Supporting Information

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Fast cascade neutralization of an oxidized sensitizer by an in situ-generated ionic layer of I^- species on a nanocrystalline TiO_2 electrode

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Contents

Figure legends in ESI

Figure S1. ^{1}H NMR spectra of **TA** and **TD** in *d*-dimethylsulfoxide.

Figure S2. ^{1}H NMR spectra of 1-hexene without and with I_2 (1 eq.) and 1-hydroxy-2-iodo-ethane (6), 1,2-diiodoethane (7), and propyloxide (8) in *d*-chloroform.

Figure S3. ^{1}H NMR spectra of 1-hexene without and with I_2 (1 eq.) and 1-hydroxy-2-iodo-ethane (6), 1,2-diiodoethane (7), and propyloxide (8) in *d*-acetonitrile.

Figure S4. ^{1}H NMR spectra of 1-hexene with I_2 (1 eq.) when 1, 2, and 3 *eq*. water were added in *d*-acetonitrile.

Figure S5. Illustration of hydrogen bonds between the diasterotopic protons and water.

Figure S6. Water contact angle before and after iodization of **TA** and **TD** anchored on the surface of TiO_2 substrates.

Figure S7. (a) Transient absorption measurement system using nanosecond pulsed laser used in this study, (b) absorbance and absorption change (ΔO.D.) of N719 ground state and N719 cation, respectively, (c) linear plotted and (d) log plotted decay profiles of N719 cation probed at 790 nm.

Figure S8. Nyquist plots of complete devices (with electrolytes): N719 only (black square), N719 + **TA** (blue triangle), and N719 + **TD** (red circle).

Figure S9. Photovoltaic values obtained using the average over 4 devices for 4 individual experiments (a) photo voltage (V), (b) current density (mA/cm^2), (c) fill factor (%), and (d) power conversion efficient (%).

Figure S10. Cyclic voltammograms for calculating the density-of-state (DOS) of N719 sensitized TiO_2 electrode with and without **TA** and **TD** coadsorbents.

Figure S11. Representative photocurrent–voltage curves for devices prepared with **TA** or **TD** (N719+**TA** or N719+**TD**), in comparison with a control device (N719 only), under AM 1.5 irradiation. Identical 0.25 cm^2 active areas were defined by placing using a black metal mask on top of each device. The transparent photoactive TiO_2 layers of all electrodes are 7.0 ± 0.2μm with 2 ± 0.2μm scattering TiO_2 layers. All devices does not have soldered silver on the FTO glass.

1. Experimental Details

a. Chemicals. 1-Hexene, 1-hydroxy-2-iodo-ethane, 1,2-diiodoethane, propyloxide, tert-butanol, iodine (I_2), guanidinium thiocyanate (GuSCN), lithium iodide (LiI), 4-*tert*-butylpyridine (*t*BP), acetonitrile (AN), and valeronitrile (VN) were purchased from Sigma-Aldrich. Fluorine-doped SnO_2 (FTO) glass, Ti-nanoxide T/SP, Ti-nanoxide R/SP, cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719), 1-butyl-3-methylimidazolium bromide (BMII) were purchased from Solaronix SA.

b. Preparation of the nanocrystalline TiO_2 electrodes. Contaminants were removed by washing the fluorine-doped SnO_2 (FTO) conducting glass with detergent (Mucasol) and subsequently with DI water at 60 °C for 15 min. Organics were subsequently removed and a clean FTO glass was prepared by washing with ethanol and acetone, sequentially, at 40 °C for 10 min. The prepared FTO glass was treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and rinsed with DI water and ethanol to support the good mechanical adhesion at the interface between the transparent TiO_2 layer and the FTO conducting glass. To improve sunlight harvesting via adsorption of large amounts of sensitizers, 20 nm TiO_2 particles were screen-printed onto the $TiCl_4$-treated FTO surface. The transparent film thickness was controlled by reapplication using a similar printing process. The light scattering layer (400 nm anatase particles) was screen-printed onto the transparent layer. The thicknesses of the transparent layer and the scattering layer were measure using an Alpha-Step 500 Surface Profilometer (Tencor Instruments, USA). The double layer prepared on the FTO glass was sintered at 550 °C for 15 min according to the programmed heating procedure. After sintering, the double layer film was treated with a 40 mM $TiCl_4$ aqueous solution again at 70 °C for 15 min, then rinsed with water and ethanol. The nanocrystalline TiO_2 film was subsequently sintered again using the same programmed heating procedure. After cooling to 60 °C, the nanocrystalline TiO_2 electrode was immediately immersed in the dye solution to minimize moisture adsorption.

c. d. ^{1}H NMR measurements. ^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) system operated and *d*-acetonitrile was used.

d. Contact angle measurements. The electrodes were rinsed with acetonitrile and dried prior to use after finish the sensitization process. The water contact angles of dye-sensitized electrodes were measured using surface contact angle calculator (Surface and Electro-Optics, SEO300A). The contact angles were calculated by internal software.

e. Electrochemical impedance spectrophotometer measurements. The impedance values of devices having different coadsorbents were measured using a computer-controlled potentiostat (SP-200, BioLogic) under dark conditions. The frequency range examined was 0.05 Hz–100 kHz at room temperature. The measured spectra were fitted to simplified equivalent circuits using the Z-fit software provided by BioLogic.

f. Cyclic voltammograms measurements. The potential values were measured using a computer-controlled cyclic voltammetry (SP-200, BioLogic). The capacitive currents of electrodes at the TiO_2/BMIB interface were measured at scan rate of voltage amplitude at 0.05 V/s.

