

ELCTRONIC SUPPORTING INFORMATION

Dye-sensitized solar cells based on multichromophoric supramolecular light-harvesting materials

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MATERIALS

All chemicals, solvents, and electrolytes were purchased from Sigma-Aldrich, Across Organic, Cambridge Isotope Laboratory, and EMD chemicals and used as received unless otherwise mentioned. Solvents used in this study were dried and distilled prior to use. TEC-15 (3.0 mm) FTO-coated transparent conductive glass substrate was purchased from Hartford Glass Co., Inc, USA. Ti-Nanoxide T paste was purchased from Solaronix (Switzerland). PyPMI, PyPDICy were synthesized by following the literature procedures^{S1} and ZnPc was purchased from Sigma-Aldrich.

METHODS

NMR Titration Experiments and Determination of K_a . ¹H NMR titration experiment (CD₂Cl₂, 298 K) was carried out using Bruker Avance 600 MHz spectrometer. The concentration (2 mM) of PyPDICy was kept constant and the concentration of ZnPc was varied between 0–1.5 equiv. in each NMR tube. To determine the chemical shift of diagnostic proton signals upon complex formation, a mixture of ZnPc and PyPDICy at different ratios was allowed to reach equilibrium over 15 h. prior to recording the ¹H NMR spectrum of each sample. The binding constant (K_a) calculated taking chemical shifts of PyPDICy protons using a nonlinear least square fitting method using OriginPro 8.5.1 software. To determine the binding affinity (K_a) from ¹H NMR titration experiments (Fig. S1), PyPMI was replaced with PyPDICy to avoid competitions between the pyridine ligand and anhydride terminal. The ¹H NMR spectrum of free PyPDICy (CD₂Cl₂, 298 K) displays two doublets at 8.73 and 7.25 ppm that represent H_a and H_b of the *N*-pyridyl ring and two singlets at 8.17 and 8.11 ppm that correspond to H_c and H_d on the PDI core, respectively. Protons of 4-*tert*-butylphenoxy groups (H_e, H_f, H_g, and H_h) appear as doublets at 7.25–7.29 and 6.83–6.85 ppm region. ¹H NMR titration of PyPDICy with ZnPc (CD₂Cl₂, 298 K) caused the dramatic upfield shifts of *N*-pyridyl and PDI core protons due to the shielding effects of the perpendicular ZnPc ring-current. PyPDICy's H_b signal becomes broad and shifts to 5.80 ppm ($\Delta\delta = -1.45$ ppm), H_c shifts to 7.69 ppm ($\Delta\delta = -0.48$ ppm), and H_d to 7.98 ppm ($\Delta\delta = -0.14$ ppm). The H_a signal disappears, which is characteristic of axial coordination of pyridyl ligands with ZnPc.^{S2,3} Protons on 4-*tert*-butylphenoxy groups of PyPDICy also shift slightly upfield. The addition of >1 equiv. of ZnPc to PyPDICy did not change any further. The K_a of a 1:1 ZnPc⋯PyPDICy complex (5.8×10^4 M⁻¹, CD₂Cl₂, 298 K) was calculated from NMR chemical shifts of diagnostic H_b signal using nonlinear least-squares fitting method. This K_a value is consistent with that measured for a similar ZnPc⋯imidazole coordination complex.^{S2}

Electrospray Ionization Mass Spectrometry (ESI-MS). ZnPc···PyPDICy dyad complex formation in methanol was detected by ESI-MS technique. ESI-MS was recorded on a JEOL AccuTOF JMS-T100LC mass spectrometer using negative ionization mode.

UV/Vis Spectroscopy. UV/Vis spectra of ZnPc, PyPDICy, and ZnPc···PyPDICy complex were recorded in CH₂Cl₂ and dye coated TiO₂-FTO film, using a PerkinElmer Lambda-25 UV/Vis spectrophotometer.

