Light-to-electron conversion panchromatic supramolecular solar cells of phthalocyanine-porphyrin heterodimer adsorbed onto nanocrystalline SnO_2 electrodes

Navaneetha K. Subbaiyan[a] and Francis D'Souza[a*]

Electronic Supporting Information

Experimental Procedure

Chemicals: The free-base and zinc(II) derivatives of tetrakis(N-methyl pyridyl)porphyrin chloride, M(TMPyP), free-base and zinc(II) derivatives of phthalocynanine sulfonic acid derivatives, M(PcS) were procured from Frontier Scientific, Inc. (Logan UT) and used as received. Millipore water was used in all of the experiments.

Preparation of FTO/SnO_2/Zn(PcS):Zn(TMPyP) electrodes: A 110 mg of SnO_2 colloidal solution (Alfa Aesar, 15%) was dissolved in 10 mL of ethanol; a 500 μL of NH_4OH was added to this solution for stability. About 2 mL of colloidal solution placed on optically transparent electrode, fluorine doped indium tin oxide (FTO) (Pilkington TEC-8, 6-9 Ω/square) and dried in air on a warm plate. The electrodes were annealed in an oven for an hour in air at 673 K. The thickness of the electrode profiled using surface profiler was around 5±0.2 μm. SnO_2 electrodes were dipped in 0.2 mM of Zn(PcS) solution in 40% by volume water:methanol solution for 90 min. After washing, in methanol, the electrodes were heated on a warm hot plate for 10 min. Next, the FTO/SnO_2/Zn(PcS) electrode was dipped in 0.2 mM of Zn(TMPyP) in methanol solution for 3 hours. The FTO/SnO_2/Zn(PcS):Zn(TMPyP) electrode was rinsed in methanol solution and dried on a warm plate for 10 min before testing. A similar procedure was used to prepare other hetero dimer modified electrodes.

Instrumentation: Absorption spectral measurements were carried out with a Shimadzu UV2550 UV-Vis spectrophotometer. The steady-state fluorescence emission was monitored by using a Cary Eclipse spectrofluorometer. Photoelectrochemical experiments were performed in a two-electrode configuration using porphyrin adsorbed FTO/SnO_2 electrode and a platinum foil as a counter electrode. The two electrodes were separated using 0.7 cm Teflon spacer. A mixture of

(TBA)I/I_2 in acetonitrile was used as redox mediator. The photocurrent-photovoltage (I-V) characteristics of the solar cells were measured using a Model 2400 Current/Voltage Source Meter of Keithley Instruments, Inc. (Cleveland, OH) under illumination with an AM 1.5 simulated light source using a Model 9600 of 150-W Solar Simulator of Newport Corp. (Irvine, CA). A 340-nm filter was introduced in the light path to eliminate UV radiation. The light intensity was monitored by using an Optical Model 1916-C Power Meter of Newport. Incident photon-to-current efficiency (IPCE) measurements were performed under ~2.5 mW cm^2 monochromatic light illumination conditions using a setup comprised of a 150 W Xe lamp with a Cornerstone 260 monochromator (Newport Corp., Irvine, CA).

Electrochemical impedance measurements were performed using EG&G PARSTAT 2273 potentiostat. Impedance data were recorded under forward bias condition from 100 kHz to 100 mHz with an A.C amplitude of 10 mV. Data were recorded under dark and A.M 1.5 illumination conditions applying corresponding V_{oc} for each electrode. The data were analyzed using ZSimpwin software from Princeton Applied Research.

