ELCTRONIC SUPPORTING INFORMATION

Multichromophoric dye-sensitized solar cells based on supramolecular zinc-porphyrin···perylene-imide dyads

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MATERIALS

Chemicals, solvents, and electrolytes were purchased from Sigma-Aldrich, Acros Organic, Cambridge Isotope Laboratory, and EMD Chemicals and used as obtained. TiO_2 T-paste (20 nm particles) was purchased from Solaronix and FTO-coated glass substrate (resistance ~10-14 Ω) was purchased from TEC Glass. **ZnP-1**, **PyPMI-2**, and **PyPDICy-3** were synthesized by following the literature procedures[S1] (Scheme S1) and purified by SiO_2 column chromatography. ^{1}H spectra were recorded at 298 K in deuterated solvents on Bruker Avance 400 MHz and 600 MHz spectrometers.

Synthesis and Characterization

All reactions were performed under N_2 atmosphere using dry solvents unless otherwise specified. Analytical thin layer chromatography (TLC) was performed on silica gel 60-F_{254} (Merck) plates and detected under UV lamp and/or by developing with I_2. Column chromatography was performed on silica gel 60 (SorbTech). ^{1}H NMR spectra were recorded at 298 K in appropriate deuterated solvents using Bruker Avance 400 MHz and Bruker Avance 600 MHz spectrometers. Electrospray Ionization mass spectra (ESI-MS) were recorded on a JEOL AccuTOF JMS-T100LC ESI mass spectrometer.

PDI 5. Commercially available tetrachloro-perylene bisanhydride **4** (5.0 g, 9.4 mmol) was heated under reflux in propionic acid (120 mL), into which octylamine (5.5 mL) was added dropwise over 30 minutes and refluxed for 12 h. After allowing the reaction mixture to cool to room temperature the mixture was poured on water and the resulting precipitate was filtered and washed with H_2O. This product was used in the next step without further purification. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.66 (s, 4H), 4.19 (t, J=7.7, 4H), 1.76 (p, J=7.7, 4H), 1.45 (p, J=7.7, 4H), 1.40 (p, J=7.7, 4H), 1.29 (m, 12H), 0.89 (t, J=7.0, 6H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 13.83, 22.64, 27.07, 28.01, 29.21, 29.30, 31.81, 40.83, 123.37, 128.64, 131.47, 132.63, 135.19, and 162.19 ppm. (MALDI-TOF) *m/z* 750 [M-].

PDI 6. PDI 5 (4.0 g, 5.3 mmol), *tert*-butyl phenol (6.4 g), and K_2CO_3 were heated under reflux in N-methyl pyrrolidinone (135 mL). After cooling the reaction mixture to room temperature, the mixture was poured on AcOH (200 mL) and stirred for 1 h. H_2O was then added to the solution and the resulting precipitate was filtered and dried under vacuum. The crude product was further purified by column chromatography on silica gel ($CHCl_3$/Hexane 3:1) to obtain 5.1 g. of PDI **6** as a purple powder (80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (s, 4H), 7.23 (d, J=8.6, 8H), 6.83 (d, J=8.7, 8H) 4.11 (t, J=7.5, 4H), 1.29 (s, 18H), 1.25 (s, 18H), 0.89–0.82 (m, 34H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 13.82, 22.61, 27.04, 28.00, 29.17, 29.27, 31.19, 31.79, 34.25, 40.50, 119.16, 119.48, 119.82, 120.47, 122.65, 126.59, 132.87, 147.31, 153.18, 155.76, and 163.12 ppm. MALDI-TOF MS (*m/z*) 1206 [M^-].

PDA 7. PDI **6** (5.0g, 4.1 mmol) and KOH (30 g) were heated under reflux in isopropanol (300 mL). After cooling the reaction mixture to room temperature, it was stirred in acetic acid (100 mL) for 1h, H_2O was added, and the resulting precipitate was filtered and dried under vacuum to obtain 3.9 g of product (95% yield). This compound was used in the next step without further purification. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.17 (s, 4H), 7.30 (d, J=8.6, 8H), 6.87 (d, J=8.6, 8H), 1.30 (s, 36H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 31.15, 31.17, 34.31, 118.67, 119.27, 121.39, 121.46, 126.69, 126.85, 133.43, 148.00, 152.60, 156.31, and 159.79 ppm. MALDI-TOF MS (*m/z*) 985 [M^-].

