8-Hydroxylquinoline as a Strong Alternative Anchoring Group for Porphyrin-sensitized Solar Cells

Hongshan He[1,2,*], Ashim Gurung[1] and Liping Si[1]

[1]Center for Advanced Photovoltaics, South Dakota State University, Brookings, SD 57007, USA; [2]Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, USA.

Experimental section

All solvents were treated by standard methods prior to use. Reagent grade 8-hydroxy-5-quinolinecarboxaldehyde was purchased from Leadgen Labs and used without further purification. All other chemicals were analytical grade and used as received. Elemental compositions were determined using a commercial C, H, and N analyzer. The N719 dye was obtained from Solaronix. The FTO (fluorine-tine-oxide) glass with sheet resistance 8 Ω/cm^2 from Hartfort Glass (USA) was used for cell fabrication. The scanning electron microscope (SEM) images were taken on a Hitachi S3400 microscope. 5-(4-Carboxylpheny)-10, 15,20-triphenylporphyrin zinc was prepared as described previously. Absorption spectra were obtained on an HP Agilent 8543 UV-visible spectrophotometer in CH_2Cl_2 at room temperature. The steady-state fluorescence spectra were obtained on a fluorimeter (FS920, Edinburg Instrument, Inc, UK) with a Xenon arc lamp as light source. The decay curves of fluorescence were measured on a fluorimeter using time-correlated single-photon-counting technique (LifeSpec II, Edinburg Instrument, Inc.). The diode laser (EPL 375, Edinburg Instrument, Inc, UK) with wavelength at 375 nm was used as light source. The pulse repetition frequency was 20 MHz. The lifetimes were obtained by exponential fitting of deconvoluted decay curves.

Synthesis of TPPZn-OQ

A solution of benzaldehyde (54 mmol) and 8-hydroxy-5-quinolinecarboxaldehyde (35 mmol) in propionic acid (250 mL) was heated to reflux with mechanical stirring. Then freshly distilled pyrrole (72 mmol) in propionic acid (50 mL) was added slowly to the solution in half an hour. Upon cooling to room temperature, methanol (300 mL) was added to the reaction mixture. The resultant solution was kept in a refrigerator overnight. After filtration the solid was dissolved in a minimum amount of chloroform and chromatographed on a silica gel column with chloroform eluent. The second band gives the desired $TPPH_2$-OQ. The compound was dissolved in chloroform and zinc acetate dehydrate in methanol was added and stirred at room temperature overnight. The final porphyrin TPPZn-OQ was after purification on chromatography. The composition of the samples was characterized by elemental analysis and ^1H NMR.

X-ray crystallographic analysis

Single crystals of $TPPH_2$-OQ were obtained by slow evaporation of solvent from the respective complexes in 1:1 (v:v) mixtures of methanol and dichloromethane at room temperature. A crystal was mounted on glass fibers for data collection. Diffraction measurements were made on a CCD-based commercial X-ray diffractometer using Mo Kα radiation (λ= 0.71073 Å). The frames were collected at 125 K with a scan width 0.3° in ω and integrated with Bruker SAINT software package using narrow-frame integration algorithm. The unit cell was determined and refined by least squares upon the refinement of XYZ-centeroids of reflections above $20\sigma(I)$. The data were corrected for absorption using SADABS program. The structures were refined on F^2 using the Bruker SHELXTL (version 5.1) software package. Crystal data for $TPPH_2$-OQ: C47H30N5O3, MW = 712.76, triclinic, space group = P-1, a = 11.339(2), b =12.618(3), c = 13.623(3) Å, α = 83.97(3), β = 89.30 (3), γ = 87.94(3)°, V = 1936.9(7) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.222 Mgm^{-3}, μ(Mo-Kα) = 0.078 mm^{-1}, F(000) = 742, T = 298(2) K. 16915 reflections were measured, of which 6747 were unique (Rint = 0.0742). Final R_1 = 0.2535 and wR1 = 0.1278 values were obtained for 2468 observed reflections with $I>2\sigma(I)$, 504 parameters, and GOF = 1.261. The overall quality of the structure was not good; however, it is clear that OQ unit was linked to the porphyrin successfully.

