS, the final product **3b** was obtained.

X-ray crystallography. Single crystals of porphyrin **2b** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a CH₂Cl₂/THF solution of **2b**. The compound was crystallized in the form of its THF adduct. Crystal structure and refinement parameters

are given in Table 1. A drawing of the structure is shown in Figure 1, while selected bond distances and angles are listed in Table 2 (full list of bond distances and angles are provided in Table S3 in Supporting Information). The structure consists of a Zn-metallated porphyrin unit in which the metal atom is coordinated by four pyrrole N-atoms. The Zn-N (pyrrole) bond lengths were found to be within the range of 2.053-2.065 Å. In general, a 4-coordinate Zn metal atom located in the center of a porphyrin unit has the ability to bind Lewis bases on both sides of the molecular framework. In the present case, there is only one THF solvent molecule axially coordinated on one side, with a Zn-O1 distance of 2.190(2) Å, resulting in a 5-coordinate, square-pyramidal geometry. The THF molecule was found to exhibit a two-fold orientation disorder (Figure S1). In this coordination environment, the Zn metal atom appears to deviate from the mean plane of the pyrrole N-atoms by 0.22 Å, as it has typically been observed in related structures.^{66, 67} The 4-*tert*-butyl-phenyl and bipyridyl groups located at opposite positions at the periphery of the porphyrin macrocycle were found to be in an almost perpendicular orientation with respect to the porphyrin framework, with dihedral angles of ~95° and ~110°, respectively.

Photophysical properties. UV-Vis absorption spectra of Znpor-py (**3a**) and Znpor-bpy (**3b**) in THF solutions are shown in Figure 2 (black color). Both compounds exhibit similar absorption profiles with typical porphyrin absorption characteristics, which include a strong Soret band appearing at 400-450 nm and moderate Q-bands at 550-650 nm. These are attributed to π - π^* transitions within the D- π -A conjugated macrocyclic porphyrin rings.²⁰

The absorption spectra of porphyrins **3a** and **3b** adsorbed onto TiO₂ films were also recorded (Figures **2a** and **2b**, red color). Both porphyrins show similar absorption profiles, indicating that their light harvesting efficiencies are very similar. Furthermore, the Soret and Q-absorption bands of the adsorbed dyes on TiO₂ films appear broader and red-shifted, with respect to the corresponding solution spectra. The broadening of the absorption bands is

attributed to the electronic coupling between the dyes and the TiO₂ semiconductor.⁶⁸⁻⁷¹ Furthermore, the absorption characteristics of the adsorbed dyes provide information for their aggregation morphology on the TiO₂ electrode. *H*-aggregates, in which molecules are aligned parallel to each other with strong intermolecular interactions, tend to induce a non-radiative deactivation process⁷² and leads to blue shift of the absorption bands. In contrast, *J*-aggregates, in which the molecules are arranged in a head-to-tail direction, induce relatively high fluorescence efficiency with a bathochromic shift in optical absorption band. The redshift observed in the absorption bands of the two porphyrins **3a** and **3b** is thought to result from the formation of *J*-aggregates on the TiO₂ surface (shown for **3a**/TiO₂ in Scheme 3).

The fluorescent emission spectra of porphyrins **3a** and **3b** in THF were also recorded and shown in Figure 3. Both the porphyrins exhibit two peaks of unequal intensities at 612 nm and 672 nm, respectively, upon excitation at 565 nm. We have also recorded the fluorescent emission spectra of porphyrins adsorbed onto TiO₂ film as shown in Figure 3. After the adsorption of porphyrin dye onto TiO₂ film, the fluorescence bands were slightly red-shifted and broadened as compared to those of the dyes in solutions. The red-shift of the fluorescence is probably due to the interaction with the nanoparticles (anchoring effect) or with other dye molecules.

Electrochemistry. In order to study the feasibility of electron injection and dye regeneration processes in the Znpor-py (**3a**) and Znpor-bpy (**3b**) sensitized solar cells, cyclic voltammetry measurements of the two porphyrins in THF solutions, using tetrabutyl ammonium tetrafluoroborate as supporting electrolyte, were performed. As shown in the cyclic voltammograms in Figure 4, both porphyrins **3a** and **3b** exhibit one oxidation process, at $E_{1/2}^{\text{ox}} = +1.23$ and $+1.21$ V vs SCE, respectively, which corresponds to removal of an electron from the π -ring system of the zinc-porphyrin, resulting in the formation of the corresponding porphyrin radical cation, and one reduction process, at $E_{1/2}^{\text{red}} = -1.11$ and -1.09

V vs SCE, respectively, which is attributed to the reduction of the porphyrin unit, forming a porphyrin radical anion.

For efficient electron injection from the excited state of a sensitizer into the TiO₂ conduction band of a DSSC, the LUMO energy level of the sensitizer (which corresponds to its first reduction potential) should be higher (more negative) than the TiO₂ conduction band edge (-0.74 V vs SCE). Both porphyrins **3a** and **3b** exhibit $E_{1/2}^{\text{red}}$ values, which are more negative than TiO₂ conduction band edge, suggesting there is sufficient driving force for electron injection from their excited state into the TiO₂ conduction band. On the other hand, in order to ensure efficient regeneration of sensitizer (after electron injection) in a DSSC, the HOMO energy level (which corresponds to its first oxidation potential) should be lower (more positive) than the redox potential of the electrolyte employed in the DSSC (0.4 V vs SCE for I₃⁻/I⁻). The oxidation potentials of both porphyrins **3a** and **3b** are more positive than the corresponding electrolyte redox potential, and therefore, regeneration of porphyrin dyes, after the electron injection, is thermodynamically feasible.⁷³

DFT calculations. In order to gain insight into the molecular and electronic structures of Znpor-py (**3a**) and Znpor-bpy (**3b**), DFT calculations at the B3LYP/6-31G(*) level of theory were performed in THF. The geometry-optimized structures of the two porphyrins are depicted in Figure 5, while their optimized coordinates are provided in Table S7 and S8 (Supporting Information). Both compounds display a planar central scaffold, which is in accordance with p- π conjugated systems, with the Zn atoms being coplanar with the four pyrrole rings. The meso-substituents, 4-*tert*-butyl-phenyl and either pyridyl or bipyridyl groups, are in an almost perpendicular orientation with respect to the corresponding porphyrin frameworks. In the case of both dyes **3a** and **3b**, the dihedral angles of 4-*tert*-butyl-phenyl and pyridyl group regarding the porphyrin ring were found ~67°. The electron density distributions of the frontier and near frontier molecular orbitals of compounds **3a** and **3b** are

shown in Figure 6. In general, they are primarily extended over the zinc-porphyrin units and partly delocalized over the corresponding meso-substituents. For example, in case of Znpor-bpy (**3b**) (the porphyrin with the better photovoltaic performance), HOMO-1, HOMO, LUMO, and LUMO+1 are essentially porphyrin-based π molecular orbitals, which is in agreement with the Gouterman's four orbital model of porphyrins.⁷⁴ Furthermore, in HOMO and HOMO-2 there are additional contributions over the 4-*tert*-butyl-phenyl group, while in LUMO+1 and LUMO+2 there is significant delocalization over the bipyridyl group. Similar electron density distributions of the frontier molecular orbitals were also found for Znpor-py (**3a**) (Figure 6). Therefore, the calculated electron density distributions of both compounds favor intramolecular electron transfer, upon photoexcitation, from the 4-*tert*-butyl-phenyl donor (D) group to the pyridyl acceptor/anchoring (A) groups through the porphyrin π system (which is consistent with the D- π -A description of the two compounds), and promote electron injection, upon their binding onto TiO₂.

The calculated dipole moments μ of Znpor-py (**3a**) and Znpor-bpy (**3b**) were found to be 4.58 and 5.57 D, respectively (Table 3). The larger μ value for the latter implies an enhanced ability for directed intramolecular electron transfer and electron injection into TiO₂, which is in accordance with the observed longer electron lifetime and enhanced photovoltaic performance of the corresponding solar cell (see electrochemical impedance spectroscopy and photovoltaic measurements results).

The theoretically calculated HOMO-LUMO gaps for **3a** and **3b** in THF were found to be 2.719 eV, which are not significantly different from the HOMO-LUMO gaps estimated from cyclic voltammetry measurements.

FTIR spectra. To get structural information on the attachment of Znpor-py (**3a**) and Znpor-bpy (**3b**) on the TiO₂ surface of DSSCs, FTIR spectra of the two dyes in neat form and when adsorbed on TiO₂ films were recorded (as shown in Figure 7 for **3a** and **3a**/TiO₂). The

spectra of both porphyrins in pure form exhibit similar absorption characteristics, with bands for the stretching vibrations of C=C and C-N at 1602 and 1452 cm^{-1} for **3a** and 1581 and 1454 cm^{-1} for **3b**. Upon adsorption of the porphyrins onto TiO_2 , a new absorption band appears at 1634 cm^{-1} , which can be assigned to the pyridyl group coordinated to a Lewis acid site of the TiO_2 surface.^{48, 75}

Photovoltaic performance. Current-voltage (J - V) characteristics of the DSSCs sensitized by Znpor-py (**3a**) and Znpor-bpy (**3b**) are shown in Figure 8a, while the corresponding photovoltaic parameters are compiled in Table 4. The optimum values of the short circuit current J_{sc} , open circuit voltage V_{oc} , and fill factor FF parameters were found to be 8.58 mA/cm^2 , 0.63 V and 0.66 for the **3a**-based solar cell, and 10.52 mA/cm^2 , 0.69 V, and 0.70 for the **3b**-based solar cell, which correspond to overall PCE values of 3.57 and 5.08%, respectively.