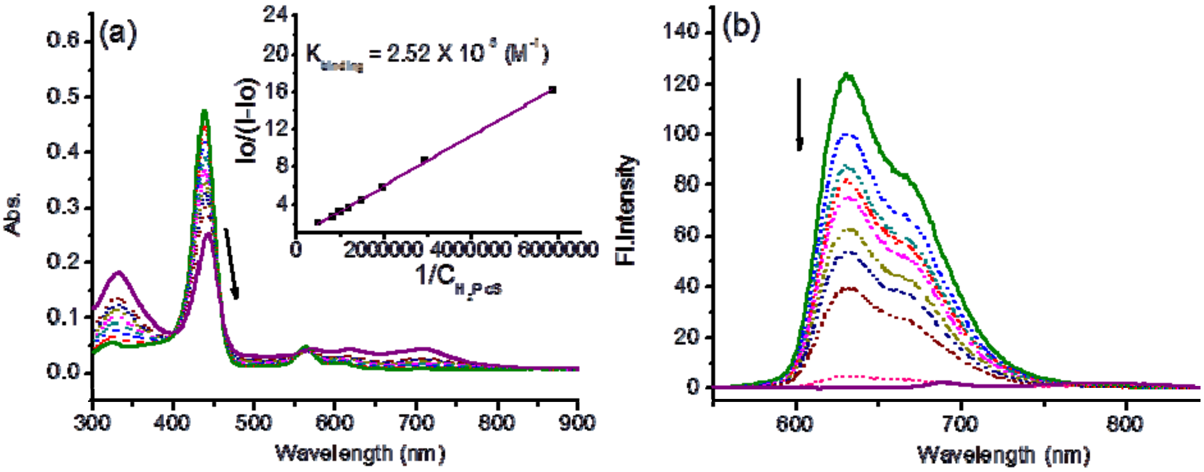

Fig. S1 (a) Absorption spectral changes observed for Zn(TMPyP) (3 ml of 1.75 μM) on increasing addition H_2(PcS) (5-10 μL of 0.551 mM each addition) in methanol-water. (b) Corresponding fluorescent spectral changes observed for Zn(TMPyP) (3 ml of 1.75μM) on increasing addition H_2(PcS) (5-10 μL of 0.551 mM each addition) in methanol-water excited at 438 nm Fig. a inset shows Benesi-Hildebrand plot showing linear dependence of the inverse of δA (change in absorbance) at 438 nm on the inverse of the H_2(PcS) concentration.