Fabrication of DSCs

The nanocrystalline TiO_2 paste from the Dyesol was coated on a commercial fluorine-tin-oxide (FTO) using doctor-blade method. After air-drying for about 30 minutes, the sample was put into an oven for sintering (500°C for 30 min) in ambient oxygen. The samples were then coated a scattering layer with larger size (diameter ~ 400 nm) and sintered again at 500°C for 30 minutes. The sample was then cooled to the room temperature and was immersed in a $TiCl_4$ aqueous solution (20 mM) for one hour. The film was air-dried and sintered again at 500°C for 30 minutes. The film was then put into the dye solution (~ 0.3 mM in methanol/CH_2Cl_2, v:v, 9:1) at room temperature and kept for four hour. The film was then taken out, flushed with methanol, and vacuum dried for one hour. The thickness of the film was ~ 6.6 µm from cross-view images of scanning electron microscope (SEM). The counter-electrode was prepared by sputtering a 16 nm-thick film of the Pt on the FTO glass. A mask made from the Parafilm was used as a spacer for two electrodes and sealing material. The electrolyte solution was injected from two pre-cut channels in the mask. The outside of the final cell was sealed by hot glue. The electrolyte is an acetonitrile solution having 0.6 M 1-propyl-2,3-dimethylimidazolium iodide, 0.05 M I_2, 0.1 M LiI, 0.1 M guanidine thiocyanate and 0.5 M *tert*-butylpyridine.

Solar cell characterization

The applied potential and cell current were measured using an Agilent 4155C semiconductor parameter analyzer using a 450W Xenon light source. The light intensity at the surface of cell was calibrated to 100 mW/cm^2, equivalent to one sun at air mass 1.5G condition. Efficiency (η) and the fill factor (ff) were calculated by η (%) = $P_{max} \times 100/(P_{in} \times A)$ and FF = $P_{max}/(I_{SC} \times V_{OC})$, where P_{max} is the maximum output power of cells (mW), Pin is the power density of the light source (mW/cm^2), Isc is the short-circuit current (mA), V_{oc} is the open-circuit voltage (V), A is the active area (0.16 cm^2) of the cell. Incident photon to charge carrier efficiency (IPCE) experiments were performed on an Agilent semiconductor parameter analyzer with an Xe arc lamp and an Newport monochromator. Monochromatic light was incident on the sample through focusing lenses. The National Renewable Energy Laboratory (NREL) calibrated photodetector was used as a reference. The samples were scanned from 350 - 850 nm and the voltage was recorded. The IPCE was calculated using the equation IPCE = (Sample Voltage × Reference voltage)/Reference IPCE. The reference IPCE was supplied by the NREL calibrated DSSC under AM1.5 photon flux. Electron impedance spectroscopy (EIS) measurements were performed on an HP 4192A LF impedance analyzer (5 Hz-13 MHz) set up in two electrode configuration. 10 mV of AC perturbation was applied ranging between 5 - 10^5 Hz. The measurements were performed in dark under forward bias condition from 0 to 1 V. A simplified Randles type model was used to fit the data to extract the series resistance (R_S), which accounts for transport resistance of TCO, the combined charge transfer resistance for electron recombination at

TCO/electrolyte and TiO_2/electrolyte interface (R_{ct}), and the constant phase element representing capacitance at TCO/electrolyte/TiO_2 interface (CPE1).

Stability tests

The TiO_2 films on a microscope slides prepared as aforementioned were immersed in an acetic acid solution in acetonitrile (10 mL) in a beaker at room temperature. The beaker was covered by Parafilm. After three hours the films were taken out, flushed with fresh acetonitrile solvent and images were taken. The samples were put back to the same acidic solution for continued monitoring.