Cyclic Voltammetry. Cyclic voltammetry (CV) experiments were performed on a Princeton Applied Research VersaStat-3-200 potentiostat/galvanostat instrument using a standard three electrode electrochemical cell having glassy carbon working electrode, Pt-wire counter electrode, and Ag/AgCl (3 N aq. NaCl) as reference electrode. All CVs were recorded at room temperature (100 mV/s scan-rate) for (a) ZnPc (1 mM), (b) PyPDICy (1 mM), and (c) 1:1 ZnPc···PyPDICy complex (1 mM each) in CH₂Cl₂ using 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte.

DEVICE CONSTRUCTION AND MEASUREMENTS.

Preparation of Dye-Functionalized TiO₂/FTO Working Electrode. Nanoporous TiO₂ paste coated FTO (F: SnO₂) transparent conductive oxide (TCO) glasses were used as substrates for working electrode. A ca. 5 μm thick nanocrystalline TiO₂ (Ti-Nanoxie T, solaronix) film was deposited on FTO glass by doctor-blade technique. The mesoporous TiO₂ electrodes were sintered up to 450 °C, for 30 min.^{S3} The nanoporous TiO₂ electrodes (at room temp condition) were functionalized with ZnPc, PyPMI, and ZnPc···PyPMI dyad. TiO₂/FTO electrodes were immersed into either PyPMI (0.15 mM in CH₂Cl₂) or pyridine-4-carboxylic acid (0.15 mM in EtOH) solution for 15 h. After being washed in solvent (CH₂Cl₂) and dried in air, PyPMI or pyridine-4-carboxylic acid functionalized TiO₂/FTO surfaces were immersed further into ZnPc (2 mM in CH₂Cl₂) for 30 min and then washed and dried in air again. These electrodes were used as the working electrode or photoanode. Photoanode surfaces were confirmed by UV/Vis spectroscopy.

We have also tried to immobilize a pre-assembled ZnPc···PyPMI dyad on TiO₂/FTO surfaces. However, in this case, the population of the dyes on surfaces and the device efficiency are significantly lower than that of the devices constructed in two steps—i.e.; first by immobilizing PyPMI on TiO₂/FTO surfaces and then coordinating ZnPc with the surface bound PyPMI. This is presumably because the two-step process allows the vertically oriented PyPMI dyes to cover surfaces uniformly, and then form the dyad with ZnPc in the second step through axial coordination. On the other hand, when a TiO₂/FTO surface was immersed into a 1:1 mixture of ZnPc/PyPMI (i.e., a preformed dyad), the dyes could be attached to the surface randomly—for instance ZnPc could be physisorbed on the surface directly instead of coordinating through a PyPMI ligand—which could diminish the dye uptake, randomize their orientations, and decrease the device performance.

Preparation of Pt/ITO Counter Electrode. Pt-coated (30 nm) ITO glass substrate was prepared with standard procedure by magnetron sputtering technique at Advanced Material Research Institute (AMRI), The University of New Orleans, Louisiana.

Preparation of I⁻/I₃⁻ Electrolyte. I⁻/I₃⁻ electrolyte were prepared from a mixture of 1 M LiI and 0.6 M I₂ in propylene carbonate.

Construction of DSSCs. For DSSCs construction, the dye-functionalized photoactive area of the working electrode was confined to 0.25cm². Then the dye-functionalized TiO₂/FTO working electrode and Pt/ITO counter electrode, separated by Dyesol (Australia) 30 μm thick thermoplast hot-melt sealing foil were sealed and I⁻/I₃⁻ electrolyte (in propylene carbonate) was injected between the two electrodes via counter electrode.

DSSC Measurements. Photovoltaic performances of three DSSCs based on ZnPc, PyPMI, and ZnPc···PyPMI and ZnP···PyPMI dyes were measured using a light source (300 W Xenon lamp, Model 67005 Oriel Instruments, USA) and Keithley source meter (Model 2400) under illumination of 100

mW/cm². The *I/V* curve was recorded using Labview program. The intensity of light was measured using a reference cell (Oriel, USA) and was corrected by a standard air-mass filter (Oriel, USA). The light intensity was maintained by Oriel optical neutral density filters.