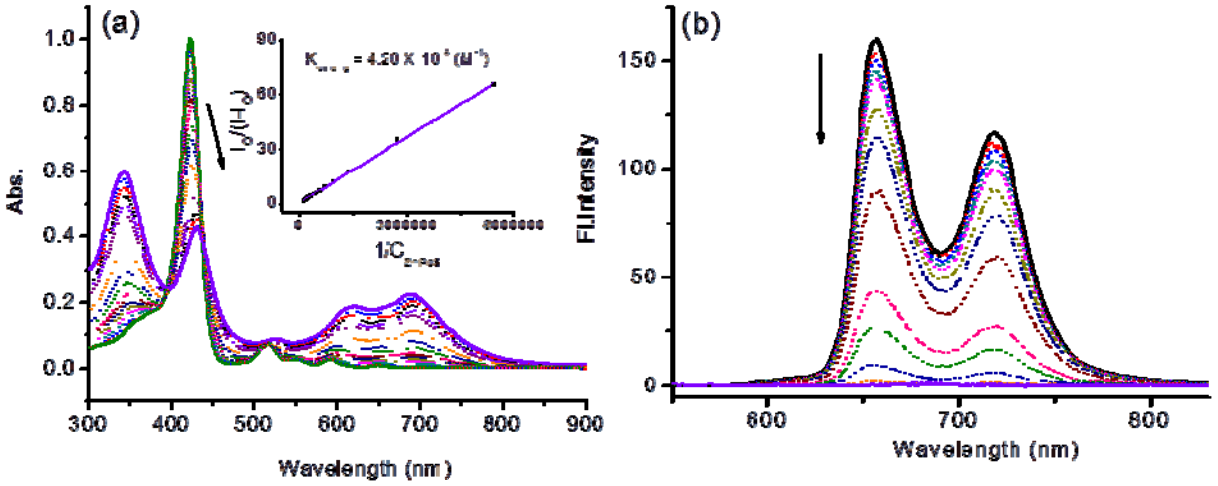

Fig. S2. (a) Absorption spectral changes observed for H_2(TMPyP) (3 ml of 1.45 μM) on increasing addition Zn(PcS) (5-10 μL of 0.512 mM each addition) in methanol-water. (b) Corresponding fluorescent spectral changes observed for H_2TMPyP (3 ml of 1.45 μM) on increasing addition Zn(PcS) (5-10 μL of 0.512 mM each addition) in methanol-water excited at 438 nm. (c) Fig. a inset shows Benesi-Hildebrand plot showing linear dependence of the inverse of δA at 438 nm on the inverse of the Zn(PcS) concentration.