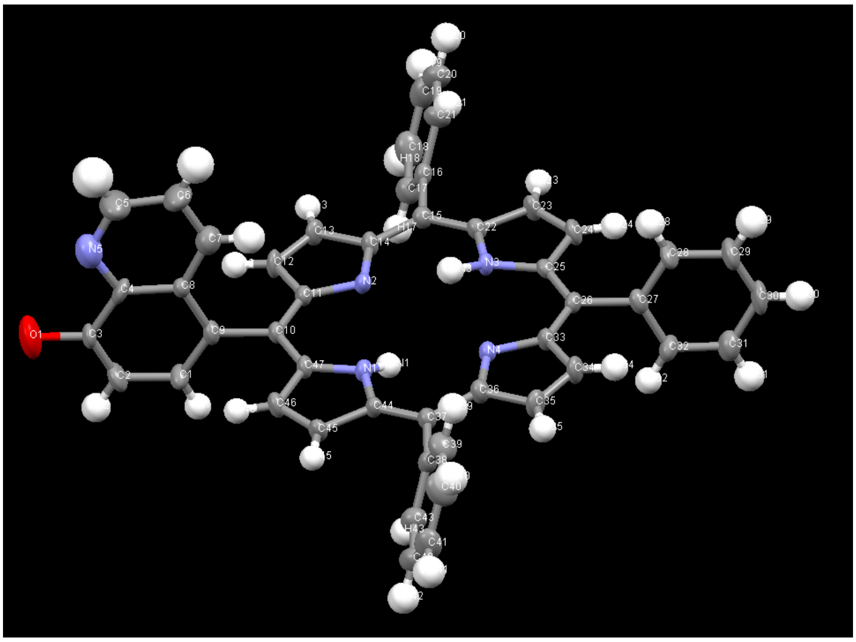


Figure S1. ORTEP diagram of $TPPH_2$-OQ with 30% thermal ellipsoid probability.

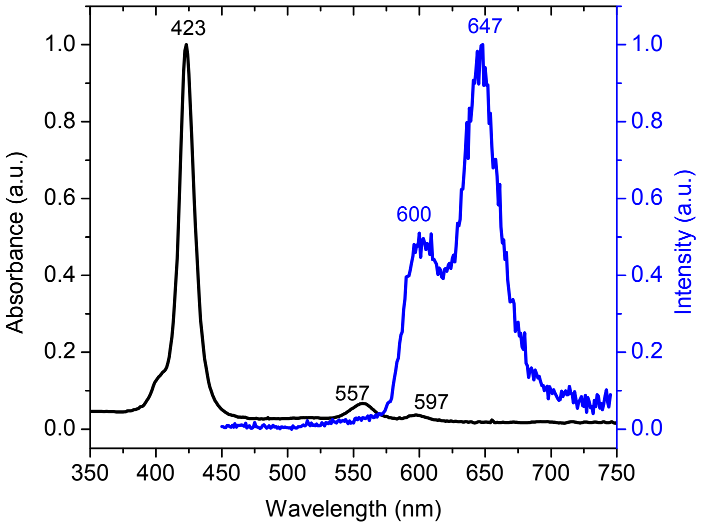


Figure S2. Normalized absorption and fluorescence spectra of TPPZn-OQ in CH_2Cl_2 at room temperature.

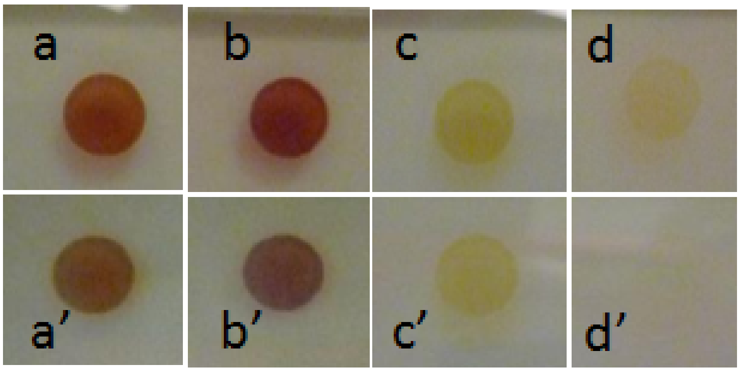


Figure S3 Optical images of porphyrin dye coated TiO_2 film before and after immersing in electrolyte. a, b, c, and d are TiO_2 NP films coated with TPPZn-OQ, TPPZn-COOH, 5-(p-hydroxylphenyl)-10,15,20-triphenylporphyrin zinc, and 5-(p-pyridine)-10,15,20-triphenylporphyrin zinc. a', b', c' and d' are those films that have been immersed in electrolyte for 30 minutes. These experiments indicated strongly that N and O atoms chelate to TiO_2 nanoparticles and the 8-hydroxylquinoline (OQ) is an excellent binding group.

