SUPPORTING INFORMATION

Combined experimental and theoretical investigation of the hemi-squaraine/TiO_2 interface for dye sensitized solar cells.

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I. COMPUTATIONAL DETAILS

Unsupported dye. In order to rationalize the photochemical properties of the CT1 molecule, structure and electron distribution have been calculated for the isolated system. Density functional theory (DFT) has been adopted by employing three functionals among those proposed in literature as the most promising for the excitation properties calculations of organic molecules[1,2]. They include hybrid B3LYP[3], PBE0[4] and the HSEH06[5,6,7] range corrected functionals. All calculations have been performed with 6-311+G(d,p) basis set[8] with Gaussian09[9] package. Time dependent DFT (TD-DFT) excited state provides information about the energy of the lowest vertical excitations energies, E_g^{calc}, oscillator strengths, f^{cal}. Solvent effects (EtOH and DMF) have been incorporated adopting the polarized continuum model (PCM) as implemented in the Gaussian09 package. Ground state calculations with all the selected functionals result in comparable molecular structures and electron distributions. All methods describe the molecule as almost planar, with an averaged value of the torsion angle τ defined around the –C-C- bond connecting the squaric and the benzo-indole groups close to 19°. The PBE0/6-311+G(d,p) electron distribution of HOMO, HOMO-1 and LUMO are depicted in Fig. SI1. Results from the TD-DFT calculations are reported in Table SI1. Computed excitation gaps provided by PBE0, B3LYP and HSEH06 (404, 418, 410 nm, respectively) are in good agreement with the experimental optical gap, 434 nm (2.83 eV). All methods describe the excitation mainly due to a HOMO→LUMO transition with a percentage from 65 to 70%, Table SI1.

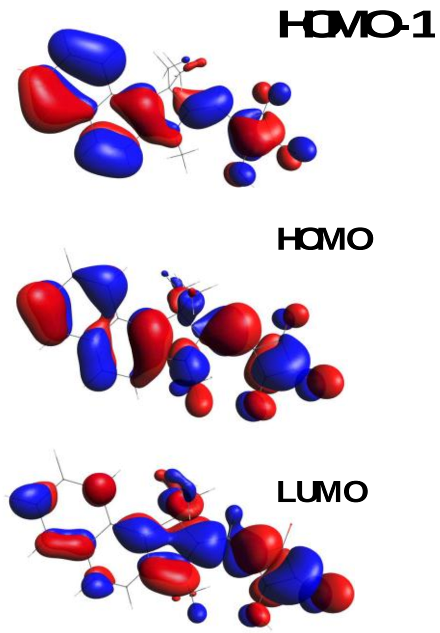

Fig. SI1 Frontier orbitals isodensity surfaces of CT1 molecule. PBE0/6311+G(p,d) results.

Functional	E_g^{calc}	f^{cal}	Main MO transition with their probabilities
PBE0	3.07 (404)	0.92	HO→LU 66 %
HSE0S6	3.03(410)	0.88	HO→LU 70 %
B3LYP	2.97(418)	0.86	HO→LU 70 %

Table SI1. Lowest computed vertical excitation energies E_g^{calc} in eV (nm in parentheses) and corresponding oscillator strengths f^{cal} of CT1 dye. Main molecular orbital (MO) transition with their probabilities are also reported using PBE0/6-311+G(d,p).

Supported dye. The attachment of CT1 to the anatase (101) surface has been studied by DFT calculations within the gradient corrected (GGA) Pendew-Burke-Ernzerhof (PBE)[10] functional that is employed to describe the exchange-correlation effects. We applied a Hubbard U term on the Ti-3d orbitals to improve the quality of GGA in describing the electronic structure of metal oxide surface (U_{Ti} = 6.68 eV)[11]. The Kohn-Sham equations are solved using ultrasoft pseudopotential for describing the electron-ion interaction and expanding the electronic wave functions in plane waves (PW). For all calculations we adopted plane wave basis set with a cutoff of 30 Ry for the wave functions and 300 Ry for the charge density and potentials. Surface calculations were performed in (1x3) orthorombic supercells containing five O-Ti-O trilayer slabs and 10 Å of vacuum to avoid spurious interaction between periodic images. The Brillouin Zone (ZB) sampling was done by employing an 6×6×6 Monkhorst-Pack mesh for the bulk calculations and an 6×6×1 or equivalent grid for the surface calculations[12].Structures were relaxed by minimizing the atomic forces and convergence was assumed when the maximum component of the residual forces on the ions was less than 10^{-4} Ry/Bohr. All the calculations were carried out using the Quantum Espresso code[13].