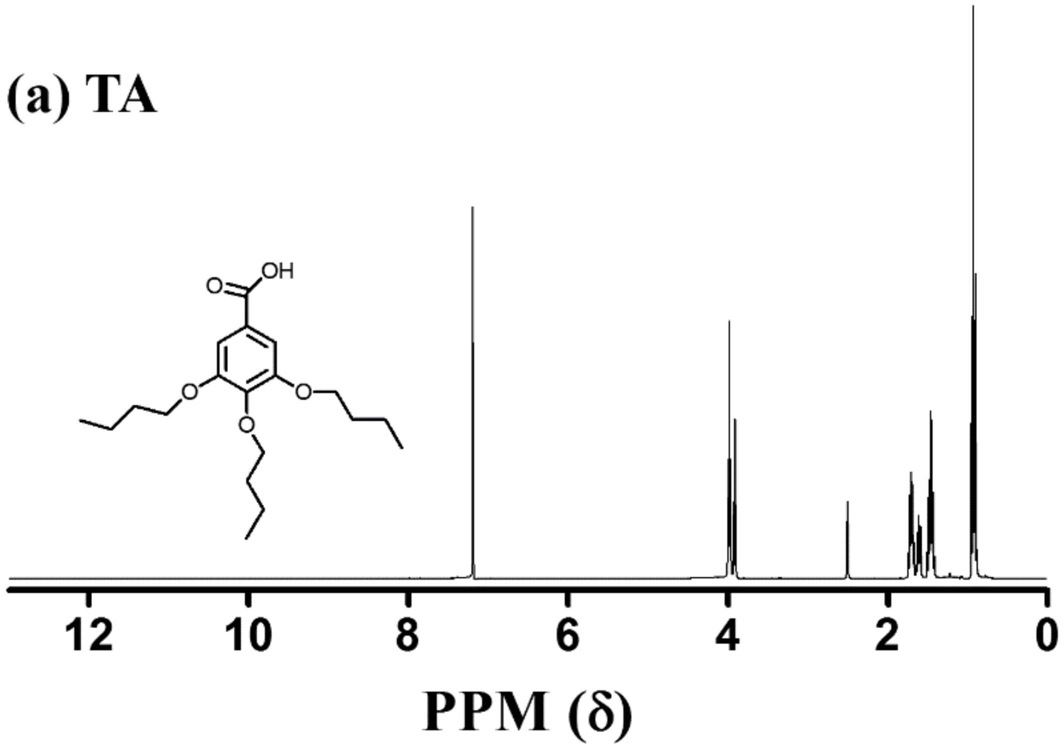
g. UV-Vis absorption measurements. The dye-coated films were rinsed with acetonitrile and dried prior to use. UV-Vis spectrophotometry (using an Optizen POP spectrophotometer) was used to measure the amount of dye adsorbed onto the TiO_2 films.

j. Photoelectrochemical measurement. A 450 W xenon light source (Model No. 94022A, Oriel) was used to apply an illumination power of 100 mW/cm^2 (the equivalent of one sun at AM1.5) to the surface of the solar cell to simulate solar light irradiation. The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR-cutoff filter (KG-5, Schott). Comparison of the simulated light to the true solar spectrum in the region 350–750 nm determined a spectral mismatch of less than 2%. The *I-V* characteristics were obtained by measuring the photocurrent generated by the cells (under an applied external bias) using a Keithley model 2400 digital source meter (Keithley, USA). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively.

h. IPCE measurement.

The IPCE spectra were recorded as functions of wavelength (370 -550) under a constant white light bias of approximately 5 mW cm^{-2} supplied by an array of white light emitting diodes using a power source with a monochromator (Zahner GmbH) and a multimeter and chopped at approximately 4 Hz.

2. Synthesis of TA and TD[1-3]



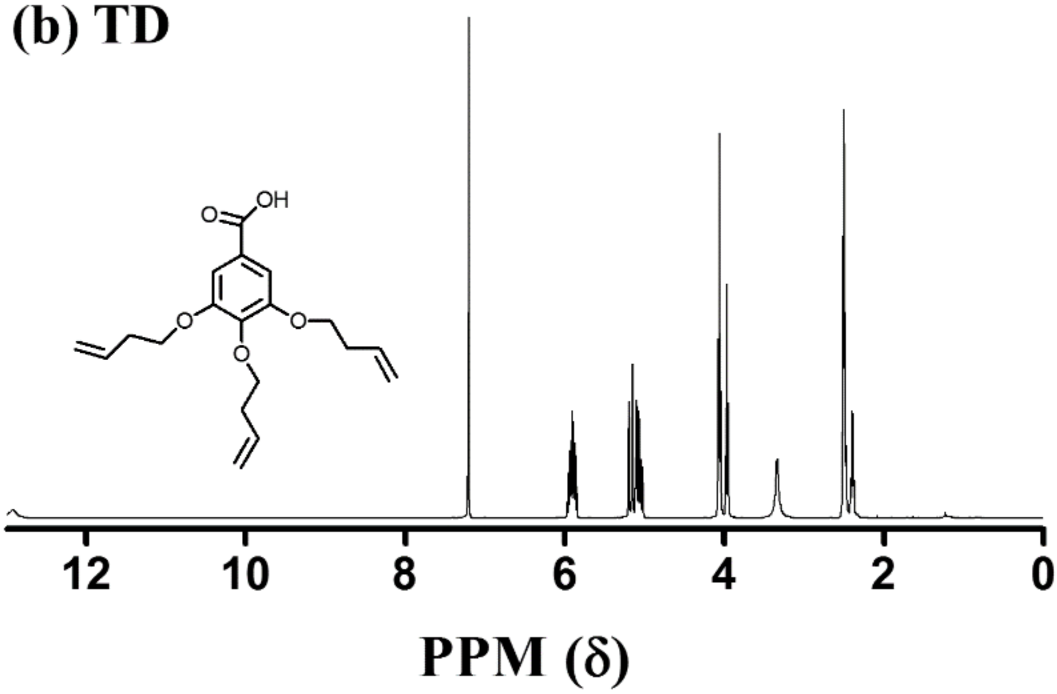


Figure S1. ^{1}H NMR spectra of **TA** and **TD** in *d*-dimethylsulfoxide.