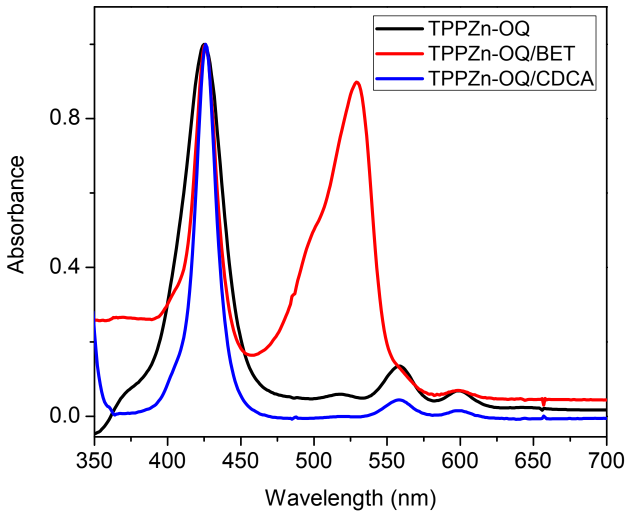


Figure S4 The absorption spectra of TPPZn-OQ, TPPZn-OQ/BET, and TPPZn-OQ/CDCA on TiO_2 films. The spectra were recorded in CH_3CN solvent. The narrowing of Soret bands of TPPZn-OQ and TPPZn-COOH after addition of CDCA on their absorption spectra indicated strongly that aggregation is suppressed in TPPZn-OQ porphyrin.

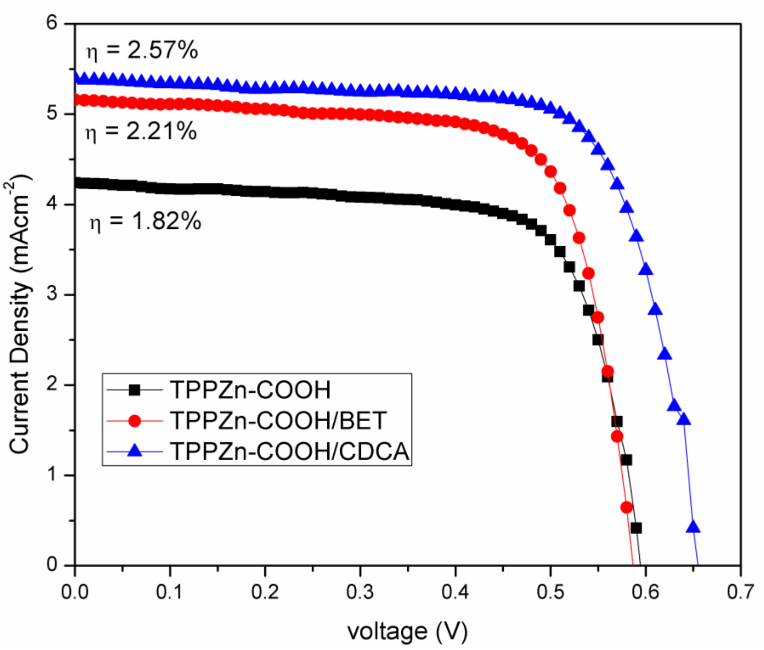


Figure S5. The *J-V* curves of TPPZn-COOH, TPPZn-COOH/BET, and TPPZn-COOH/CDCA sensitized solar cells