PyPMI-2. A mixture of PDA **7** (1.0 g, 1.01 mmol), imidazole (25 g) and pyridine (20 mL) was heated to 150 °C. 4-Aminopyridine (0.086 g, 0.91 mmol) dissolved in pyridine (15 mL) was added drop-wise to PDA **7** solution over 5 h. and the reaction mixture heated at 150 °C for 15 h. After cooling it to room temperature, the mixture was stirred in acetic acid (250 mL) for 1 h, excess water was then added and the resulting precipitate was filtered and dried under vacuum. Purification achieved by column chromatography on silica gel ($CHCl_3$/EtOAc 15:1, $CHCl_3$) to give 0.38 g of product (35% yield) as a purple powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.75 (d, J=5.9, 2H), 8.19 (s, 2H), 8.17 (s, 2H), 7.31–7.26 (m, 10H), 6.88 – 6.84 (m, 8H), 1.31 (s, 18H), 1.28 (s, 18H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 31.14, 31.16, 34.27, 34.30, 118.33, 119.13, 119.26, 119.66, 120.20, 120.68, 121.41, 121.58, 121.83, 122.58, 123.88, 126.72, 126.81, 133.08, 133.49, 143.16, 147.71, 147.87, 150.99, 152.69, 152.88, 156.03, 156.27, 159.89, and 162.56 ppm. HRMS (ESI-TOF): *m/z* for $C_{69}H_{61}N_2O_9$ calcd. 1061.43770; found 1061.43935 (M^+).

PyPMICy-3. PyPMI-2 (0.20 g, 0.18 mmol) and imidazole (10 g) were heated to 150 °C in pyridine (10 mL). Cyclohexylamine (45 µL, 0.40 mmol) dissolved in pyridine (15 mL) was added dropwise over 5 minutes and the reaction mixture refluxed at 150 °C for 15h. After cooling to room temperature the mixture was stirred in acetic acid (60 mL) for 1h, excess water was then added and precipitate filtered and dried under vacuum. Purification achieved by column chromatography on silica gel ($CHCl_3$, $CHCl_3$/EtOAc 15:1) to give 0.13 g of product (60% yield) as a dark purple powder. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.75 (d, J=6.1, 2H), 8.18 (s, 2H), 8.11 (s, 2H), 7.29-7.25 (m, 10H), 6.85 (d, overlapped, 8H), 1.30 (s, 18H), 1.28 (s, 18H) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 25.48, 26.52, 29.05, 29.68, 31.16, 31.19, 34.23, 34.26, 119.02, 119.20, 119.38, 119.66, 119.88, 120.37, 121.51, 121.86, 123.50, 123.94, 126.61, 132.73, 133.18, 143.31, 147.37, 147.39, 150.92, 153.08, 153.14, 155.52, 156.16, 162.66, and 163.45 ppm. HRMS (ESI-TOF): *m/z* for $C_{75}H_{72}N_3O_8$ calcd. 1142.53194; found 1142.52749 (M^+).

Porphyrin. Porphyrin was synthesized from *p*-*t*-butyl benzaldehyde and pyrrole according to a literature procedure[S1b] and purified by column chromatography on silica gel (CH_2Cl_2/Hexane 1:1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.89 (s, 8H), 8.17 (d, J=8.0, 8H), 7.81 (d, J=4, 8H), 1.62 (s, 36H), –2.86 (s, 2H) ppm.

ZnP-1. Porphyrin was metallated with $Zn(AcO)_2$ according to literature procedure[S1c] and purified by column chromatography on silica gel (CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.98 (s, 8H), 8.16 (d, J=8, 8H), 7.81 (d, J=12, 8H), 1.62 (s, 36H) ppm. ESIMS (*m/z*) 901.3 [M^+].

METHODS

Electrospray Ionization Mass Spectrometry (ESIMS). For the detection of **ZnP-1···PyPDICy-3** complex in methanol, ESIMS was recorded on a JEOL AccuTOF JMS-T100LC mass spectrometer using negative ionization mode (Fig. S1).

UV/Vis Spectroscopy. UV/Vis spectra of **ZnP-1**, **PyPDICy-3**, and **ZnP-1···PyPDICy-3** complex were recorded in CH_2Cl_2 (Fig. S2) as well as on TiO_2-coated FTO surface, using a PerkinElmer Lambda-25 UV/Vis spectrophotometer.