A principal reason for the higher PCE value of the **3b**-based solar cell is its higher J_{sc} value, which is reflected in its higher incident photon-to-electron conversion efficiency (IPCE) response. The IPCE spectra of the two solar cells are shown in Figure 7b. In general, they exhibit very similar IPCE profiles (as shown in the normalized IPCE spectra of the DSSCs in the inset of Figure 8b), but the IPCE response of the solar cell sensitized by **3b** is higher than the IPCE response of the solar cell sensitized by **3a**. In general, the monochromatic IPCE for a DSSC is given by the expression^{7, 76}

$$\text{IPCE}(\lambda) = \eta_{\text{LHE}} \eta_{\text{inj}} \eta_{\text{cc}}$$

where η_{LHE} is the light harvesting efficiency (which is related to the absorption profile of the sensitizing dye and the amount of dye adsorbed onto the TiO_2 surface), η_{inj} is the electron injection efficiency (which is related to the electron injection rate from the excited state of the sensitizer into the TiO_2 conduction band), and η_{cc} is the charge collection efficiency (which is related to the recombination rate of injected electrons with the oxidized dye or redox couple

in the electrolyte). We have measured the dye loading onto the TiO₂ film using dye desorption method and found this is about 3.4×10^{-7} mol/cm² and 3.12×10^{-7} mol/cm² for **3a** and **3b**, respectively. Considering that the dye loading is similar for both the dyes leading to similar LHE, we assume that the major factors that lead to a higher IPCE response for the **3b**-based solar cell should be η_{inj} and η_{cc} . This can be justified by the chemical structures of the two sensitizers, since **3b** can be considered to be a molecule with a double-pyridine anchoring group, compared to the single pyridine group of **3a**, which has the potential coordinate stronger and increase the interfacial electron transfer process, and therefore leading to a higher η_{inj} value. Moreover, both DSSCs showed two times higher IPCE value at the Soret band than at the Q bands. This could be attributed to better overlapping between the LUMO+2 and LUMO+3 orbitals of the porphyrins and the TiO₂ conduction band when both dyes were excited at the of the Soret band wavelengths. As can be seen in the fluorescence spectra of porphyrin dyes adsorbed on TiO₂ (Figure 3), the fluorescence intensity was more quenched for **3b** porphyrin as compared to **3a**, also suggested the photo-induced charge transfer is more pronounced in for later, leading to higher J_{sc} and PCE for **3b** sensitized DSSC.

The enhanced photovoltaic performance of the **3b**-based solar cell is also related to its enhanced V_{oc} parameter. In general, the V_{oc} value of DSSC is determined by the potential difference between the quasi Fermi level of TiO₂ (E_{CB}) and the HOMO energy level of the redox couple (E_{redox}) in the electrolyte, as described by the following relationship.⁷⁷

$$V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q} \ln\left(\frac{N_{CB}}{n}\right) - \frac{E_{redox}}{q}$$

Where k is the Boltzmann's constant, T is the temperature, q is the electronic charge, N_{CB} is the effective electron density of states at TiO₂ conduction band edge, n is the concentration of injected electrons in TiO₂ conduction band edge. Since the same electrolyte redox couple

was used for both **3a**- and **3b**-based DSSCs, their different V_{oc} values result from differences in the quasi Fermi level of TiO_2 conduction band. The quasi Fermi level of TiO_2 is influenced by the balance between electron injection and charge recombination, i.e. the number of electrons in the TiO_2 conduction band. The higher V_{oc} value of the **3b**-sensitized DSSC could be attributed to a larger number of electrons in the TiO_2 conduction band, which results from a more effective interfacial electron injection caused by the bipyridine anchoring group. In addition, the higher V_{oc} value of the solar cell sensitized by **3b** is also determined by the recombination rate of the injection electrons with the redox active species of the electrolyte (I_3^-), as discussed in the following paragraphs.

To shed light in the relationship between the electron transfer kinetics and the corresponding photovoltaic properties of the two DSSCs, electrochemical impedance spectroscopy (EIS) measurements were carried out. The Nyquist and Bode plots for the two DSSCs in dark, under a forward bias of -0.64 V, are shown in Figures 9a and 9b, respectively. The Nyquist plots of both solar cells show three semicircles in the frequency ranges 10^5 - 10^3 , 10^3 -1, and 1 - 10^{-2} Hz which corresponds to impedances at counter electrode/electrolyte interface, TiO_2 /dye/electrolyte interface, and diffusion process in electrolyte, respectively.^{78, 79} The larger radius of the middle frequency semicircle signal of the **3b**-sensitized solar cell, compared to that of the **3a**-based solar cell, indicates a higher charge recombination resistance (R_{rec}) at the TiO_2 /dye/electrolyte interface (63 vs $42\Omega cm^2$, respectively). In other words, the **3b**-based solar cell exhibits a slower charge recombination rate, which leads to a more effective charge recombination retardation between injected electron into the TiO_2 conduction band and oxidized species (I_3^-) in the electrolyte. The characteristic middle frequency signal in the Bode phase plot of a DSSC is also related to the charge recombination rate. In particular, the reciprocal of the peak frequency maximum (f_{max}) of this signal is related to electron lifetime (τ_e) according to the relationship

$$\tau_e = \frac{1}{2\pi f_{\max}}$$

As shown in Figure 9b, the peak frequency for the **3b**-based solar cell is lower than that for the **3a**-based solar cell, which leads to a longer electron lifetime for the former cell (31 vs 18 ms for **3b** and **3a**, respectively). In other words, the DSSC sensitized by **3b** exhibits a slower charge recombination rate, which is consistent with the presence of the bipyridine anchoring group in the molecular structure of **3b** that offers more pathways for electron injection into the TiO₂ conduction band, compared to the simple pyridine group in **3a**.

These results are further supported by measurement of the *J-V* characteristics of the two DSSCs under dark conditions (Figure 10), since the dark current is a measure of the recombination process in a DSSC. Due to the fact that the dark current of the **3b**-based DSSC is found to be lower than that of the **3a**-based DSSC, the former device exhibits a higher charge recombination resistance at the TiO₂/dye/electrolyte interface.

As mentioned above, the reason for the enhanced photovoltaic performance of the **3b**-sensitized solar cell, compared to the **3a**-based solar cell, can be associated with the molecular structures of the corresponding sensitizers. Since the two porphyrins exhibit very similar light absorption characteristics, their difference results only from the anchoring groups they use for attachment to the TiO₂ photoanodes. Both compounds are bound to the acid sites of TiO₂ through their *N*(pyridyl) atoms. It has been recently shown that *N*(pyridyl) containing anchoring groups provide efficient adsorption of the sensitizers onto the TiO₂ surface and support an excellent electronic coupling between the levels of the excited sensitizer and those of TiO₂.^{34, 50} The presence of bipyridyl group in **3b**, which offers two effectively bound pyridyl groups, in contrast to only one pyridyl group in **3a**, results in more effective binding and formation of a more compact layer of **3b** onto the TiO₂ surface, and provides more electron transfer pathways to the TiO₂ surface, leading to a faster and more efficient electron injection process (Scheme 4), which is demonstrated by its longer electron

lifetime. The coordination geometries of the two dyes onto TiO_2 surface might also play a significant role. The presence of a pyridyl group in Znpor-py (**3a**) results in a perpendicular edge-to-face attachment of the porphyrin unit with respect to the TiO_2 surface, while in case of Znpor-bpy (**3b**), the two pyridyl groups of the bipyridyl anchoring moiety result in a coordination geometry with a slightly tilted porphyrin unit with respect to the TiO_2 surface. Considering that in both cases porphyrin units form *J*-aggregates upon their adsorption onto TiO_2 (see Photophysical measurements), in case of the **3b**-sensitized solar cell the tilted porphyrin units form a more compact hydrophobic layer at the TiO_2 surface than in the **3a**-based solar cell, which causes retardation of the I_3^- diffusion onto the TiO_2 electrode and results in a more effective suppression of charge recombination (RC) between the injected electron and electrolyte redox couple (Scheme 4). Nevertheless, advanced spectroscopic techniques, in combination with computational studies, are needed in order to investigate in detail the relationship between adsorption geometry and electron transfer between the adsorbed porphyrin unit and the TiO_2 surface.

CONCLUSIONS

Herein, we present the synthesis of two porphyrins with the D- π -A molecular architecture, which are functionalized with terminal pyridyl and bipyridyl acceptor groups, namely Znpor-py (**3a**) and Znpor-bpy (**3b**). The *N*-containing units of the two porphyrins have the potential to act as anchoring groups on the TiO_2 surface, while photophysical and electrochemical measurements of the two compounds, supported by theoretical DFT calculations, revealed the presence of suitable HOMO and LUMO energy levels for utilization as sensitizers in DSSCs. Photovoltaic measurements of the corresponding DSSCs showed an enhanced photovoltaic performance for the Znpor-bpy (**3b**)-sensitized solar cell, as a result of its higher short circuit current J_{sc} and open circuit voltage V_{oc} parameters. This was attributed to the more effective

binding of the bipyridine anchoring group onto the TiO₂ surface and the formation of a more compact dye layer on the Znpor-bpy (**3b**) based solar cell photoanode, which result in higher charge injection efficiency, and more effective suppression of recombination of the injected electrons with I₃⁻ in the electrolyte. These arguments are supported by EIS measurements, which show higher charge recombination resistance R_{rec} , and longer electron lifetime τ_e for the Znpor-bpy (**3b**)-based solar cell.

ASSOCIATED CONTENT

Supporting Information. CIF for **2b** (THF), ORTEP diagram and Tables with X-ray crystallographic information for **2b** (THF), ¹H NMR and ¹³C NMR spectra of compounds **1a**, **2a**, **3a**, **1b**, **2b**, and **3b**, and optimized coordinates from DFT calculations for **3a** and **3b**.