3. ^{1}H NMR study in *d*-chloroform

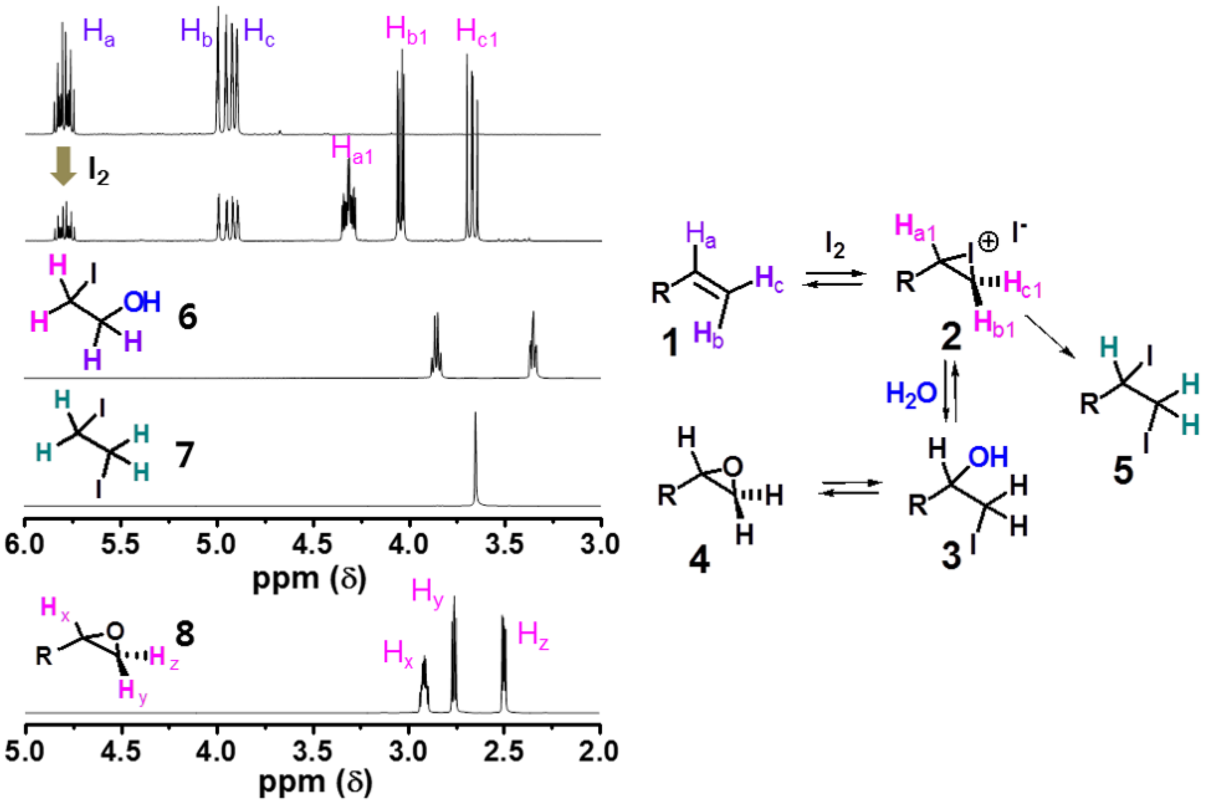


Figure S2. ^{1}H NMR spectra of 1-hexene without and with I_2 (1 eq.) and 1-hydroxy-2-iodo-ethane (6), 1,2-diiodoethane (7), and propyloxide (8) in *d*-chloroform.

The addition of I_2 to the 1-hexene (**1**) solution may undergo further reactions generating chemicals **3-5** as shown in the scheme (right side). However, we only observed three new peaks (H_{a1}, H_{b2}, and H_{c3}) in the range 3.5 – 4.5 ppm, of which pattern was identical to the peaks provided by propyloxide (8), indicating that the H_{b2} and H_{c3} protons retained their diastereotopic environments. This result suggested that the ionic iodized species **2** was generated and that further reactions toward **3** (hydrolysis) or **5** (fully iodization) did not proceed. These results were corroborated by comparing the ^{1}H NMR spectra of 1-hydroxy-2-iodo-ethane (**6**) and 1,2-diiodoethane (**7**) with the peak positions corresponding to the homotopic protons.

