Supplementary Information

Efficient Passivated Phthalocyanine-Quantum Dot Solar Cells

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Materials and methods for the synthesis of new compounds.

All chemicals were reagent-grade, purchased from commercial sources, and used as received. Column chromatography was performed using SiO_2 (40-63µm) TLC plates coated with SiO_2 60F254 and visualized by UV light. NMR spectra were measured with a Bruker AC 300. Fluorescence spectra were recorded with Perkin-Elmer LS 55 Luminescence Spectrometer, UV/Vis spectra were recorded with a Helios Gamma spectrophotometer and IR spectra with Nicolet Impact 400D Spectrometer. Mass spectra were obtained from Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF). CV measurements were performed in a conventional three-electrode cell using a µ-AUTOLAB type IIIpotentiostat/galvanostat at 298 K, over benzonitrile and deaerated sample solutions (~0.5 mM), containing 0.10 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as supporting electrolyte. A glassy carbon (GC) working electrode, $Ag/AgNO_3$ reference electrode and a platinum wire counter electrode were employed. Ferrocene/ferrocenium was used as an internal standard for all measurements.

Preparation on Sensitized TiO_2.

The electrode configuration was a transparent layer DSL 18NR-T (20 nm average particle size) and a scattering layer WERO-4 (300_400 nm particle size distribution). The FTO (SnO_2:F) coated glass was previously covered by a compact layer of TiO_2 deposited by spray pyrolysis of titanium(IV)bis(acetoacetonato) di(isopropanoxylate). These electrodes were sintered at 450 °C for 30 min.

The mesoporous TiO_2 electrodes were *in situ* sensitized by CdS and CdSe QDs grown by SILAR. For CdS growth the electrodes were successively immersed in two different solutions for 1 min each: one consisting of 0.05 M $Cd(OAc)_2$ dissolved in ethanol, another of 0.05 M Na_2S in methanol/Milli-Q ultrapure (1:1). Following each immersion, rinsing and drying was undertaken using pure methanol and a N_2 gun, respectively. All these processes constitute one SILAR cycle. A SILAR of CdSe to obtain the Se precursor, we followed, 0.03 M $Cd(NO_3)_2$ dissolved in ethanol, for generated *in situ* Se_2^- we used 0.03 M of SeO_2 that is diluted in ethanol with $NaBH_4$. For sensitization, electrodes were dipped successively in these solutions inside a glove box under N_2 atmosphere. Following each immersion, rinsing and drying was undertaken using pure ethanol and a N_2 gun, respectively.

Solar Cell Configuration.

The cells were prepared by assembling the counter-electrode and a QD-sensitized electrode using a scotch spacer (thickness 50 µm) and with a droplet (10 µL) of polysulfide electrolyte. Polysulfide electrolyte was 1 M Na_2S, 1 M S, and 0.1 M NaOH solution in Milli-Q ultrapure water. We have used Cu_2S counter-electrodes. The Cu_2S counter-electrodes were prepared by immersing brass in HCl solution at 70°C for 5 min and subsequently dipping it into polysulfide solution for 10 min, resulting in a porous Cu_2S electrode.[1] The area of the cells was 0.24 cm^2.

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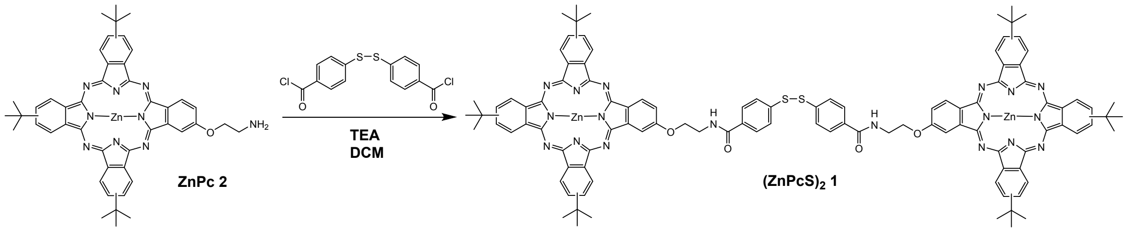
[1] G. Hodes, J. Manassen, D. Cahen, *J. Electrochem. Soc.,* 1980, **127**, 544-549.

Electrode and Cell Characterization.