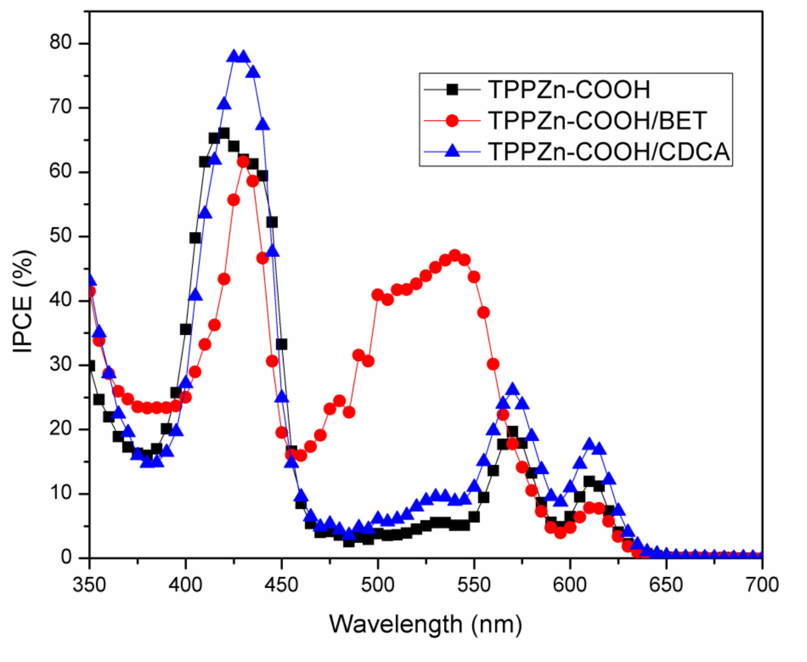
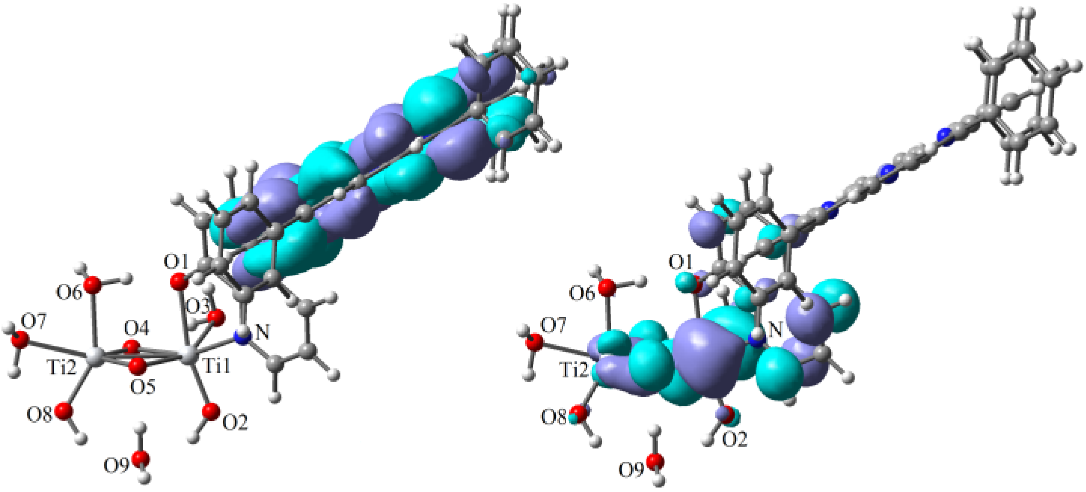


Figure S6. The IPCE curves of TPPZn-COOH, TPPZn-COOH/BET, and TPPZn-COOH/CDCA sensitized solar cells

Theoretical calculations

The theoretical calculations were performed at density functional theory level. The single-crystal structures were used as framework for the construction of initial input structures of calculations. Geometry optimization and electronic structure calculations were performed using B3LYP functional and 6-31G(D) basis set in acetonitrile solution by means of the conductor-like polarizable continuum model (CPCM) solvation model, as implemented in the Gaussian 09 program package. The acetonitrile was used to mimic the solvents in electrolyte. Molecular orbitals were visualized by GaussView 3.0 software. The method has been used widely for geometry optimization and electronic calculations of porphyrins derivatives for its accuracy, which was further validated by very similar bond angles and bond lengths in optimized structures of TPPZn-OQ to its single-crystal structures. Geometry-optimized structures, as well as initial input structure, are shown in Figure S7 and S8. For TPPZn-COOH, two O atoms from carboxylic group bind to two Ti atoms as propose in initial structure. The porphyrin resides vertically on the TiO_2 surface. Each Ti atom is five-coordinate with Ti-O bond length 2.2457 Å. For TPPZn-OQ, O and N atoms bind to same Ti. The bond lengths of Ti-O and Ti-N are 2.2337 and 2.2043 Å.