4. ^{1}H NMR study in *d*-acetonitrile

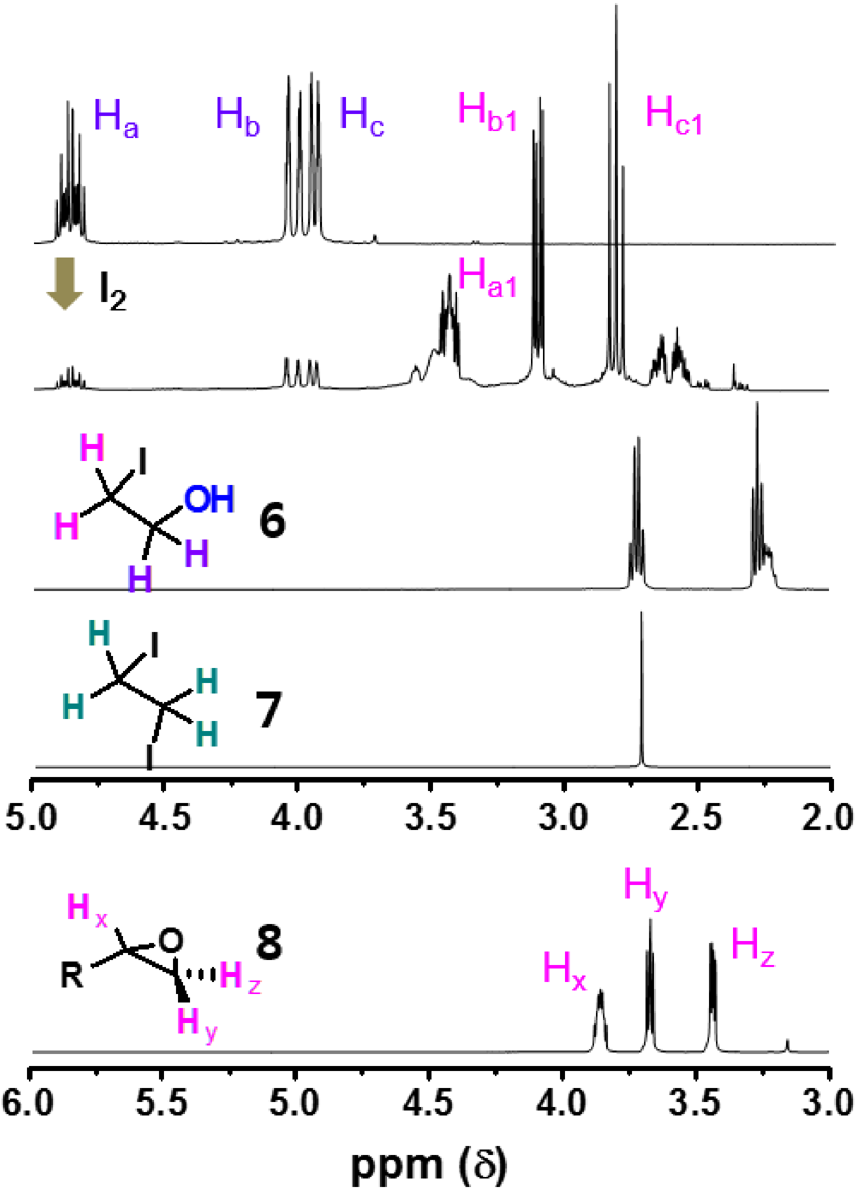


Figure S3. ^{1}H NMR spectra of 1-hexene without and with I_2 (1 eq.) and 1-hydroxy-2-iodo-ethane (6), 1,2-diiodoethane (7), and propyloxide (8) in *d*-acetonitrile.

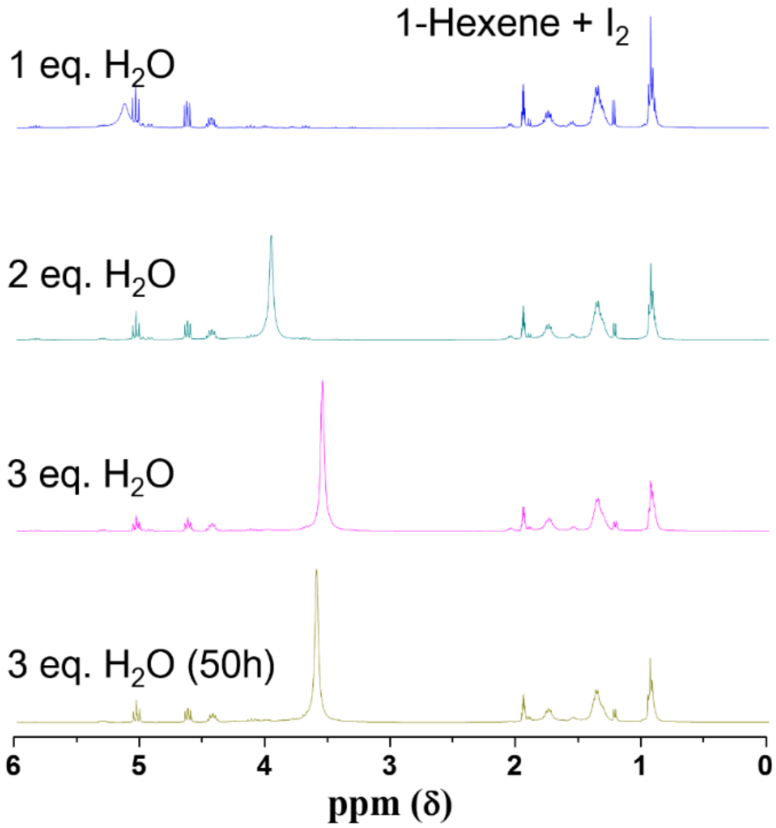


Figure S4. ^{1}H NMR spectra of 1-hexene with I_2 (1 eq.) when 1, 2, and 3 *eq*. water were added in *d*-acetonitrile.

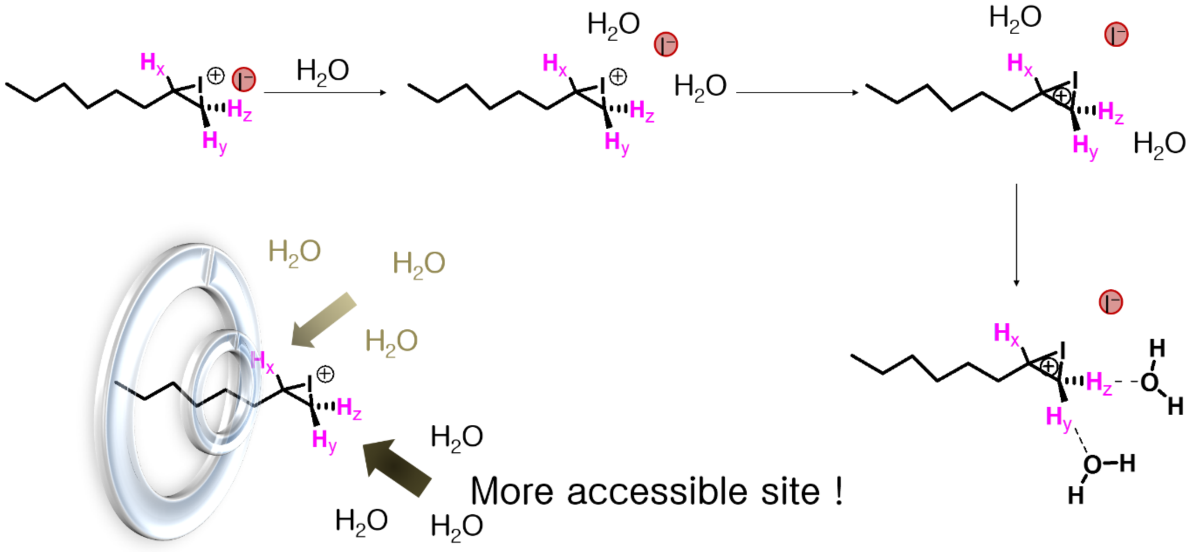


Figure S5. Illustration of hydrogen bonds between the diasterotopic protons and water.[4,5]