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ACKNOWLEDGEMENT

Financial support from the European Commission (FP7-REGPOT-2008-1, Project BIOSOLENUTI No 229927) and the Special Account for Research of the University of Crete are greatly acknowledged.

Table 1. Crystal structure and refinement parameters for **2b** (THF).

empirical formula	C ₄₄ H ₃₈ N ₆ OZn	
formula weight	732.17	
crystal system	monoclinic	
space group	C2/c	
unit cell dimensions	a = 21.201(7) Å b = 10.863(2) Å c = 32.160(6) Å	α = 90° β = 98.94(4)° γ = 90°
volume	7317(3) Å ³	
Z	8	
density (calculated)	1.329 g/cm ³	
absorption coefficient	0.715 mm ⁻¹	
reflections collected	47595	
data / restraints / parameters	9536 / 0 / 509	
final R indices [I>2σ(I)]	R1 = 0.0680, wR2 = 0.0981	
goodness-of-fit on F ²	1.035	

Table 2. Selected bond distances and angles for **2b** (THF).

Bond distances (Å)			
Zn1–N1	2.053(3)	Zn1–N4	2.065(3)
Zn1–N3	2.055(3)	Zn1–O1	2.190(2)
Zn1–N2	2.062(3)		
Bond angles (deg)			
N1–Zn1–N3	165.88(9)	N3–Zn1–N4	89.93(11)
N1–Zn1–N2	90.13(12)	N2–Zn1–N4	168.88(9)
N3–Zn1–N2	88.43(12)	N1–Zn1–O1	95.50(11)
N1–Zn1–N4	88.77(12)	N3–Zn1–O1	98.61(11)
C6–C5–C21–C22	95.1(4)	C14–C15–C31–C32	113.9(4)

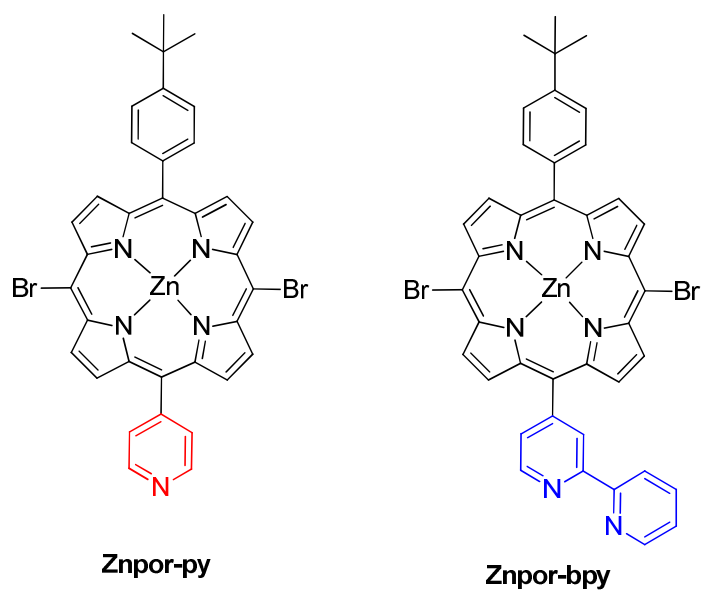
Table 3. DFT calculated properties of Znpor-py (**3a**) and Znpor-bpy (**3b**).

Compound	HOMO/eV	LUMO/eV	HOMO-LUMO gap/eV	Dipole moment μ /D
Znpor-py (3a)	-5.353	-2.634	2.719	4.58
Znpor-bpy (3b)	-5.360	-2.641	2.719	5.57

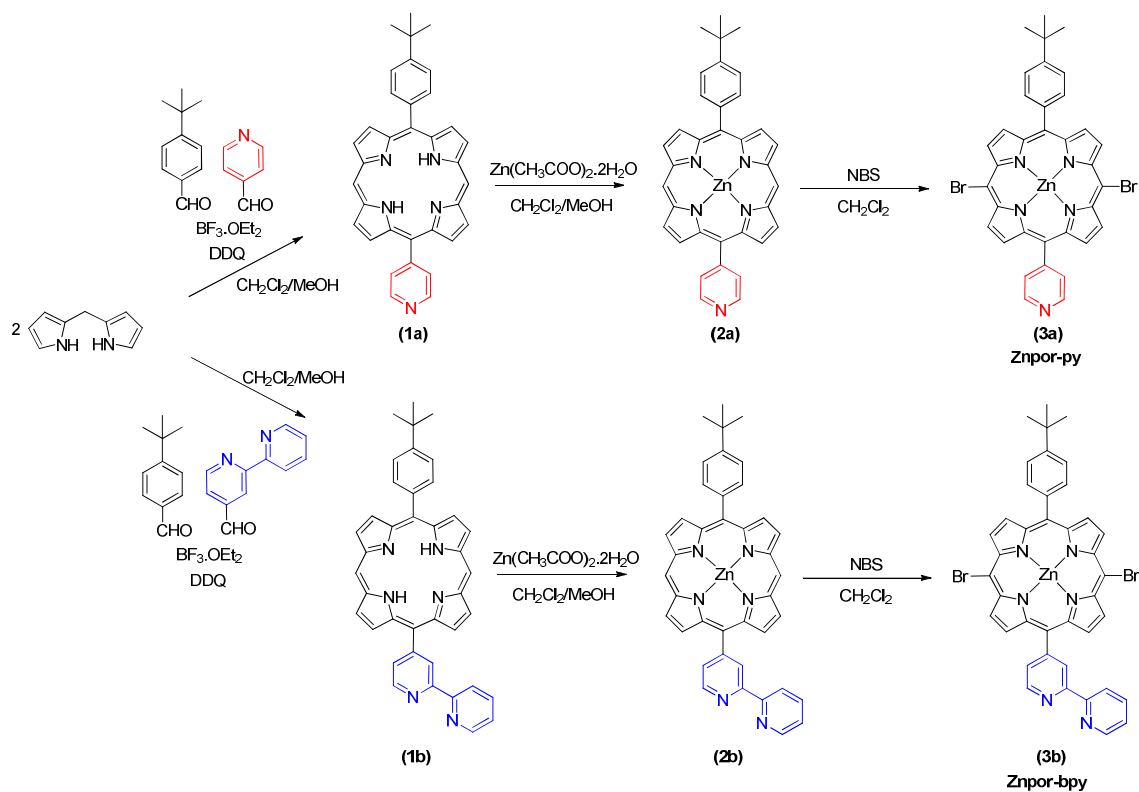
Table 4. Photovoltaic and electrochemical impedance spectroscopy parameters of DSSCs sensitized by Znpor-py (**3a**) and Znpor-bpy (**3b**).

DSSC sensitized by:	$J_{sc}/\text{mA}/\text{cm}^2$ ^[a]	V_{oc} ^[b] /V	FF ^[c]	PCE/% ^[d]	$R_{rec}/\Omega\text{cm}^2$ ^[e]	$R_{tr}/\Omega\text{cm}^2$ ^[f]	τ_e/ms ^[g]
Znpor-py (3a)	8.58	0.63	0.66	3.57 (3.48) ^[i]	42	34	18
Znpor-bpy (3b)	10.52	0.69	0.70	5.08 (4.96) ^[i]	63	23	31

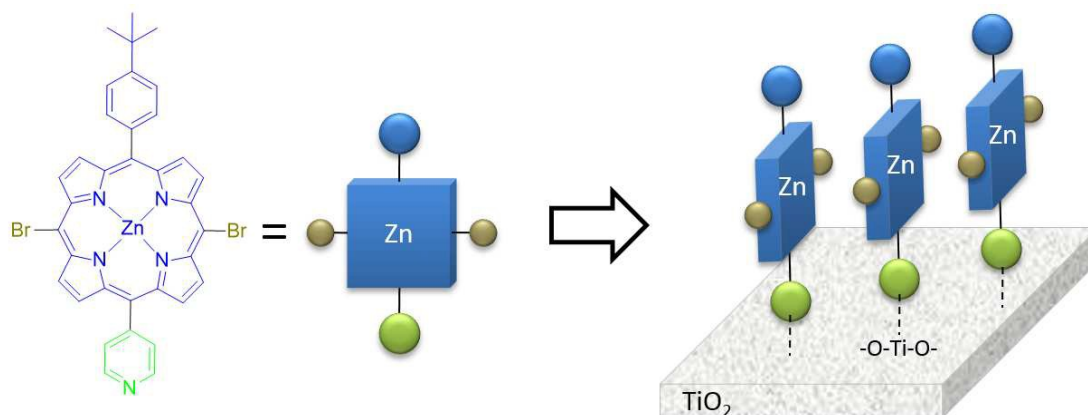
[a] short circuit current, [b] open circuit voltage, [c], fill factor, [d] photoconversion efficiency, [e] charge recombination resistance at the TiO₂/dye/electrolyte interface, [f] charge transport resistance, [g] electron lifetime and [i] average of eight devices.