The *J-V* curves were performed using a solar simulator at AM 1.5 G, where the light intensity was adjusted with an NREL-calibrated Si solar cell to 1 sun intensity (100 mW cm^{-2}). The IPCE measurements were performed employing a 150 W Xe lamp coupled with a monochromator controlled by a computer; the photocurrent was measured using an optical power meter 70310 from Oriel Instruments, using a Si photodiode to calibrate the system.



Synthesis of $(ZnPcS)_2$ 1

A solution of 49 mg (0.061 mmol) of 2-(2´-aminoethoxy)-9,16,23-tri-tert-butylphtalocyaninato zinc (II)[2] and TEA (0.061 mmol) in DCM (0.5 ml) was added to a solution of 10 mg (0.03 mmol) of 4,4'-dithiobis-benzoyl chloride[3] in 200 µl of DCM at 0°C. After 3 h of stirring at 0°C, the reaction mixture was diluted with DCM and washed with NH_4Cl (aq), $NaHCO_3$(aq) and H_2O. The organic layer was dried with Na_2SO_4 and concentrated in vacuum. The crude was purified by column chromatography (DCM:AcOEt/85:15), yielding 54 mg of **$(ZnPcS)_2$ 1** (96%).

- ^{1}H-NMR (TFA-*d₁*) 1.68 [s, 54H, 6x$(CH_3)_3C$], 4.27 (s, 4H, CH_2N), 4.76 (s, 4H, CH_2O), 7.65-7.83 (m, 10H, ArH), 8.52 (s, 6H, ArH), 8.98-9.51 (m, 16H, ArH).
- IR (KBr): ν= 3381, 2956, 2865, 1646, 1611, 1487, 1391, 1330, 1256, 1089, 1047, 921, 830 and 748 cm^{-1}.
- UV-Vis (DMF), λmax/nm (log ε): 351 (5.09), 610 (4.79) and 675 (5.52).
- HRMS (MALDI-TOF-MS): For $C_{106}H_{96}N_{18}O_4S_2Zn_2$ $(M+H)^+$ calc. 1877.5959 found 1877.5185.

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[2] S. Fukuzumi, K. Ohkubo, J. Ortiz, A. M. Gutiérrez, F. Fernández-Lázaro and Á. Sastre-Santos, *J. Phys. Chem. A*, 2008, **112**, 10744-10752.

[3] S. Moeno, E. Antunes, S. Khene, C. Litwinski and T. Nyokong, *Dalton Trans.*, 2010, **39**, 3460-3471.