5. Water contact angle measurement

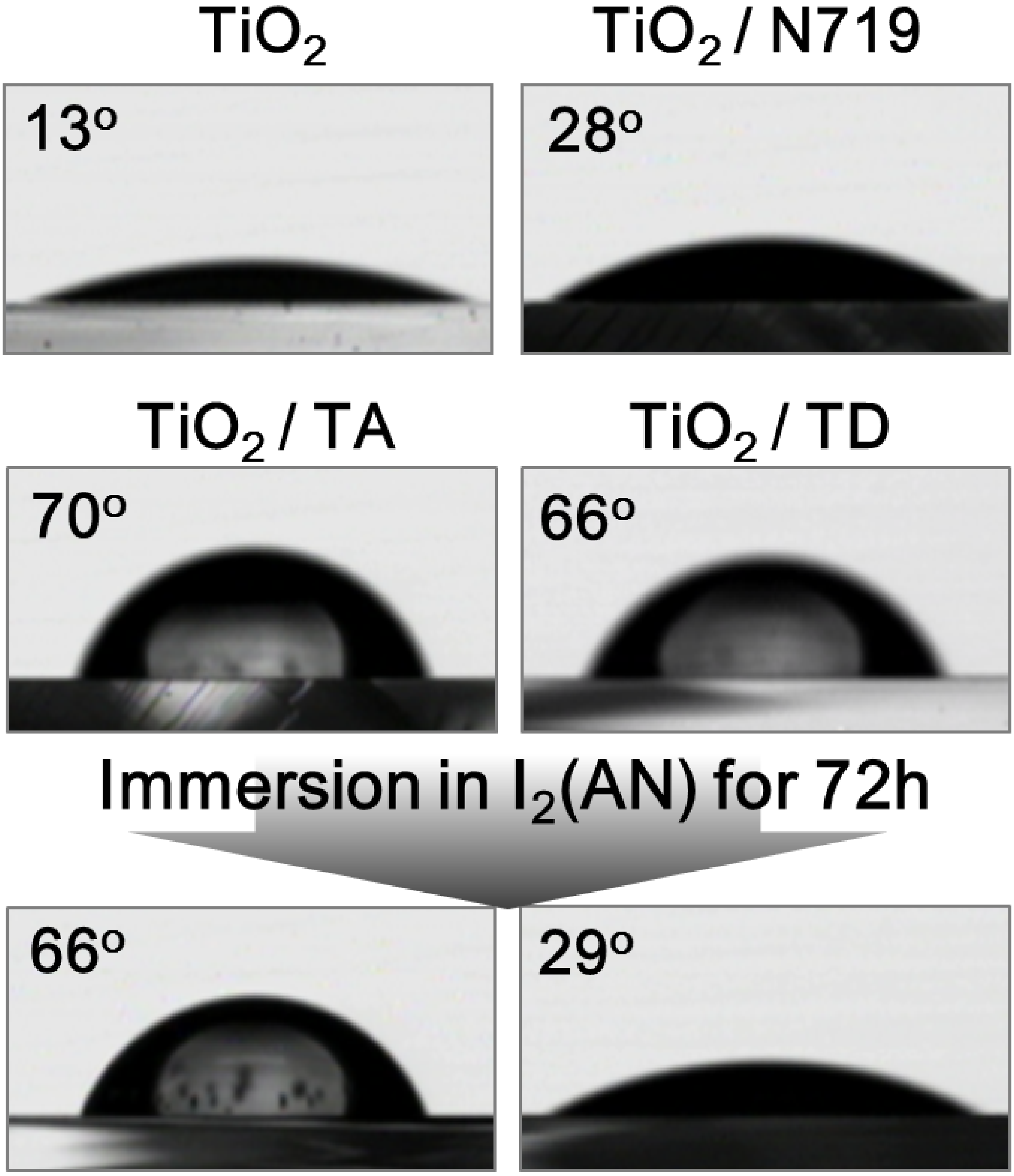


Figure S6. Water contact angle before and after iodization of **TA** and **TD** anchored on the surface of TiO_2 substrates.