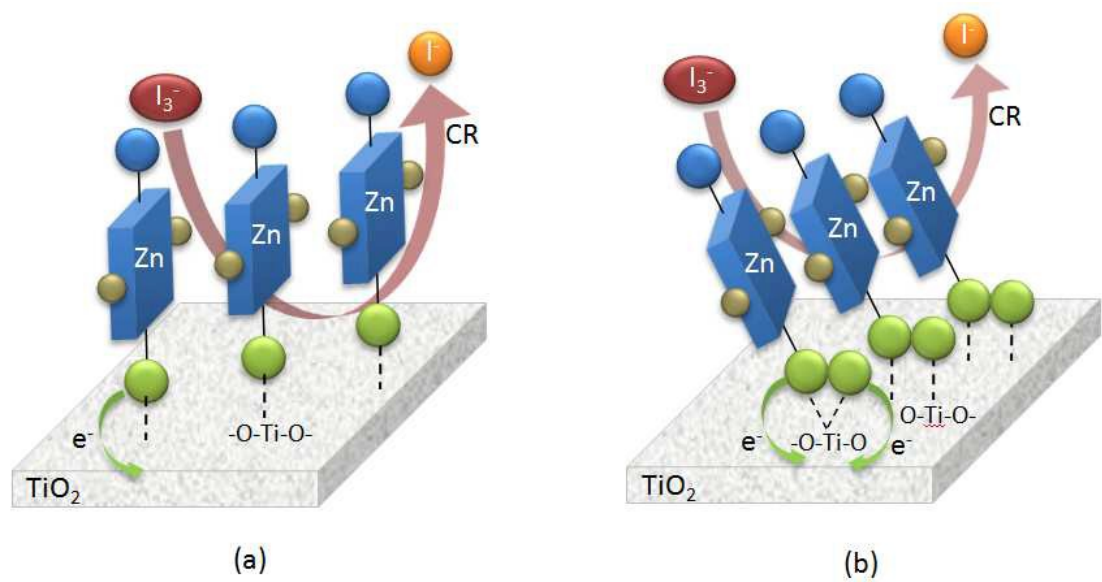
Scheme 1. Chemical structures of Znpor-py (**3a**) and Znpor-bpy (**3b**).



Scheme 2. Synthetic routes for the preparation of Znpor-py (**3a**) and Znpor-bpy (**3b**).



Scheme 3. Schematic representation of *J*-aggregate formation for Znpor-py (**3a**) when attached onto TiO₂ film.



Scheme 4. Schematic representation of the attachment of (a) Znpor-py (**3a**) and (b) Znpor-bpy (**3b**) onto TiO₂.

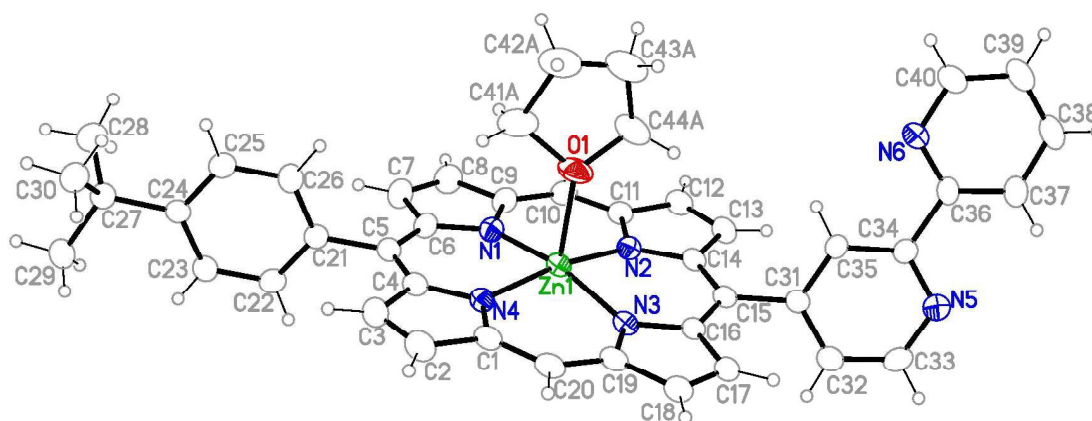


Figure 1. ORTEP representation of X-ray crystal structure of **2b** THF) with all atoms represented by thermal ellipsoids at the 35% probability level.

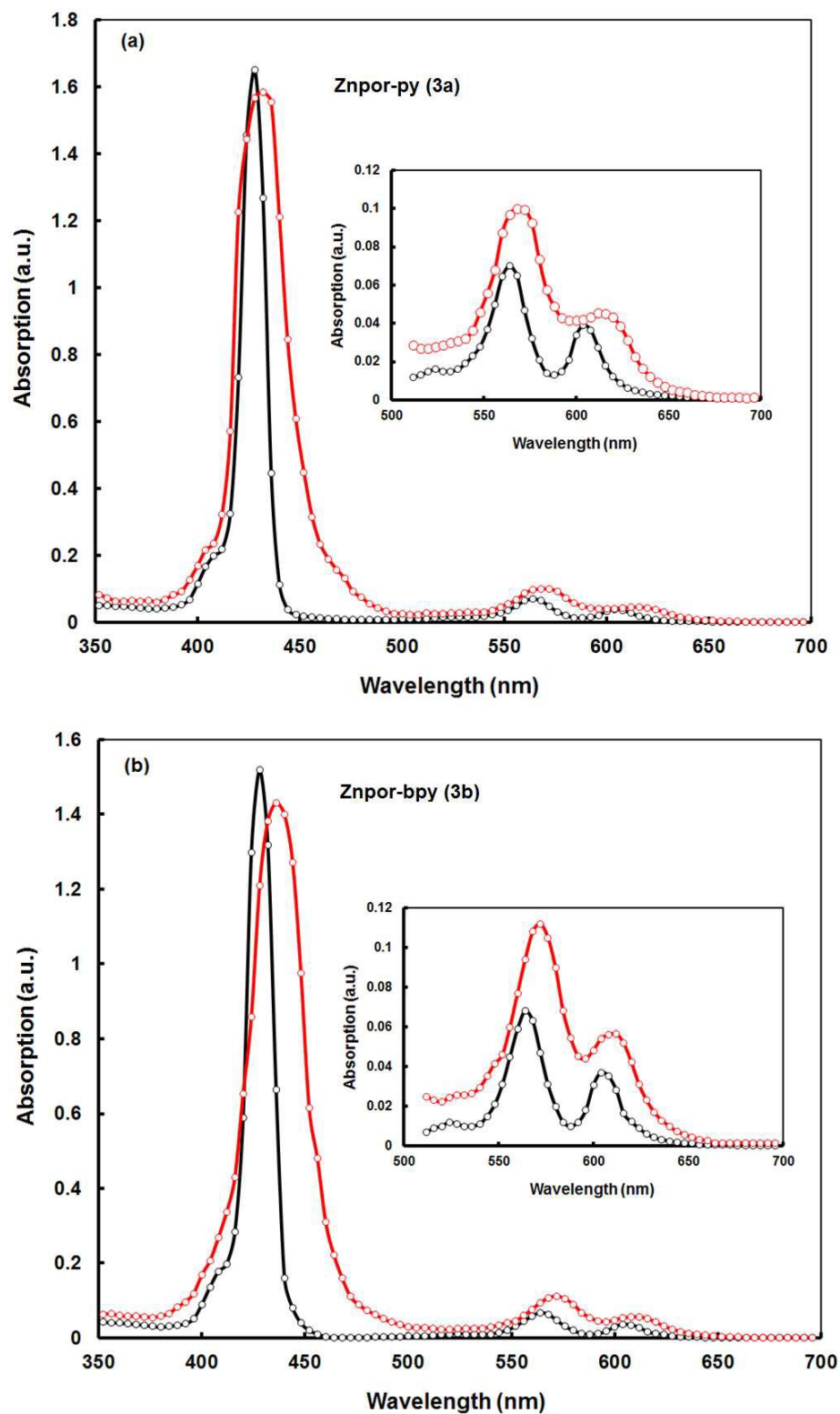


Figure 2. UV-Vis absorption spectra of (a) Znpor-py (**3a**) and (b) Znpor-bpy (**3b**) in THF solutions (black color) and adsorbed onto TiO₂ films (red color).

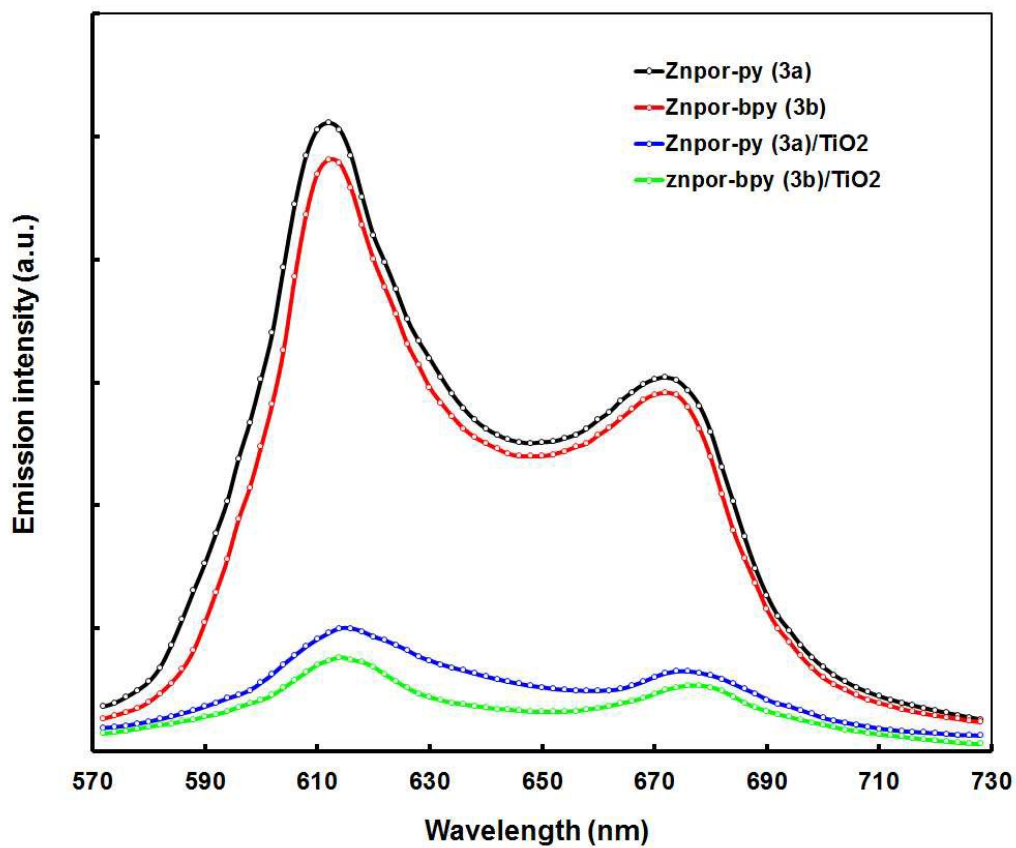


Figure 3. Fluorescence spectra of Znpor-py (**3a**) (black color) and Znpor-bpy (**3b**) (red color) in isoabsorbing THF solutions and absorbed onto TiO₂ film (Znpor-py (**3a**) (blue color) and Znpor-bpy (**3b**) (green color) upon excitation at 565 nm