Incident Photon to Converted Electron (IPCE) Measurement:

Incident photon-to-current conversion efficiency (IPCE) spectra were recorded on an Oriel setup equipped with 300 W xenon lamp as a monochromatic light source and Newport 10CGA-305 and 10CGA-570 filters. Calibration was performed with a standard silicon photo-detector (UV-Silicon Det 10×10 mm calib, Model no, 71675, Photodetector Newport Oriel Instruments, USA). The photocurrent response of DSSCs was measured using a Keithley 2400 source meter, referenced to the output of a calibrated silicon diode. The IPCE spectra were recorded using TRACQ BASIC software.

REFERENCE

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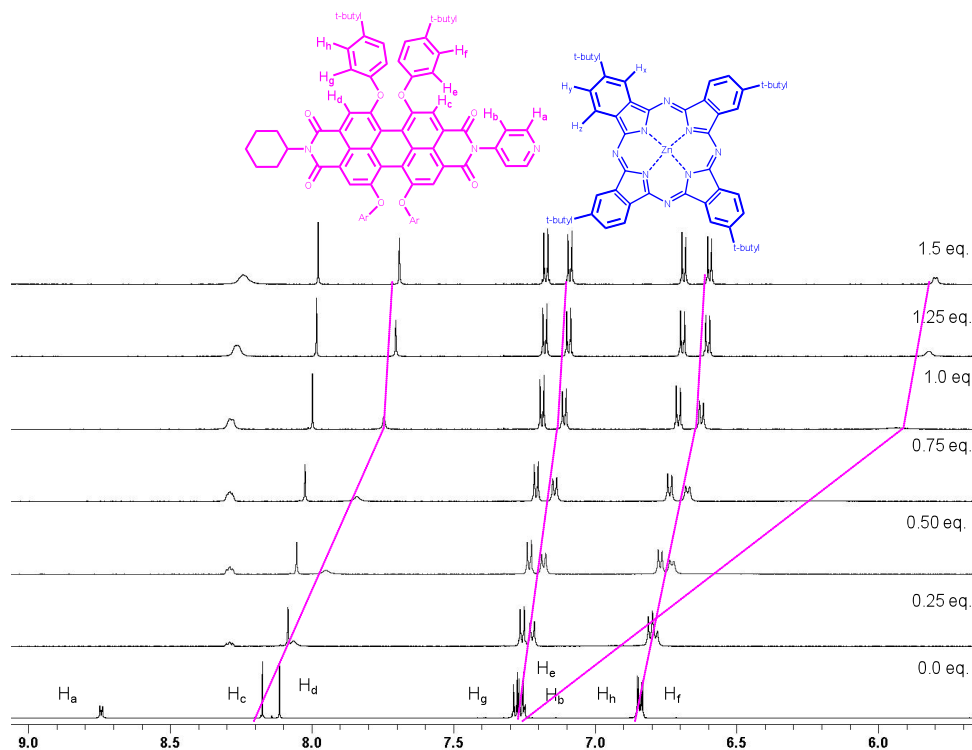


Fig.S1. ¹H NMR titration spectra of PyPDICy with ZnPc (CD₂Cl₂).