6. Transient absorption spectroscopy (TAS) study[6]

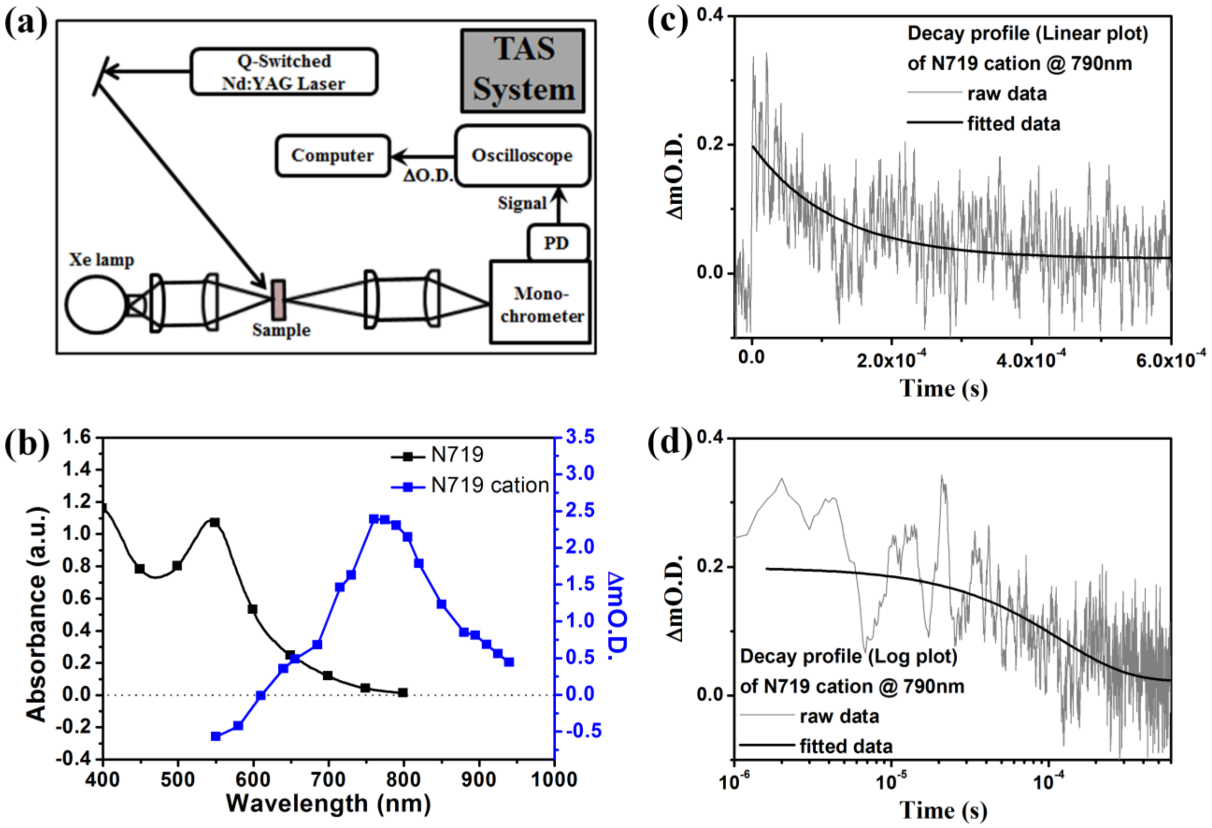


Figure S7. (a) Transient absorption measurement system using nanosecond pulsed laser used in this study. (b) Absorbance and absorption changes (ΔO.D.) of N719 ground state and N719 cation, respectively. (c) Linear plotted and (d) log plotted decay profiles of N719 cation probed at 790 nm.

(Equation S1.) $\Delta O.D. = \log((I_0 - I_{BG})/(I_{SIG} - I_{PL}))$

Equation for the time-dependent absorption decay profile from transient absorption measurement (I_0: incident light intensity, I_{BG}: back ground scattering, I_{SIG}: absorbance change of signal, I_{PL}: photoluminescence by the materials).

(Equation S2.) $y = y_0 + A_1 \times \exp(-x/t_1) + A_2 \times \exp(-x/t_2)$

Equation for fitting of decay profile obtained from transient absorption measurement (y_0: offset, A_1 and A_2: amplitude, t_1 and t_2: decay constants).

Transient absorption spectroscopy using pulsed nanosecond laser was established for the time-dependent decay profile of N719 cations. As function of probing wavelengths from 550 to 950 nm, the spectrum of N719 cationic state was obtained distinguishable to that of ground state. There were two light sources for the transient absorption measurement. One was the pulsed nanosecond laser for pumping the ground state of N719 to excited state. The other was continuous wavelength Xe lamp for probing the absorption change of N719 cations. The final absorbance change (ΔO.D.) of N719 cations was calculated using Equation S1. by excluding the background scattering and photoluminescence by probing Xe lamp and the pumping laser source, respectively. Since the absorbance change was very small with large signal to noise ratio, the stretched exponential fitting (Equation S2.) is employed for the clear calculation of decay kinetics (see the experimental details for the measurement conditions).

7. Electrochemical impedance spectroscopy (EIS) study[7]

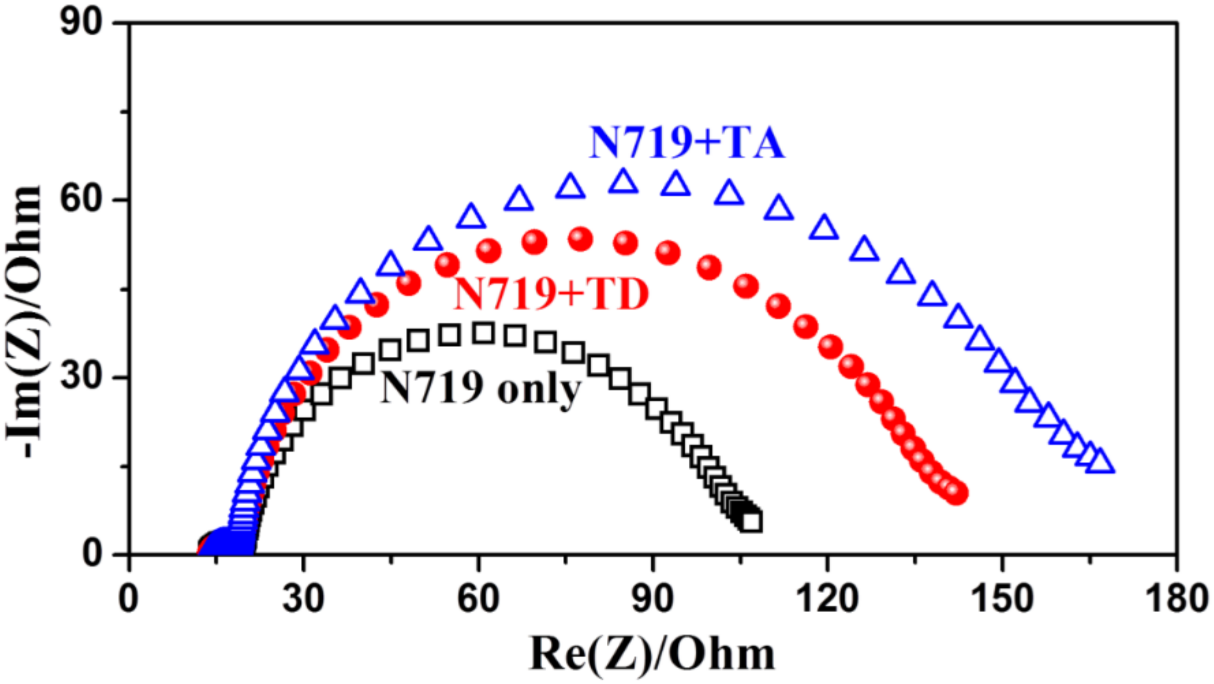


Figure S8. Nyquist plots of complete devices (with electrolytes): N719 only (black square), N719 + **TA** (blue triangle), and N719 + **TD** (red circle).