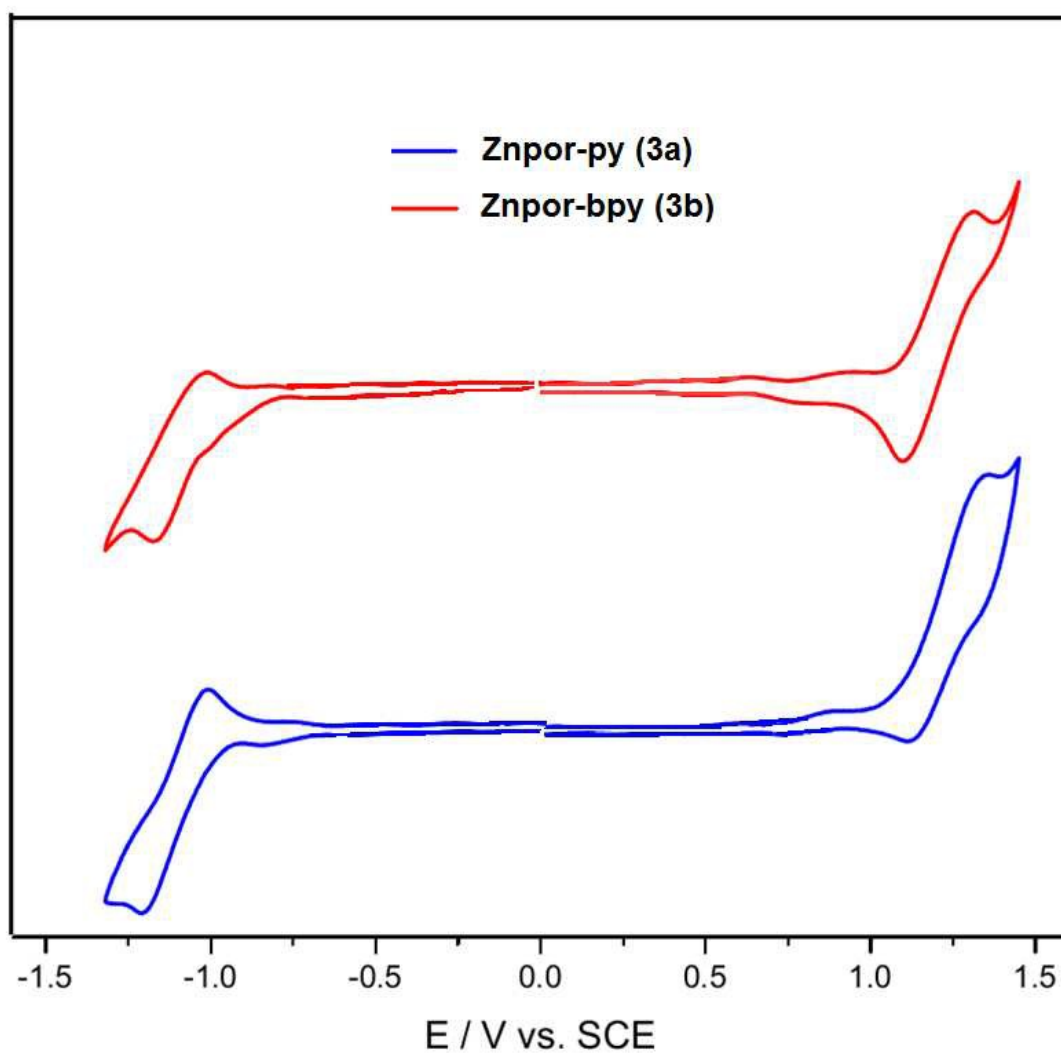


Figure 4. Cyclic voltammograms of Znpor-py (**3a**) (blue color) and Znpor-bpy (**3b**) (red color) in THF solutions.

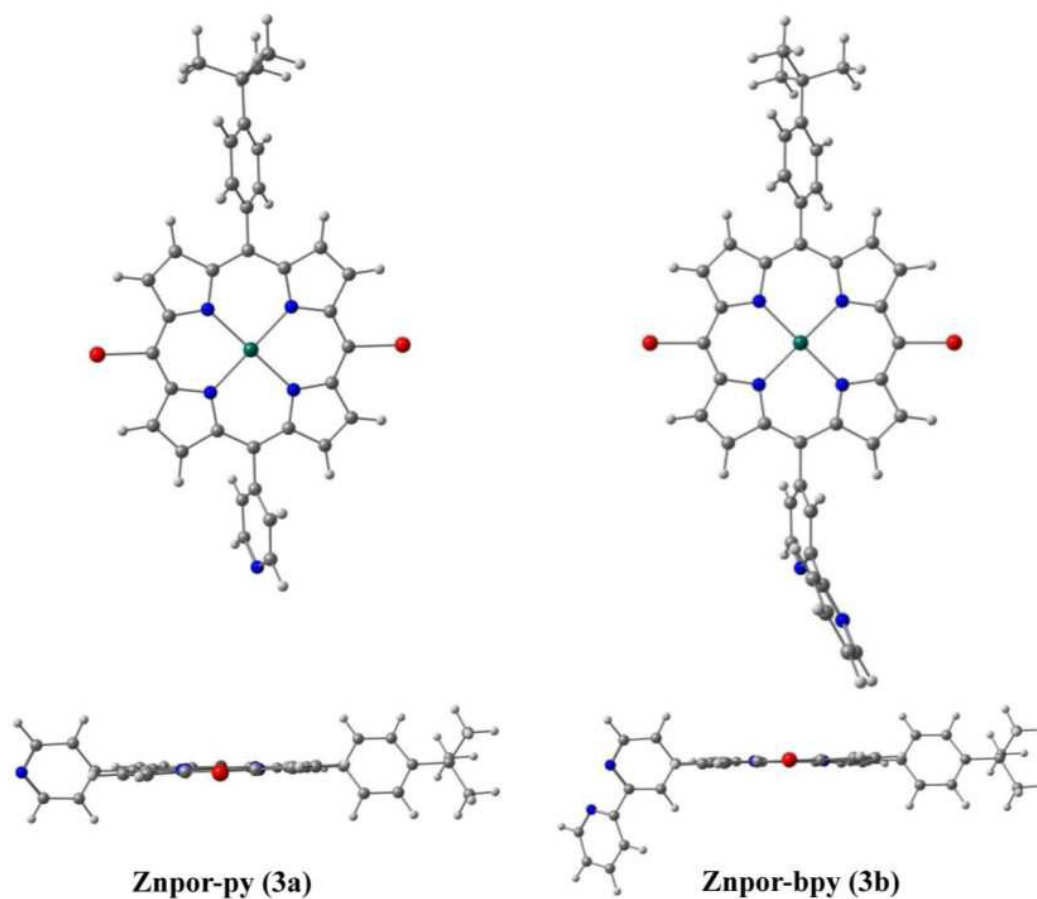


Figure 5. Different views of geometry optimized structures of Znpor-py (**3a**) and Znpor-bpy (**3b**) in THF. Carbon, nitrogen, hydrogen, bromine and zinc atoms correspond to grey, blue, white, red, green spheres, respectively.