Fig. S1 ^{1}H NMR (TFA-d_1) of **(ZnPcS)$_2$ 1**

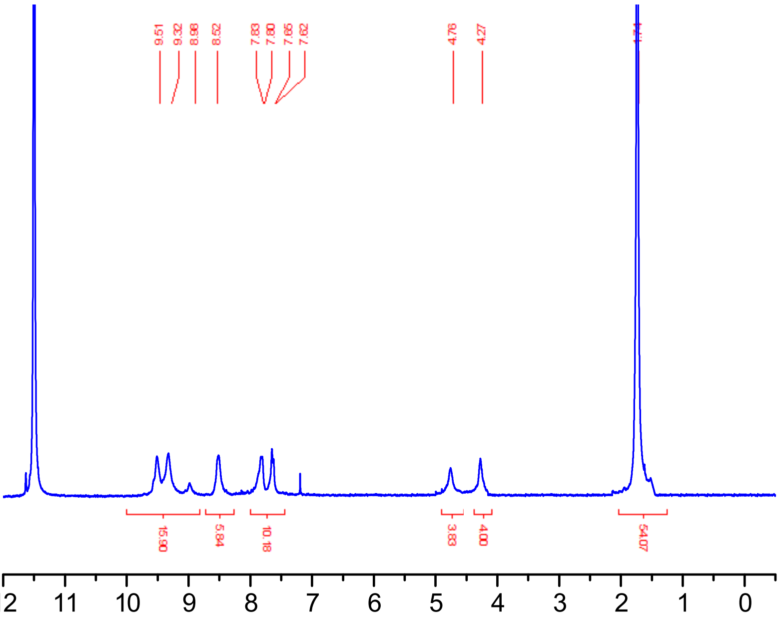

Fig. S2 MS of **(ZnPcS)$_2$ 1**

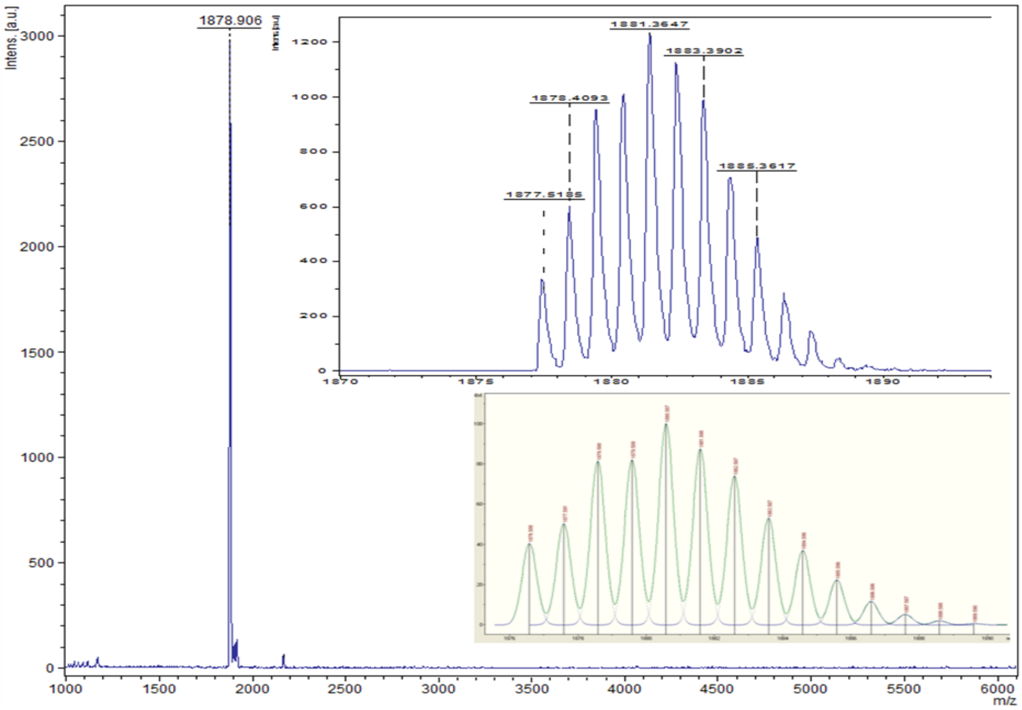

Fig. S3 IR spectrum (KBr) of **$(ZnPcS)_2$ 1**

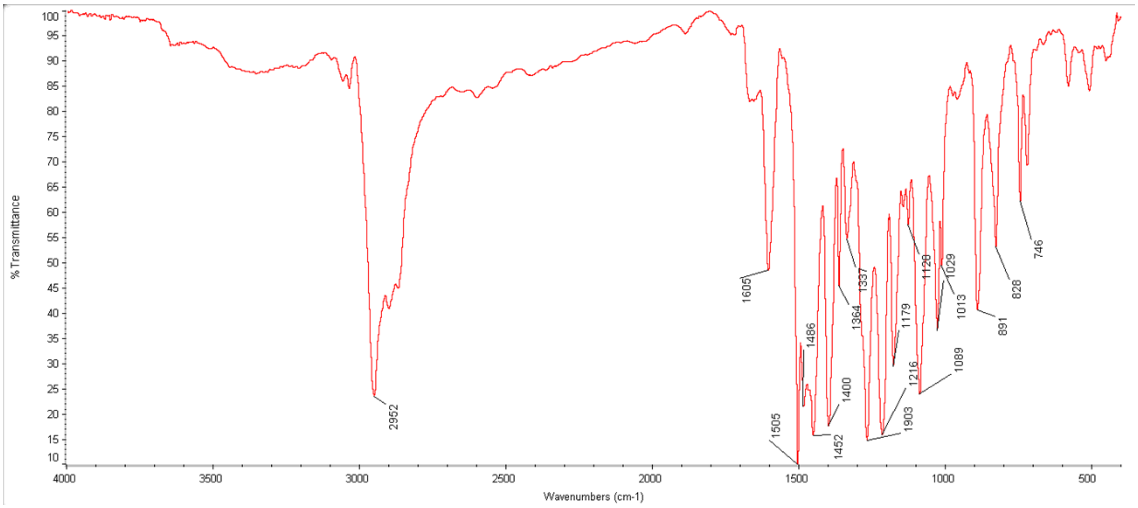

Fig. S4 UV-Vis in (DMF) of **$(ZnPcS)_2$ 1**