NMR Titration Experiments and Determination of K_a. ^{1}H NMR titration experiment (CD_2Cl_2, 298 K) was conducted using Bruker Avance 600 MHz spectrometer. **PyPDICY-3** concentration was kept constant at 2 mM and **ZnP-1** concentration was varied between 0–1.5 equiv. in each NMR tube. **PyPDICY-3** and **ZnP-1** mixtures at different ratio were allowed to reach equilibrium over 15 h. before ^{1}H NMR spectrum of each sample was recorded to determine the chemical shift of diagnostic proton signals upon complex formation. Chemical shifts of **PyPDICY-3** protons were used to calculate the binding constant through a nonlinear least square fit method using OriginPro 8.5.1.

Cyclic Voltammetry. Cyclic voltammetry (CV) was conducted on a Princeton Applied Research VersaStat-3-200 potentiostat/galvanostat instrument using a standard electrochemical cell, consisting of a glassy carbon working electrode, Pt-wire counter electrode, and Ag/AgCl (3 N aq. NaCl) reference electrode. CVs were recorded at room temperature (100 mV/s scan-rate) for (a) **ZnP-1** (0.5 mM), (b) **PyPDICy-3** (0.5 mM), and (c) 1:1 **ZnP-1**···**PyPDICy-3** complex (1 mM each) in CH_2Cl_2 using 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte (Fig. S3).

DEVICE CONSTRUCTION AND MEASUREMENTS.

Preparation of Dye-Functionalized TiO_2/FTO Working Electrode. Conductive and transparent FTO glasses were used as substrates for working electrode. A ca. 5 µm thick nanocrystalline TiO_2 (20 nm, Solaronix) film was deposited on FTO glass by doctor-blade technique. The mesoporous TiO_2 films were sintered up to 450 °C following standard temperature program.[S2] After allowing TiO_2 films to cool to room temperature, they were functionalized with **ZnP-1**, **PyPMI-2**, and **ZnP-1**···**PyPMI-2** dyad.

To functionalize TiO_2/FTO electrodes with dyes, these surfaces were immersed into either **PyPMI-2** (0.15 mM in CH_2Cl_2) or pyridine-4-carboxylic acid (0.15 mM in EtOH) solution for 15 h. This step leads to chemisborption of the anhydride or carboxylic acid group via Ti–O bond formation. After removing unbound anchoring groups by washing, **PyPMI-2** or pyridine-4-carboxylic acid functionalized TiO_2/FTO surfaces were immersed into **ZnP-1** (5 mM in CH_2Cl_2) for 30 min. to capture **ZnP-1** onto the surface via metal-ligand coordination. Unbound **ZnP-1** was washed away before using these surfaces for further analysis. Attachment of these dyes on TiO_2/FTO surfaces was confirmed by UV/Vis spectroscopy.

Preparation of Pt/ITO Counter Electrode. Pt-coated (30 nm) ITO glass substrate was prepared with standard procedure[S3] by magnetron sputtering technique at Argonne National Laboratory.

Preparation of I^-/I_3^- Electrolyte. I^-/I_3^- electrolyte was prepared from a mixture of 1 M LiI and 0.6 M I_2 in either propylene carbonate or MeCN.

Construction of DSCs. For DSC construction, the dye-functionalized photoactive area of the working electrode was first confined to 0.18 cm^2 (for I^-/I_3^- electrolyte in propylene carbonate) or 0.3 cm^2 (for I^-/I_3^- electrolyte in MeCN) by etching off the rest of the dye-coated TiO_2 surface. Then the dye-functionalized TiO_2/FTO working electrode and Pt/ITO counter electrode, separated either by Solaronix Meltonix 60 µm thick thermoplast hot-melt sealing foil (for I^-/I_3^- in propylene carbonate) or by a parafilm (for I^-/I_3^- in MeCN) spacer (does not cover the dye-functionalized photoactive area), were sealed and I^-/I_3^- electrolyte (in propylene carbonate or MeCN) was injected between the two electrodes via a drilled hole on the counter electrode.To determine the fidelity of these DSCs, i.e. error or standard deviation of energy conversion efficiency, three devices based on each given dye were prepared under the same conditions and their *I/V* characteristics were measured.

DSC Measurements. Photovoltaic performances of three DSCs based on **ZnP-1**, **PyPMI-2**, and **ZnP-1**···**PyPMI-2** dyes were measured using a light source (Light Model 66181 oriel) and Keitheley source meter (Model 2400) under illumination of 100 mW/cm^2. The *I/V* curve was recorded using Labview program. The intensity of light was measured using a reference cell (Oriel, USA) and the mismatched (from solar spectrum) was corrected by a standard air-mass filter (Oriel, USA). The light intensity was monitored by Oriel constant power supply or by optical neutral density filters.