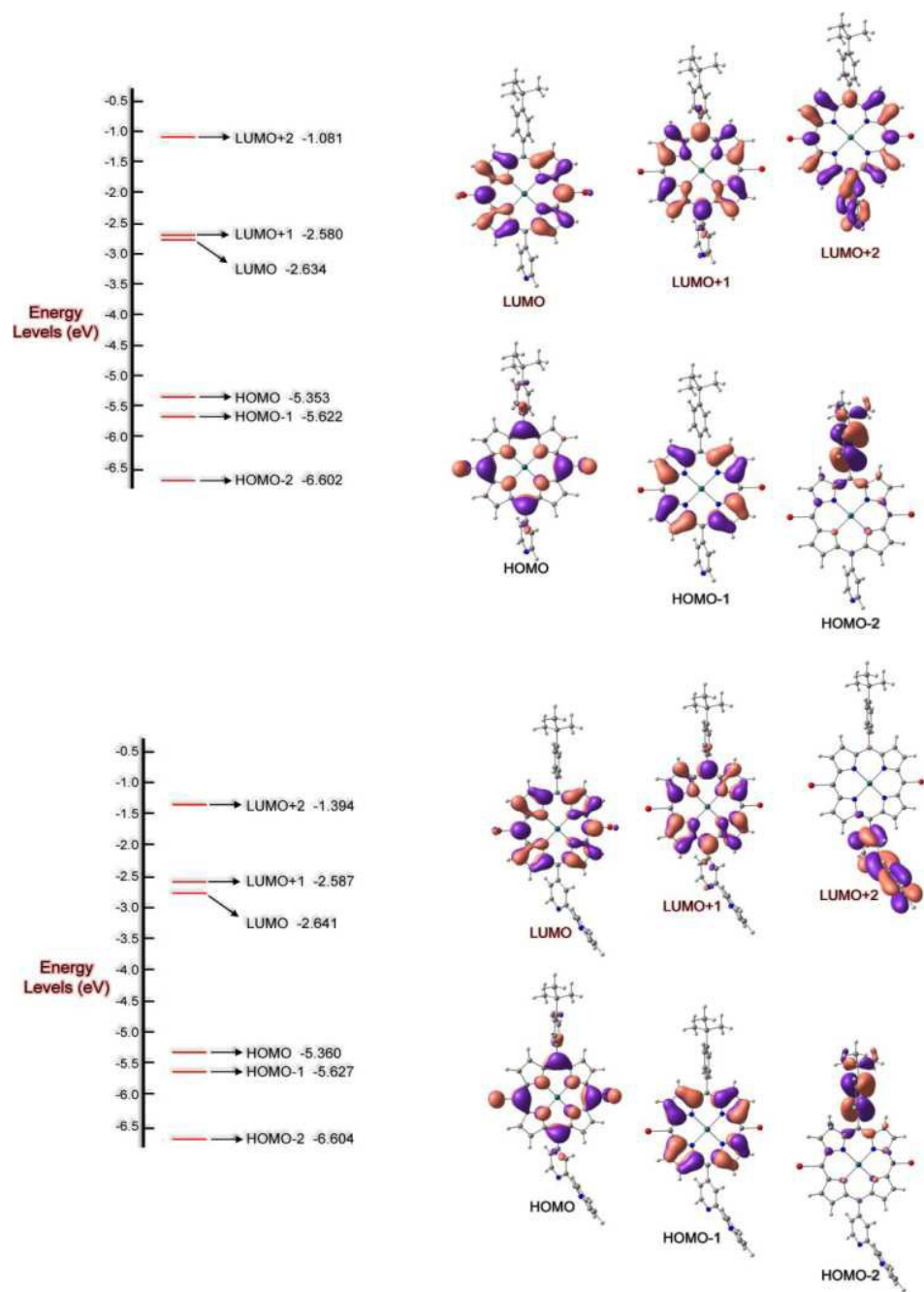


Figure 6. Frontier molecular orbitals of Znpor-py(**3a**) (upper part) and Znpor-bpy (**3b**) (lower part) and their corresponding energy levels calculated in THF.

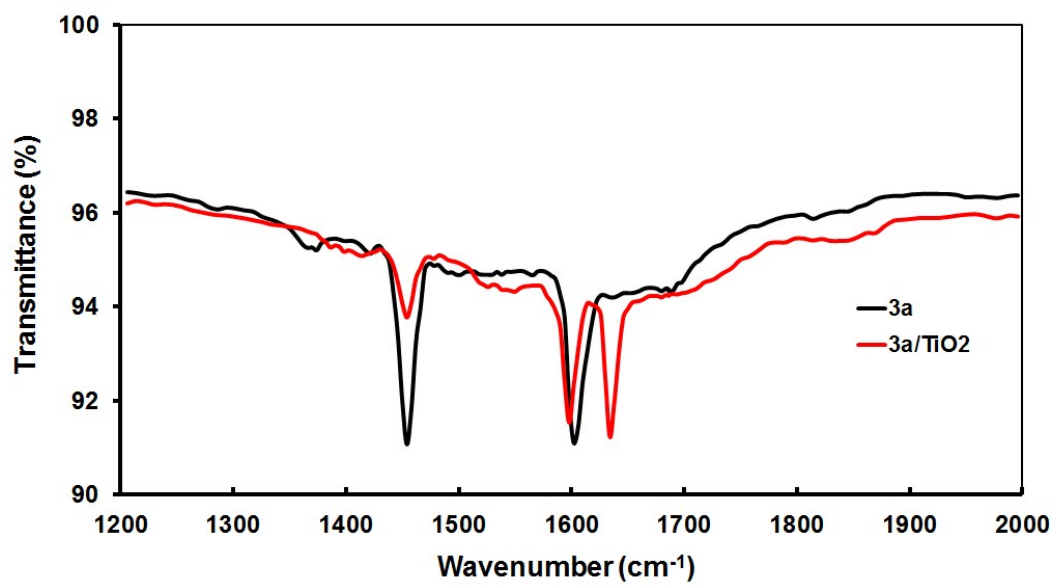


Figure 7. FTIR spectra of pristine **3a** and **3a** adsorbed onto TiO₂ film

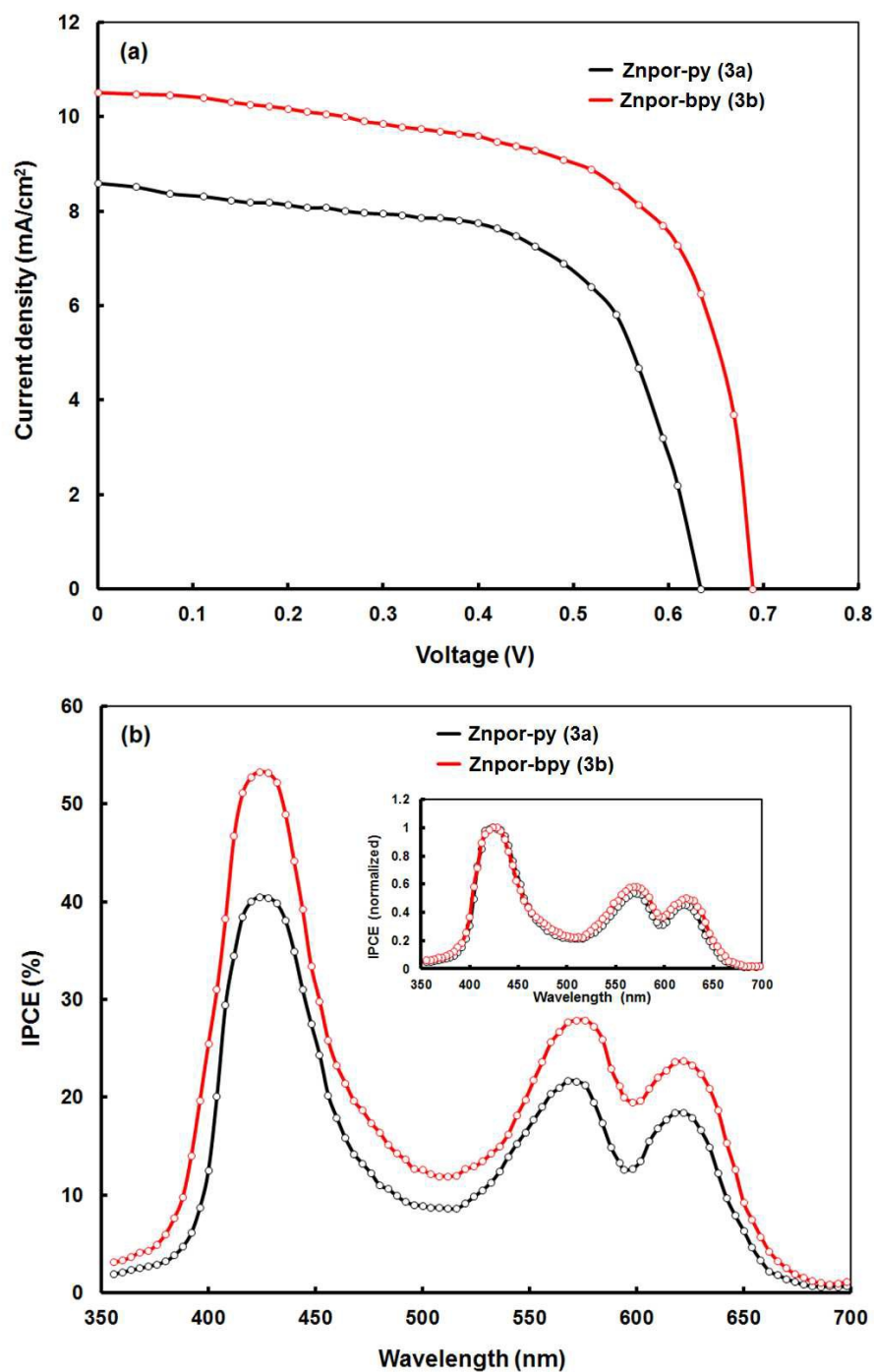


Figure 8. (a) Current-voltage (J - V) curves under illumination, and (b) IPCE spectra of DSSCs based on Znpor-py (**3a**) (black color) and Znpor-bpy (**3b**) (red color). The inset in IPCE spectra shows normalized IPCE responses at the wavelength region around the Soret and Q bands.