8. Values obtained using the average over 4 devices for 5 individual experiments

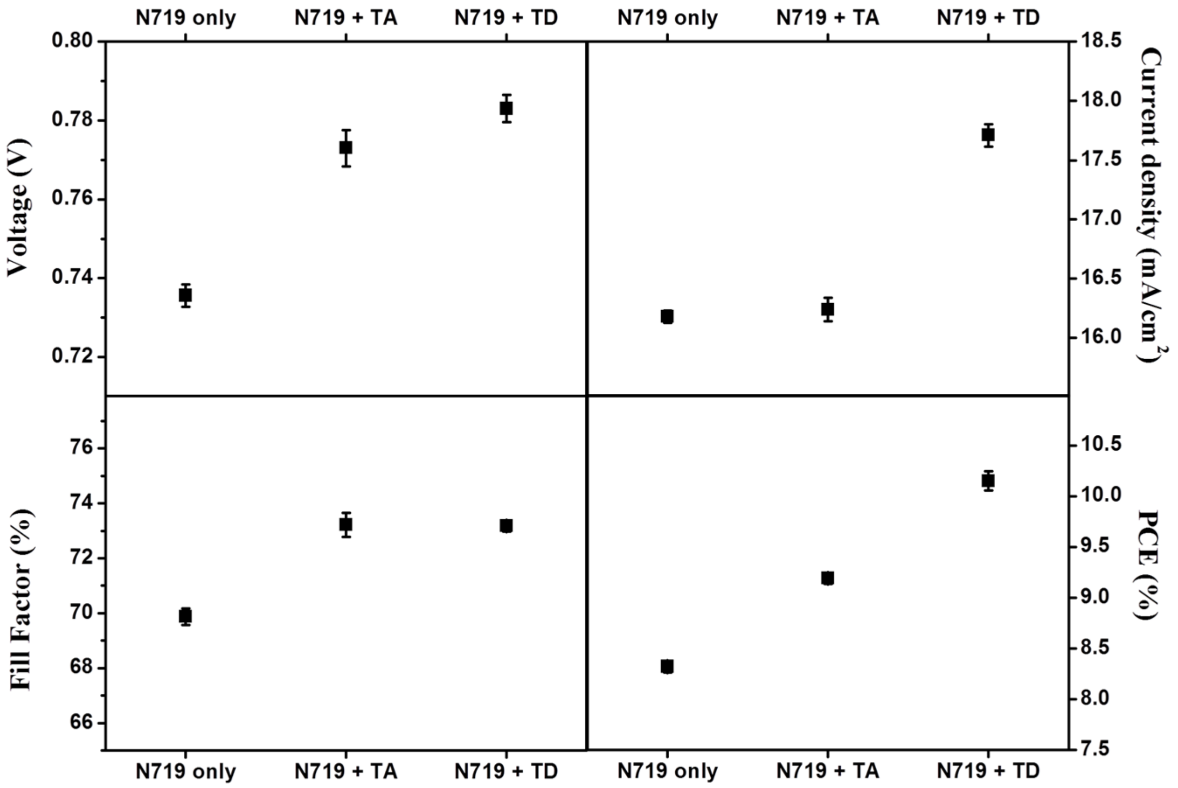


Figure S9. Photovoltaic values obtained using the average over 4 devices for 5 individual experiments (a) photo voltage (V), (b) current density (mA/cm^2), (c) fill factor (%), and (d) power conversion efficient (%).