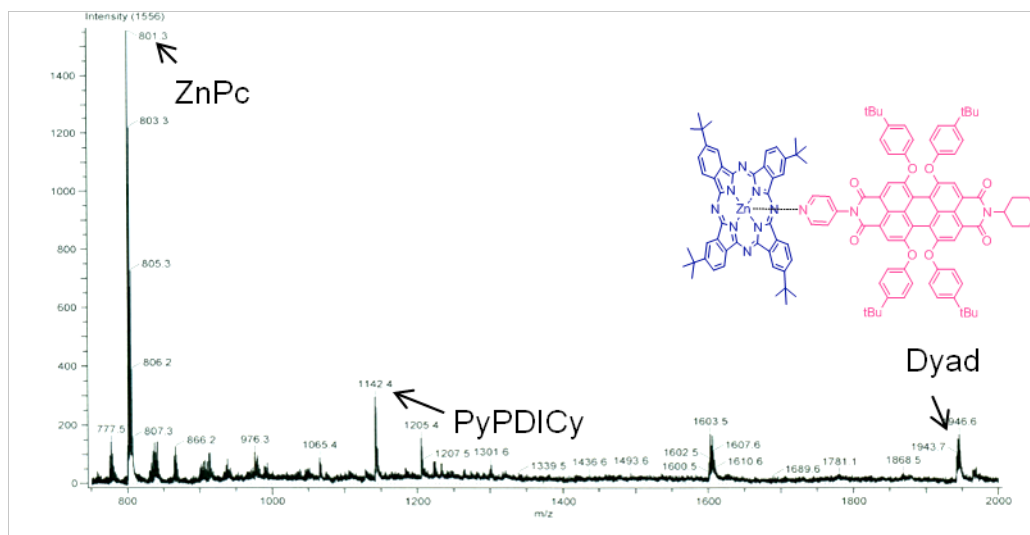


Figure S2. ESI-MS of ZnPc···PyPDICy dyad.

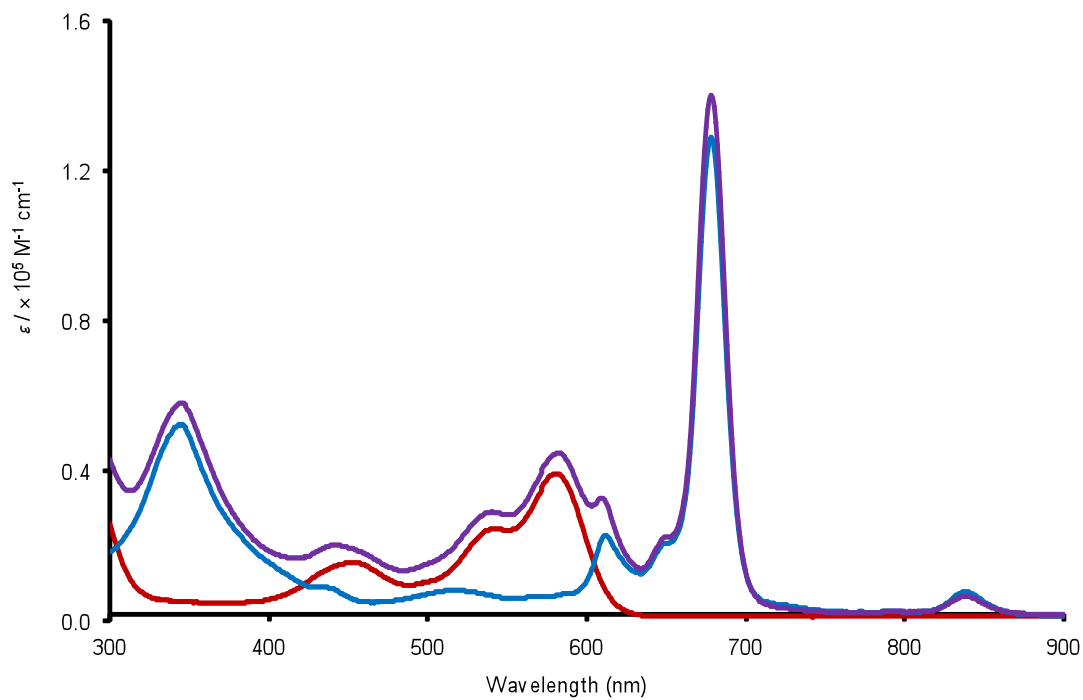


Figure S3. UV/Vis spectra of ZnPc (blue), PyPDICy (red), and ZnPc···PyPDICy dyad (purple) in CH_2Cl_2 .