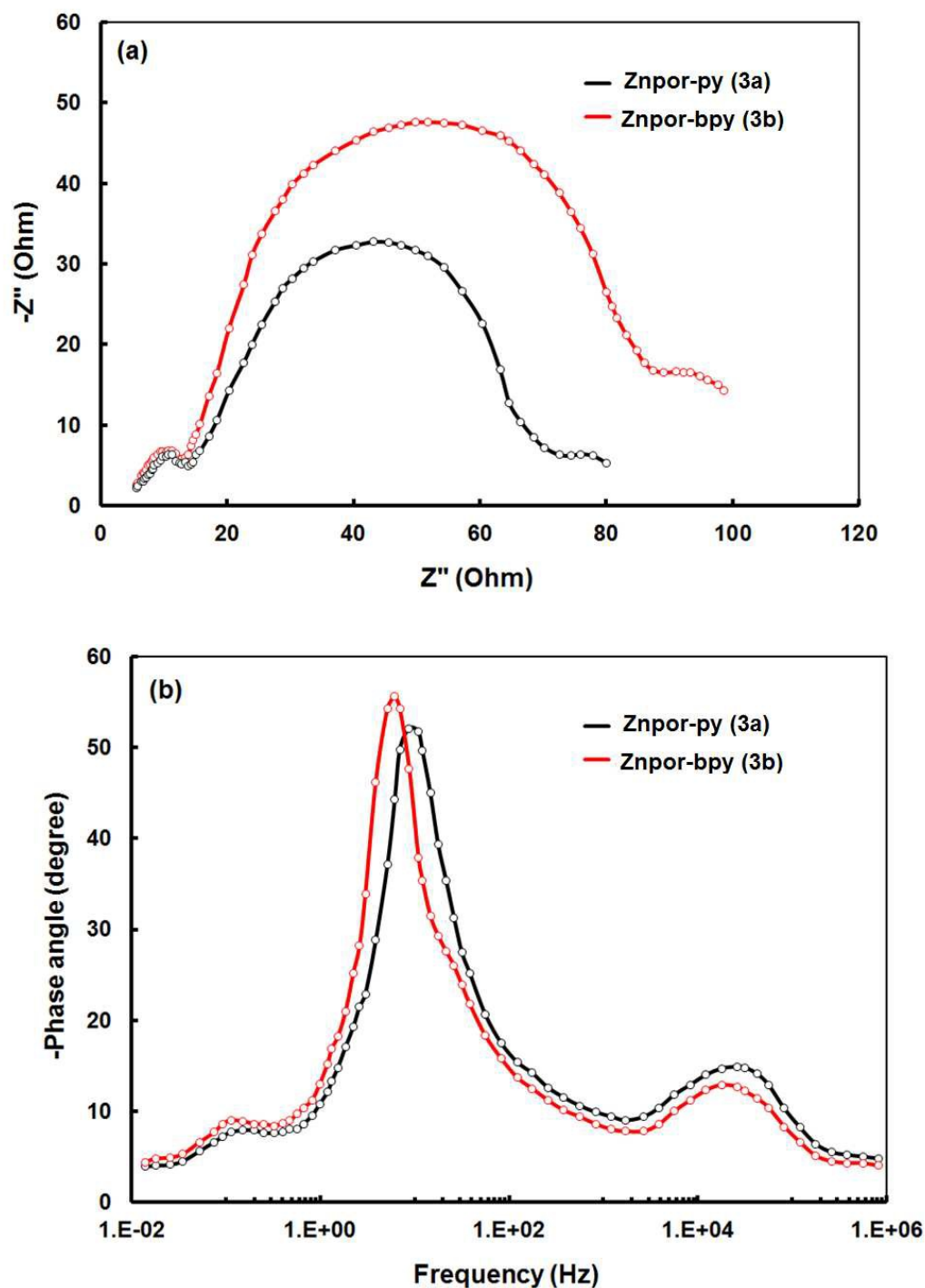


Figure 9. (a) Nyquist plots and (b) Bode phase plots of electrochemical impedance spectra of DSSCs sensitized with Znpor-py (**3a**) (black color) and Znpor-bpy (**3b**) (red color) in dark at open circuit condition.

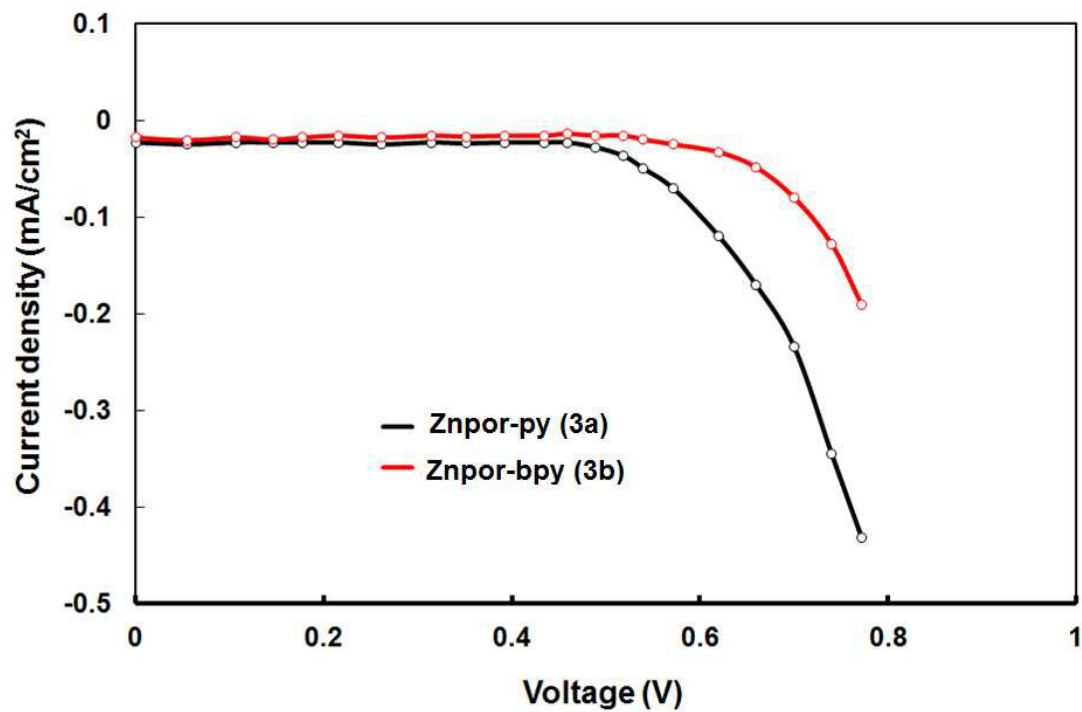
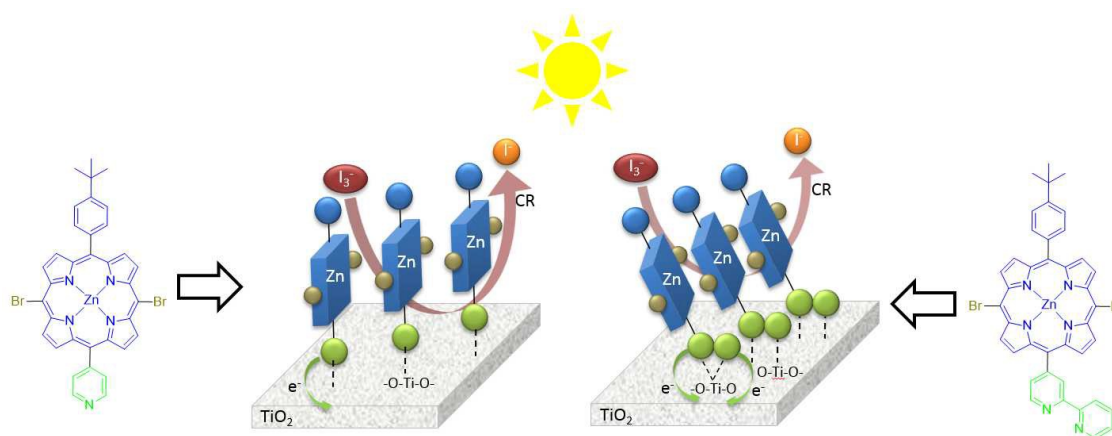


Figure 10. Current-voltage ($J-V$) curves in dark of DSSCs sensitized with Znpor-py (**3a**) (black color) and Znpor-bpy (**3b**) (red color).

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Pyridyl vs bipyridyl anchoring groups of porphyrin sensitizers for dye sensitized solar cells

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Synopsis:

Two D- π -A porphyrins, which contain either pyridyl or bipyridyl electron acceptor-anchoring groups, are synthesized and used as sensitizers for the fabrication of dye-sensitized solar cells. The device sensitized by the bipyridyl-containing dye exhibits enhanced photovoltaic performance with respect to the one that is based on the pyridyl sensitizer. This is attributed to its faster electron injection into the TiO₂ photoanode and its reduced charge recombination at the electrode/electrolyte interface, which result from the stronger binding and coordination geometry of the bipyridine anchoring group on TiO₂.

References

1. B. Oregan and M. Gratzel, *Nature*, 1991, **353**, 737-740.
2. J. N. Clifford, E. Martinez-Ferrero, A. Viterisi and E. Palomares, *Chem. Soc. Rev.*, 2011, **40**, 1635-1646.
3. A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595-6663.
4. M. Gratzel, *Acc. Chem. Res.*, 2009, **42**, 1788-1798.
5. Z. J. Ning, Y. Fu and H. Tian, *Energ. Environ. Sci.*, 2010, **3**, 1170-1181.
6. B. E. Hardin, H. J. Snaith and M. D. McGehee, *Nat. Photonics*, 2012, **6**, 162-169.
7. S. F. Zhang, X. D. Yang, Y. H. Numata and L. Y. Han, *Energ. Environ. Sci.*, 2013, **6**, 1443-1464.
8. K. Kurotobi, Y. Toude, K. Kawamoto, Y. Fujimori, S. Ito, P. Chabera, V. Sundström and H. Imahori, *Chem. -Eur. J.*, 2013, **19**, 17075-17081.
9. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa and M. Hanaya, *Chem. Commun.*, 2015, **51**, 15894-15897.
10. Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li and P. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 3799-3802.
11. F. Gao, Y. Wang, D. Shi, J. Zhang, M. K. Wang, X. Y. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Gratzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720-10728.
12. Q. J. Yu, Y. H. Wang, Z. H. Yi, N. N. Zu, J. Zhang, M. Zhang and P. Wang, *ACS Nano*, 2010, **4**, 6032-6038.
13. L. Y. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. F. Zhang, X. D. Yang and M. Yanagida, *Energ. Environ. Sci.*, 2012, **5**, 6057-6060.
14. A. Mishra, M. K. R. Fischer and P. Bauerle, *Angew. Chem. Int. Edit.*, 2009, **48**, 2474-2499.
15. M. Liang and J. Chen, *Chem. Soc. Rev.*, 2013, **42**, 3453-3488.
16. J. B. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y. J. Kim, C. Y. Yi, P. Comte, K. Pei, T. W. Holcombe, M. K. Nazeeruddin, J. L. Hua, S. M. Zakeeruddin, H. Tian and M. Gratzel, *J. Am. Chem. Soc.*, 2014, **136**, 5722-5730.
17. W. H. Zhu, Y. Z. Wu, S. T. Wang, W. Q. Li, X. Li, J. A. Chen, Z. S. Wang and H. Tian, *Adv. Funct. Mater.*, 2011, **21**, 756-763.
18. W. D. Zeng, Y. M. Cao, Y. Bai, Y. H. Wang, Y. S. Shi, M. Zhang, F. F. Wang, C. Y. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915-1925.
19. M. Zhang, Y. L. Wang, M. F. Xu, W. T. Ma, R. Z. Li and P. Wang, *Energ. Environ. Sci.*, 2013, **6**, 2944-2949.
20. H. Imahori, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809-1818.
21. W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, **248**, 1363-1379.
22. X. F. Wang and H. Tamiaki, *Energ. Environ. Sci.*, 2010, **3**, 94-106.
23. M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, **256**, 2601-2627.
24. G. E. Zervaki, V. Tsaka, A. Vatikioti, I. Georgakaki, V. Nikolaou, G. D. Sharma and A. G. Coutsolelos, *Dalton Trans.*, 2015, **44**, 13550-13564.
25. G. D. Sharma, G. E. Zervaki, K. Ladomenou, E. N. Koukaras, P. P. Angaridis and A. G. Coutsolelos, *J. Porphyrins Phthalocyanines*, 2015, **19**, 175-191.