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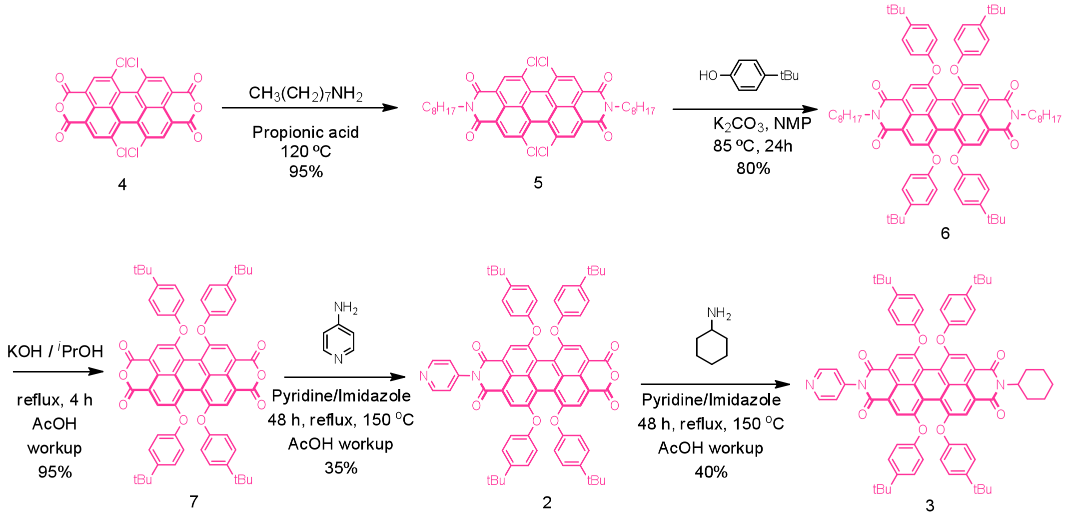
S3. A. J. Mozer, D. K. Panda, S. Gambhir, T. Romeo, B. Winther-Jensen and G. G. Wallace., *Langmuir*, 2010, **26**, 1452.



Scheme S1. Synthesis of **PyPMI-2** and **PyPDICy-3.**

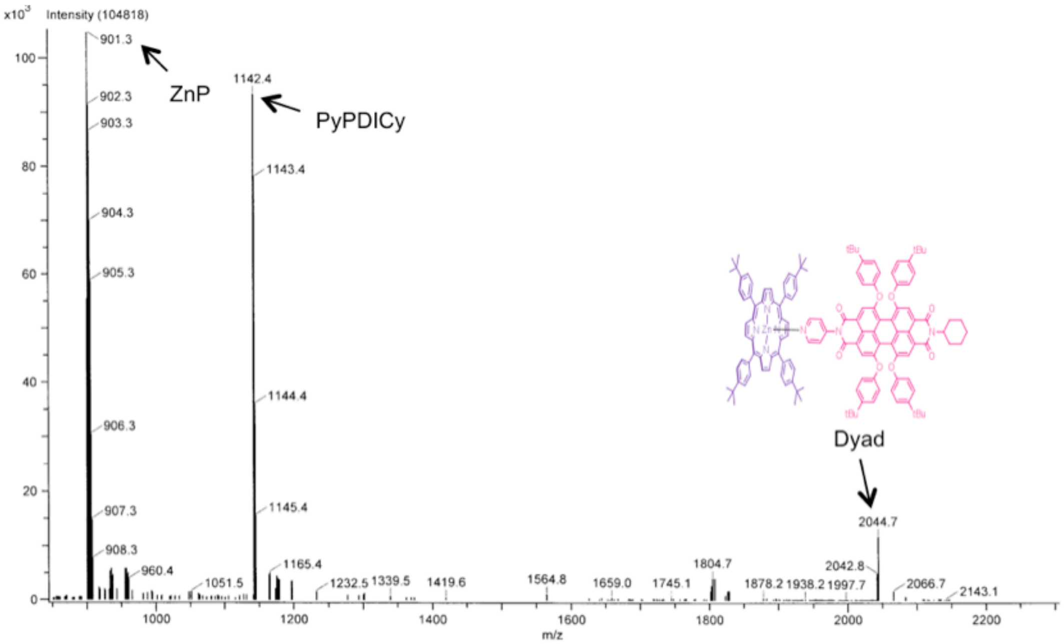


Figure S1. ESIMS of **ZnP-1···PyPDICy-3** dyad.