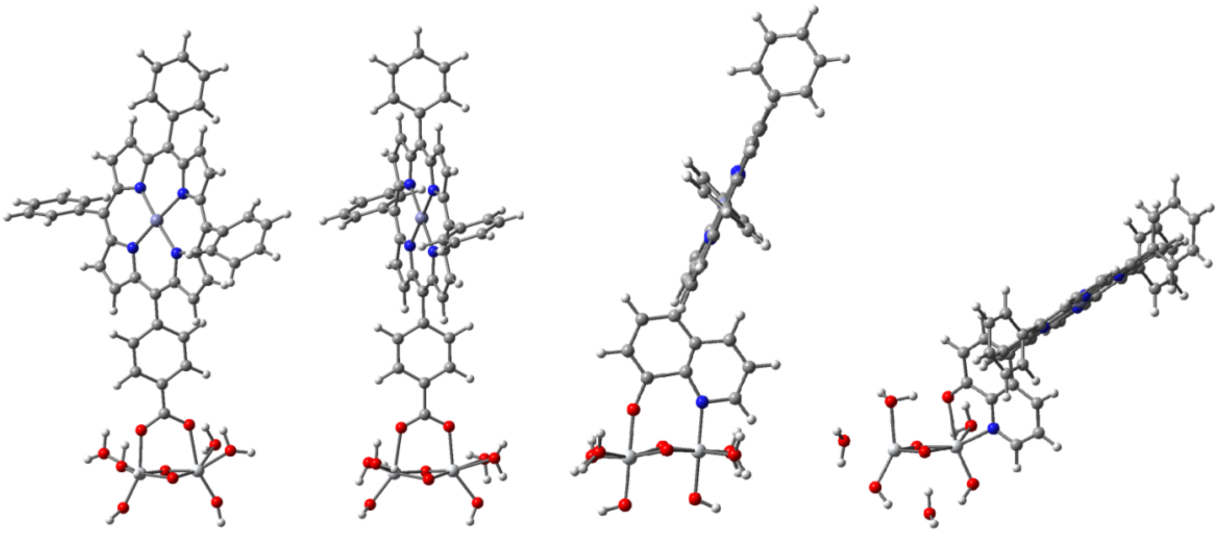
Clearly, this is due to the strong binding capability of 8-hydroxylquinoline group. One O atom that binds to Ti initially was pushed further away from this Ti with distance to two Ti atoms 3.4803 and 3.6169 Å, respectively forming a H_2O that is H-bonded to two neighboring O atoms. The LUMO (lowest unoccupied molecular orbital) is located on the porphyrin ring, whereas HOMO (highest occupied molecular orbital) is located in TiO_2 matrix with energy level 1.67 eV lower than that of LUMO. This is clearly favorable for electron injection form porphyrin ring to TiO_2 conduction band. However, the porphyrin ring resides on the TiO_2 surface with an angle ~ 30˚; the distance between the edges of porphyrin ring to TiO_2 surface in TPPZn-OQ will be shorter than that in TPPZn-COOH. This shortened distance could enhance the electron injection, but also increase the electron recombination.



LUMO (-2.1947 eV)

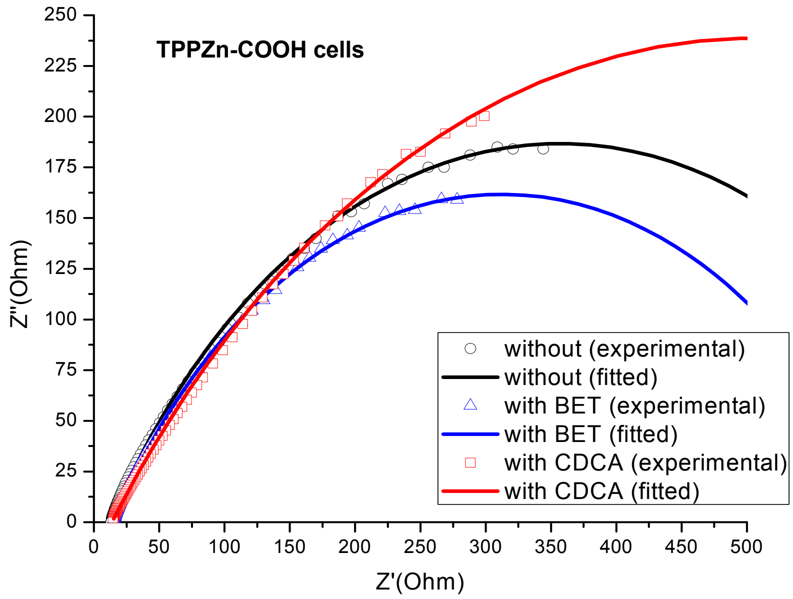
HOMO (-3.8640 eV)