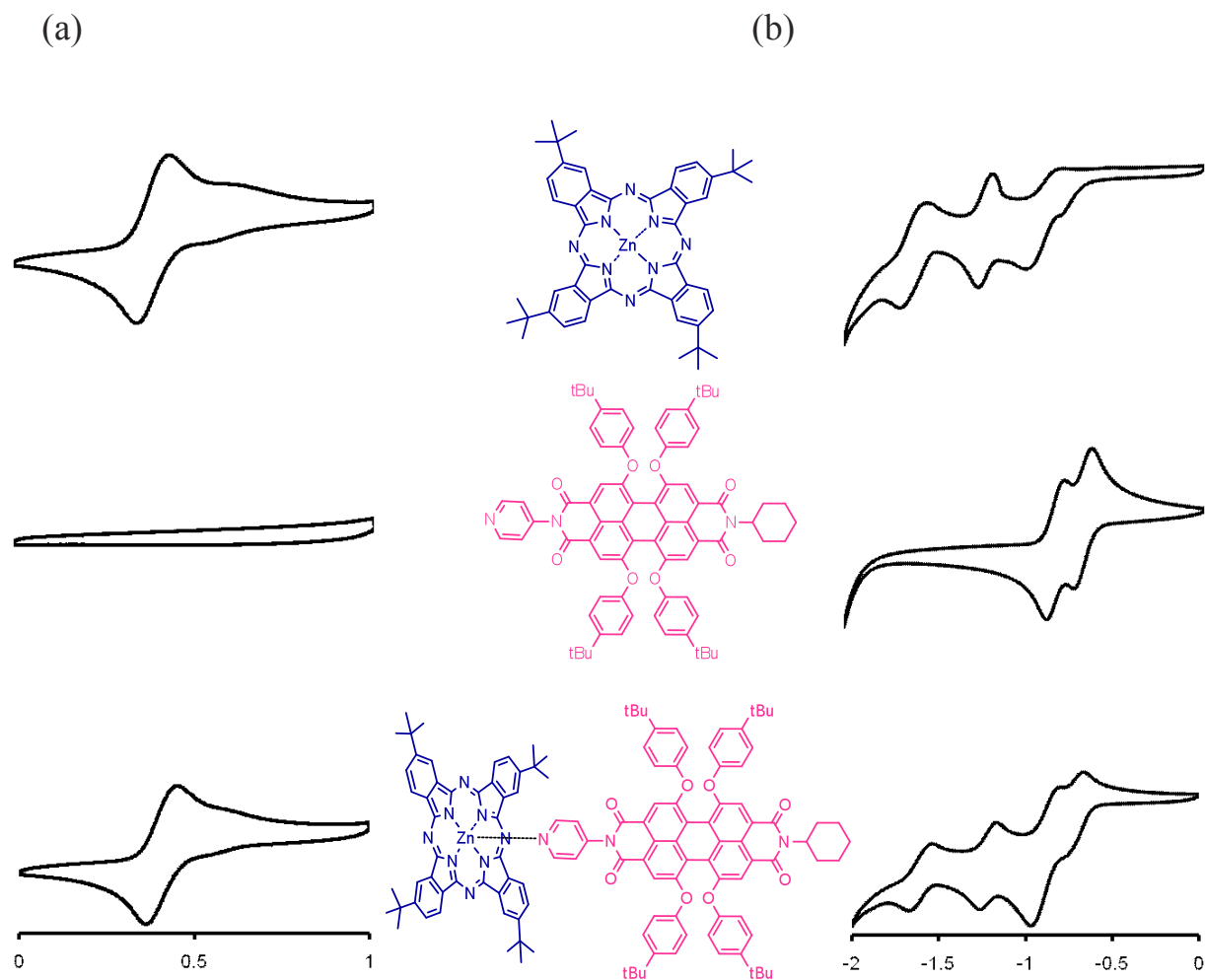


Figure S4. (a) Oxidation of ZnPc (1mM), PyPDICy (1mM), ZnPc···PyPDICy dyad (1 mM) in CH₂Cl₂ vs Ag/AgCl (0.1 M TBAPF₆). (b) Reduction of ZnPc (1mM), PyPDICy (1mM), ZnPc···PyPDICy dyad (1 mM) in CH₂Cl₂ vs Ag/AgCl (0.1 M TBAPF₆).

Table S1 E_{Ox} and E_{Red} (mV) of ZnPc, PyPDICy, and ZnPc···PyPDICy dyad (vs. Ag/AgCl in CH₂Cl₂).

Entry	E^1_{Ox}	E^2_{Ox}	E^1_{Red}	E^2_{Red}
ZnPc	+485	—	-820	-995
PyPDICy	+1340	—	-780	-950
ZnPc···PyPDICy	+445	—	-790	-960