26. V. Nikolaou, P. A. Angaridis, G. Charalambidis, G. D. Sharma and A. G. Coutsolelos, *Dalton Trans.*, 2015, **44**, 1734-1747.
27. G. E. Zervaki, E. Papastamatakis, P. A. Angaridis, V. Nikolaou, M. Singh, R. Kurchania, T. N. Kitsopoulos, G. D. Sharma and A. G. Coutsolelos, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1020-1033.
28. K. Ladomenou, T. N. Kitsopoulos, G. D. Sharma and A. G. Coutsolelos, *RSC Adv.*, 2014, **4**, 21379-21404.
29. P. A. Angaridis, T. Lazarides and A. C. Coutsolelos, *Polyhedron*, 2014, **82**, 19-32.
30. Z. E. Galateia, N. Agapi, N. Vasilis, G. D. Sharma and C. G. Athanassios, *J. Mater. Chem. C*, 2015, **3**, 5652-5664.
31. M. G. Walter, A. B. Rudine and C. C. Wamser, *J. Porphyrins Phthalocyanines*, 2010, **14**, 759-792.
32. L. L. Li and E. W. G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291-304.
33. T. Higashino and H. Imahori, *Dalton Trans.*, 2015, **44**, 448-463.
34. M. Urbani, M. Gratzel, M. K. Nazeeruddin and T. Torres, *Chem. Rev.*, 2014, **114**, 12330-12396.
35. L. Cabau, C. V. Kumar, A. Moncho, J. N. Clifford, N. Lopez and E. Palomares, *Energ. Environ. Sci.*, 2015, **8**, 1368-1375.
36. J. Luo, M. F. Xu, R. Z. Li, K. W. Huang, C. Y. Jiang, Q. B. Qi, W. D. Zeng, J. Zhang, C. Y. Chi, P. Wang and J. S. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 265-272.
37. C.-H. Wu, M.-C. Chen, P.-C. Su, H.-H. Kuo, C.-L. Wang, C.-Y. Lu, C.-H. Tsai, C.-C. Wu and C.-Y. Lin, *J. Mater. Chem. A*, 2014, **2**, 991-999.
38. A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Gratzel, *Science*, 2011, **334**, 629-634.
39. S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Gratzel, *Nature Chem.*, 2014, **6**, 242-247.
40. A. Yella, C. L. Mai, S. M. Zakeeruddin, S. N. Chang, C. H. Hsieh, C. Y. Yeh and M. Gratzel, *Angew. Chem. Int. Edit.*, 2014, **53**, 2973-2977.
41. C. Chen, X. C. Yang, M. Cheng, F. G. Zhang and L. C. Sun, *ChemSusChem*, 2013, **6**, 1270-1275.
42. B. Zietz, E. Gabrielsson, V. Johansson, A. M. El-Zohry, L. C. Sun and L. Kloo, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2251-2255.
43. T. Higashino, Y. Fujimori, K. Sugiura, Y. Tsuji, S. Ito and H. Imahori, *Angew. Chem. Int. Ed.*, 2015, **54**, 9052-9056.
44. L. Zhang and J. M. Cole, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3427-3455.
45. Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi and Y. Harima, *Angew. Chem. Int. Edit.*, 2011, **50**, 7429-7433.
46. Y. Ooyama, N. Yamaguchi, I. Imae, K. Komaguchi, J. Ohshita and Y. Harima, *Chem. Commun.*, 2013, **49**, 2548-2550.
47. Y. Ooyama, Y. Hagiwara, T. Mizumo, Y. Harima and J. Ohshita, *New J. Chem.*, 2013, **37**, 2479-2485.
48. Y. Ooyama, T. Nagano, S. Inoue, I. Imae, K. Komaguchi, J. Ohshita and Y. Harima, *Chem. -Eur. J.*, 2011, **17**, 14837-14843.
49. M. Cheng, X. C. Yang, J. J. Li, C. Chen, J. H. Zhao, Y. Wang and L. C. Sun, *Chem. -Eur. J.*, 2012, **18**, 16196-16202.
50. J. F. Lu, X. B. Xu, Z. H. Li, K. Cao, J. Cui, Y. B. Zhang, Y. Shen, Y. Li, J. Zhu, S. Y. Dai, W. Chen, Y. B. Cheng and M. K. Wang, *Chem-Asian J*, 2013, **8**, 956-962.

51. C. L. Mai, T. Moehl, C. H. Hsieh, J. D. Decoppet, S. M. Zakeeruddin, M. Gratzel and C. Y. Yeh, *ACS Appl. Mater. Interfaces*, 2015, **7**, 14975-14982.
52. D. Daphnomili, G. Landrou, S. P. Singh, A. Thomas, K. Yesudas, K. Bhanuprakash, G. D. Sharma and A. G. Coutsolelos, *RSC Adv.*, 2012, **2**, 12899-12908.
53. C. Stangel, A. Bagaki, P. A. Angaridis, G. Charalambidis, G. D. Sharma and A. G. Coutsolelos, *Inorg. Chem.*, 2014, **53**, 11871-11881.
54. J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Process Res. Dev.*, 2003, **7**, 799-812.
55. E. C. Constable, E. Figgemeier, C. E. Housecroft, J. Olsson and Y. C. Zimmermann, *Dalton Trans.*, 2004, 1918-1927.
56. B. Imperiali, T. J. Prins and S. L. Fisher, *J. Org. Chem.*, 1993, **58**, 1613-1616.
57. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A1138.
58. G. W. T. Gaussian 03; M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, rev. D.01, Gaussian, Inc., Wallingford CT, 2004.
59. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
60. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785-789.
61. D. A. Zhurko and G. A. Zhurko, *ChemCraft 1.6*, Plimus, San Diego, CA. Available at <http://www.chemcraftprog.com>.
62. M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327-335.
63. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3093.
64. G. D. Sharma, P. A. Angaridis, S. Pipou, G. E. Zervaki, V. Nikolaou, R. Misra and A. G. Coutsolelos, *Org. Electron.*, 2015, **25**, 295-307.
65. M. O. Senge, *Chem. Commun.*, 2011, **47**, 1943-1960.
66. B. S. Cheng and W. R. Scheidt, *Inorg. Chim. Acta*, 1995, **237**, 5-11.
67. W. R. Scheidt, K. M. Kadish, K. M. Smith and R. Guillard, *Academic Press*, 2000, **3**.
68. K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, *New J. Chem.*, 2003, **27**, 783-785.
69. J.-J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S. O. Kang and J. Ko, *J. Mater. Chem.*, 2008, **18**, 5223-5229.
70. K. D. Seo, M. J. Lee, H. M. Song, H. S. Kang and H. K. Kim, *Dyes Pigm.*, 2012, **94**, 143-149.
71. F. Gou, X. Jiang, R. Fang, H. Jing and Z. Zhu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 6697-6703.
72. B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410-14415.
73. C. L. Wang, C. M. Lan, S. H. Hong, Y. F. Wang, T. Y. Pan, C. W. Chang, H. H. Kuo, M. Y. Kuo, E. W. G. Diau and C. Y. Lin, *Energ. Environ. Sci.*, 2012, **5**, 6933-6940.

74. M. Gouterman, *J. Mol. Spectrosc.*, 1961, **6**, 138-163.
75. Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi and Y. Harima, *Angew. Chem. Int. Ed.*, 2011, **50**, 7429-7433.
76. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Muller, P. Liska, N. Vlachopoulos and M. Gratzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382-6390.
77. T. Marinado, K. Nonomura, J. Nissfolk, M. K. Karlsson, D. P. Hagberg, L. C. Sun, S. Mori and A. Hagfeldt, *Langmuir*, 2010, **26**, 2592-2598.
78. M. Adachi, M. Sakamoto, J. T. Jiu, Y. Ogata and S. Isoda, *J. Phys. Chem. B*, 2006, **110**, 13872-13880.
79. F. Fabregat-Santiago, J. Bisquert, E. Palomares, L. Otero, D. B. Kuang, S. M. Zakeeruddin and M. Gratzel, *J. Phys. Chem. C*, 2007, **111**, 6550-6560.