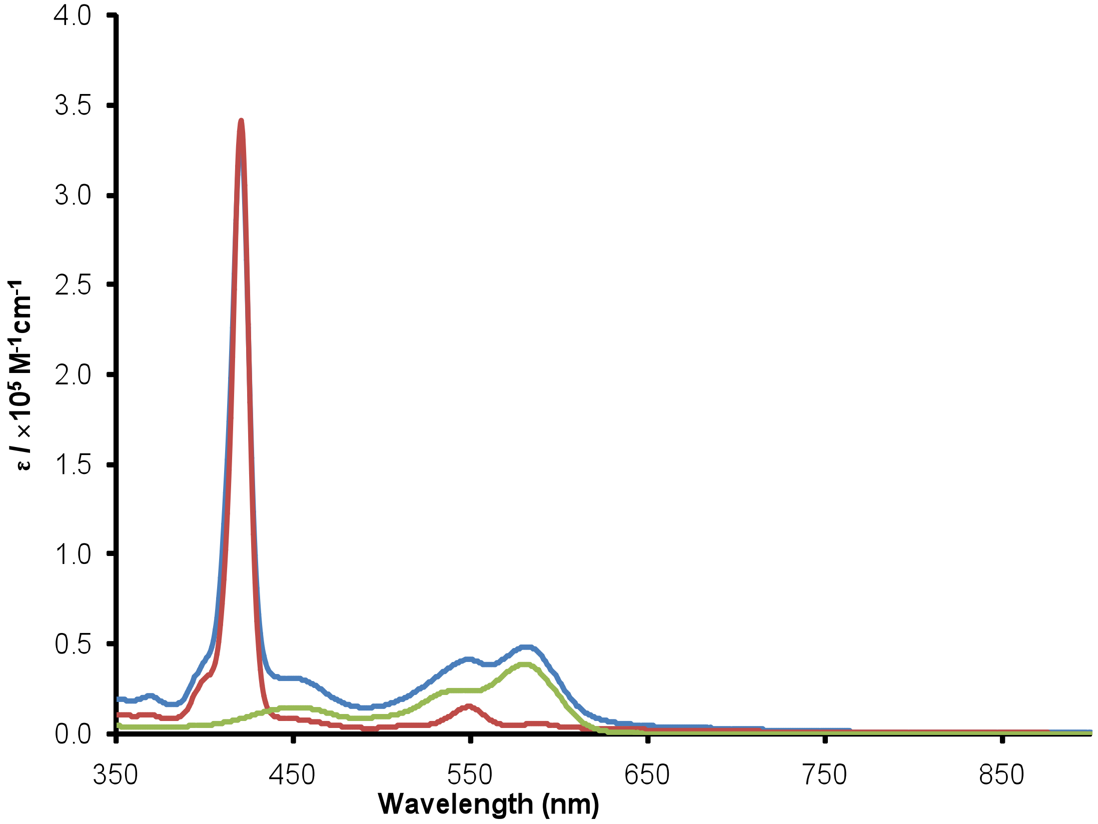


Figure S2. UV/Vis spectra of **ZnP-1** (Red), **PyPDICy-3** (Green), and **ZnP-1···PyPDICy-3** dyad (Blue) in CH_2Cl_2.