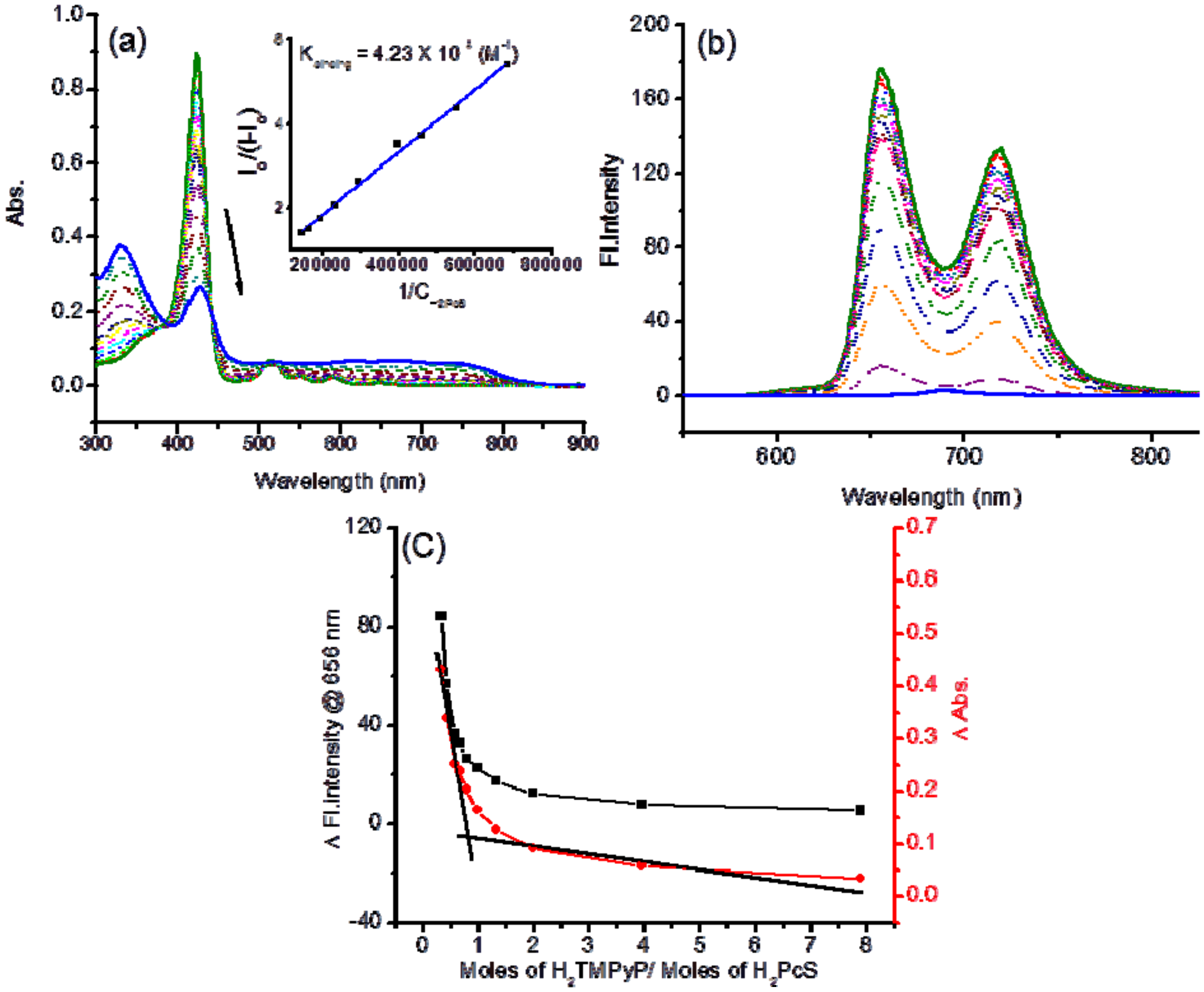

Fig. S3. (a) Absorption spectral changes observed for H_2TMPyP (3 ml of 1.45 μM) on increasing addition H_2(PcS) (5-10 μL of 0.551 mM each addition) in methanol-water. (b) Corresponding fluorescent spectral changes observed for H_2(TMPyP) (3 ml of 1.45 μM) on increasing addition H_2(PcS) (5-10 μL of 0.551 mM each addition) in methanol-water excited at 438 nm. (c) Mole ratio vs. δA or δF to obtain molecular stoichiometry. Figure a inset shows Benesi-Hildebrand plot showing linear dependence of the inverse of δA at 423 nm on the inverse of the H_2(PcS) concentration.

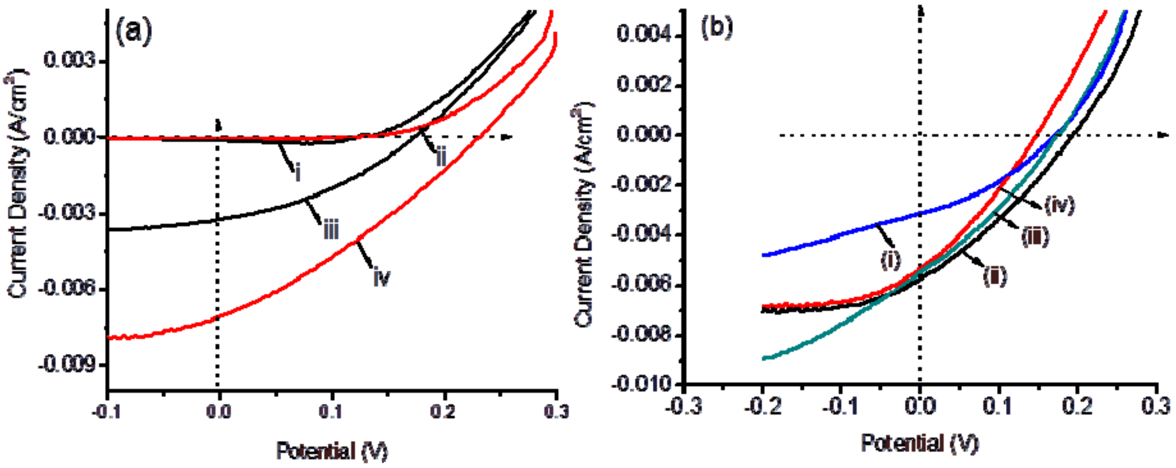

Fig. S4. (a) *J*-*V* plots of SnO_2/ZnPcS and SnO_2/ZnTMPyP:ZnPcS electrodes in dark (i and ii) and under AM1.5 light conditions (iii and iv), respectively. *J*-*V* plots of (iii) SnO_2/H_2(PcS) (i), SnO_2/Zn(PcS):H_2(TMPyP) (ii), SnO_2/ H_2(PcS):H_2(TMPyP) (iii), and SnO_2/H_2(PcS):Zn(TMPyP) under AM1.5 light conditions. The electrolyte used in this experiment consists of 0.5 M (TBA)I and 0.05 M I_2 as redox mediator.