Figure S7 Electron density distribution profiles of TPPZn-OQ after binding to that binds to Ti atom in $[Ti_2O_2\,(OH)_2(H_2O)_4]^{2+}$ model compound.



A B C D

Figure S8 The geometry-optimized structures of TPPZn-COOH (B) and TPPZn-OQ (D). Their initial input structures (A and C, respectively) are also included for a comparison.



c

Figure S9. Nyquist plots of TPPZn-COOH, TPPZn-COOH/CDCA (1:3), and TPPZn-COOH/BET (1:3) sensitized solar cells under bias of -0.60 V. The dots are experimental data; the solid lines are fitting results from Randles model.

Table S1. EIS parameters obtained by fitting experimental data with Randle's model

Sample (TPPZn-COOH cell)	Rs (Ω)	Rct (Ω)	C (F)	n	Time Constant τ (ms)
Without	12.25	688.9	3.07E-5	0.632	21.17
With BET	14.188	602.86	2.63E-5	0.63	15.88
With CDCA	13.88	982.39	7.45E-5	0.576	73.2

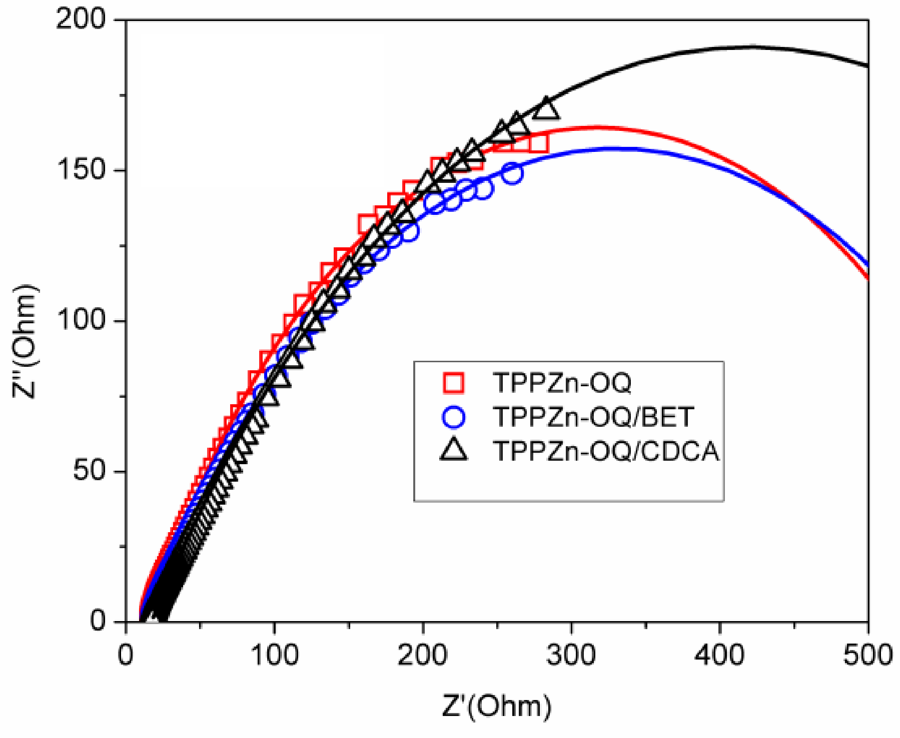


Fig. S10 Nyquist plots of TPPZn-OQ, TPPZn-OQ/CDCA (1:3), and TPPZn-OQ/BET (1:3) sensitized solar cells under bias of -0.60 V. The dots are experimental data; the solid lines are fitting results from Randles model.