9. Density of state (DOS) study using cyclic voltammeter[8,9]

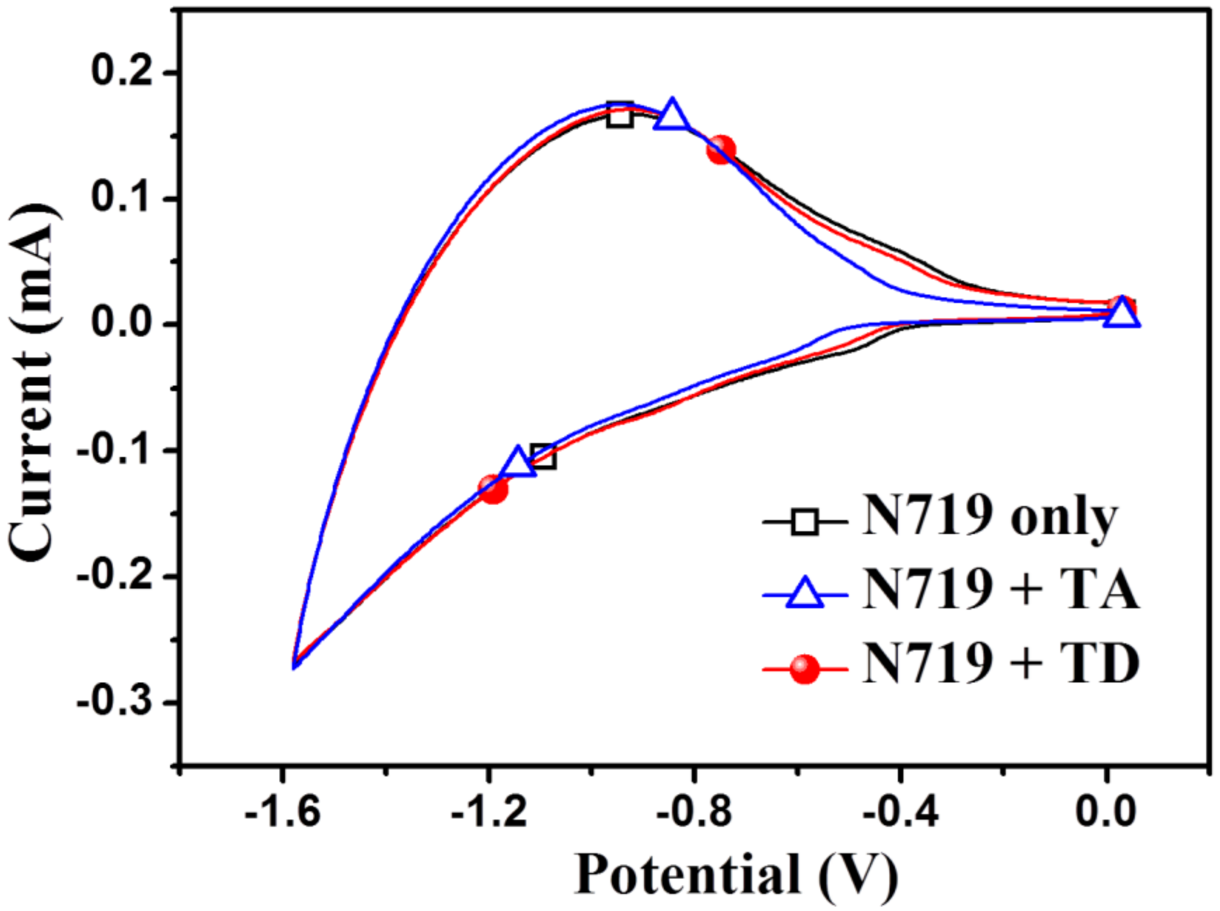


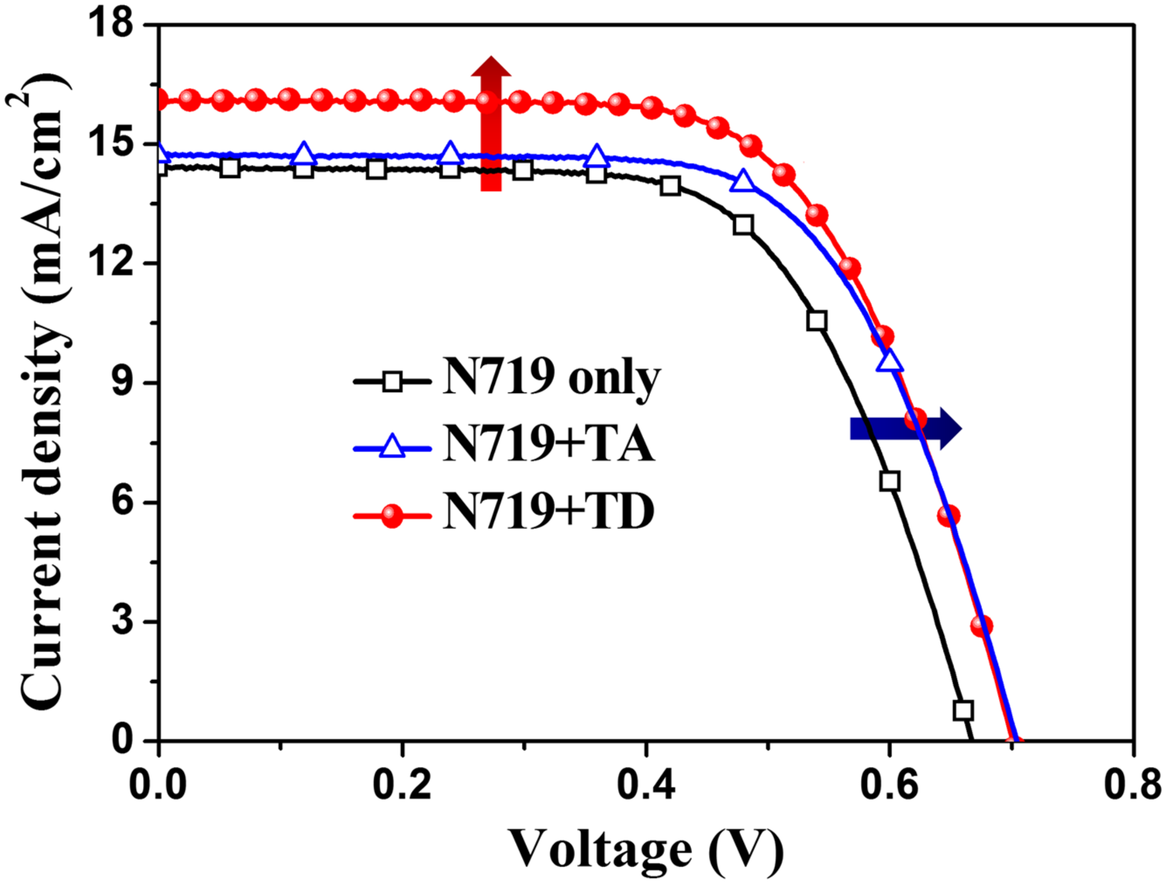
Figure S10. Cyclic voltammograms for calculating the density-of-state (DOS) of N719 sensitized TiO_2 electrode with and without **TA** and **TD** coadsorbents.

(Equation S3.) $\mathrm{d}Q/\mathrm{d}V = \mathrm{DOS}(N_A/F)$

(Equation S4.) $\mathrm{d}Q = 1/\nu * I(V)\mathrm{d}V$

Q is the total injected charge, N_A is the Avogadro constant, F is Faraday's constant, $I(V)$ is the current, V is the potential applied on the electrode, and ν represents the constant scanning rate in the cyclic voltammetry measurements. Dividing the derivative $\mathrm{d}Q/\mathrm{d}V$ by the elementary charge in Equation S3 yields DOS, while the integration of Equation S4 will give Q the total number of surface states as plotted *vs* applied potential in Figure S11.[8]

10. Photocurrent–voltage curves for devices with thin photoactive TiO_2 layers (7.0 μm).



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