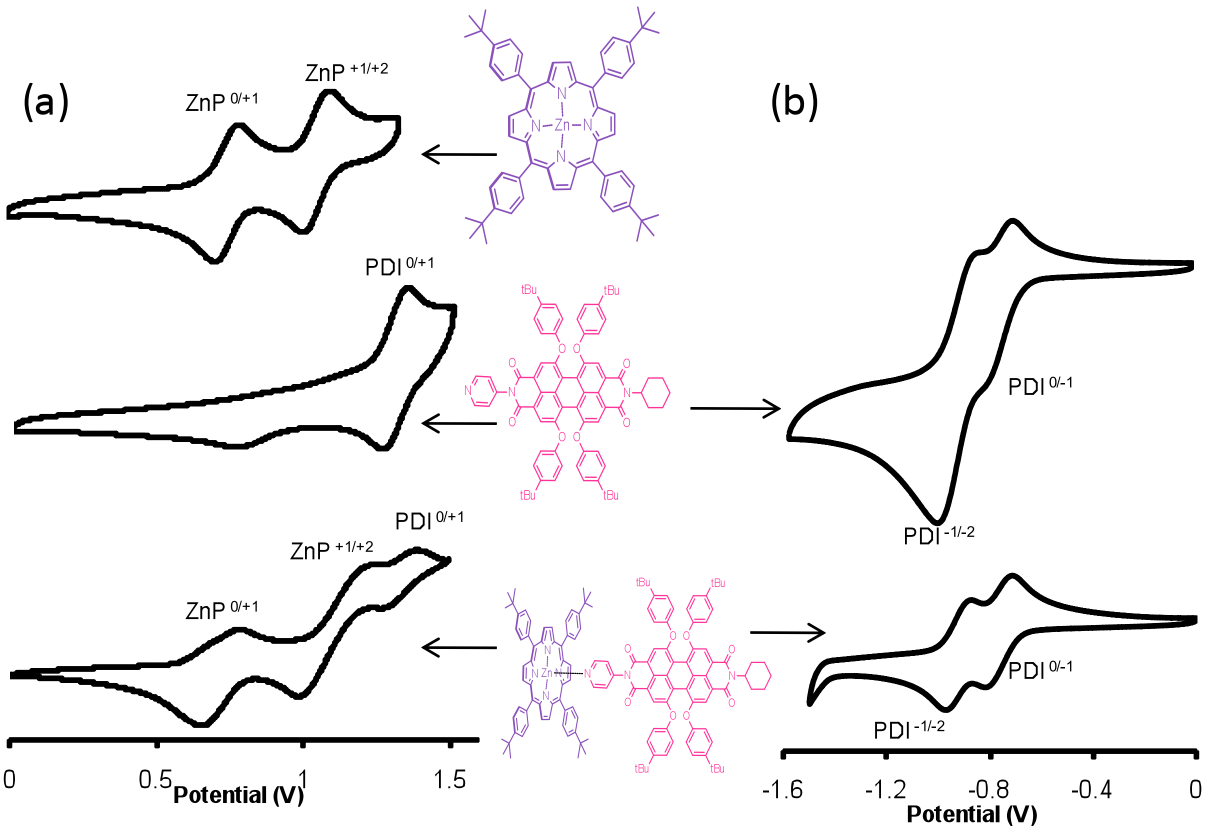


Figure S3. (a) Oxidation of **ZnP-1** (0.5 mM), **PyPDICy-3** (0.5 mM), **ZnP-1···PyPDICy-3** dyad (1 mM) in CH_2Cl_2 vs Ag/AgCl (0.1 M $TBAPF_6$). (b) Reduction of **PyPDICy-3** (0.5 mM), **ZnP-1···PyPDICy-3** dyad (1 mM) in CH_2Cl_2 vs Ag/AgCl (0.1 M $TBAPF_6$).

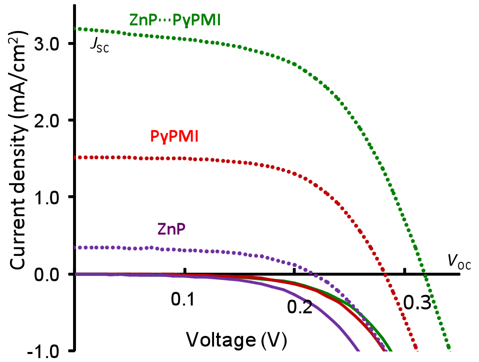


Figure S4. *I*–*V* characteristics of DSCs composed of **ZnP-1···PyPMI-2** dyad (green), **PyPMI-2** (red), and **ZnP-1** (violet) showing photocurrent generation (J_{SC} and V_{OC}) under 1.5 AM conditions (dotted lines) and negligible dark currents (solid lines). In this case, I^-/I_3^- couple (1.0 M LiI + 0.06 M I_2 in MeCN) used as a redox mediator.

Table S1. Performance of DSCs based on **ZnP-1···PyPDICy-2** dyad **ZnP-1**, and **PyPMI-2** dyes under standard illumination (100 mW/cm^2). I^-/I_3^- couple (1.0 M LiI + 0.06 M I_2 in MeCN) used as a redox mediator.

Dye Composition	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF* (%)	η (%)
ZnP-1···PyPMI-2	3.20	310	56	0.56
PyPMI-2	1.52	280	61	0.25
ZnP-1	0.35	210	54	0.03