II. SYNTHESIS AND CHARACTERIZATION OF CT1 HEMI-SQUARAINE DYE

General

All the chemicals were purchased from Sigma Aldrich and Acros Organics and used as received without further purification. TLC were performed on silica gel TLC PET-FOILS. Purity analysis were performed on a Waters HPLC apparatus (Waters 1525 Binary HPLC pump) equipped with PDA detector (Waters 2996) set at 430 nm and a Waters SunFire 4.6X250 mm C8 column. The HPLC analysis were conducted in isocratic condition with water/acetonitrile 30/70 (flow rate = 1.0 ml/min). Melting point were determinated using a Reichert’s melting point microscope instrument (the thermometer was not corrected) equipped with Reichert’s thermostat. ESI-mass analysis were recorded by direct infusion with Termo Advantage Max coupled with ESI interface. The samples were solubilized in methanol. The ^{1}H NMR spectra were recorded on a Brucker Avance 200 spectrophotometer with $CDCl_3$ and DMSO-d_6 as solvent. Chemical shift were referenced internally to tetramethylsilane (TMS, δ=0.0) in ppm. The FT-IR spectrum were recorded on a Shimadzu FTIR-8400 Spectrophotometer using KBr pellets.

Synthesis

1,1,2,3-tetramethyl-1H-benzo[e]indol-3-ium iodide **(1)**[14]

1,1,2-trimethyl-1H-benzo[e]indole (7 g, 0.033 mol) and methyl iodide (4.16 ml, 0.067 mol) were mixed in 50 ml acetonitrile in a 100 ml round bottom flask. Then the reaction mixture was refluxed under vigorously stirring for 3 h. After cooling to room temperature, the product was precipitated in 400 ml of diethyl ether, filtered off and washed two times with 50 ml of cold ethanol. The product was dried in a vacuum oven at 40 °C for 4 h giving a red-gray powder. 9.5 g (81%).

TLC: R_f (methanol/dichloromethane 1/9) = 0.30[15]; Mp (°C): 198-200[14].

^{1}H NMR (200MHz, DMSO): δ (ppm) = 8.36 (d, 1H, J = 8.5 Hz, H_{Ar}), 8.29 (d, 1H, J = 8.9 Hz, H_{Ar}), 8.22 (d, 1H, J = 8.1 Hz, H_{Ar}), 8.10 (d, 1H, J = 8.9 Hz, H_{Ar}), 7.80-7.77(m, 1H, H_{Ar}), 7.74-7.71(m, 1H, H_{Ar}), 4.09 (s, 3H, $^+$N-CH_3), 2.86 (s, 3H, -CH_3), 1.75 (s, 6H, -2 CH_3).

FTIR (KBr, cm^{-1}) ν: 3550-3250 (w), 3057 (w), 3018 (w), 3001 (w), 2983 (m), 2932 (w), 2907 (w), 2867 (w), 1637 (m), 1618 (w), 1585 (m), 1522 (m), 1464 (m), 1449 (m), 1391 (m), 1366 (m), 1217 (w), 1132 (w), 874 (m), 825 (s), 791 (m), 755 (s), 557 (m), 425 (w).

ESI-MS : m/z, $C_{16}H_{18}I_2N$ calc. 351.23, found 224.13 (M^+).

(E)-3-ethoxy-4-((1,1,3-trimethyl-1H-benzo[e]indol-2(3H)-ylidene)methyl)cyclobut-3-ene-1,2-dione (**2**).[16,17]

3,4-diethoxycyclobut-3-ene-1,2-dione (3.51 ml, 0.024 mol), 10 g (0.028 mol) 1-ethyl-2,3,3-trimethyl-3*H*-indolium iodide (**1**) and 4 ml triethylamine were dissolved in 250 ml ethanol in a 500 ml round bottom flask. Then the reaction mixture was refluxed under vigorously stirring for 19 h. The solvent was removed under vacuum from the orange mixture and the solid obtained was washed two times with 30 ml of cold ethanol. If it is necessary, the crude product was purified by column chromatography over silica gel with ethyl acetate and petroleum ether as eluent. Product was dried in vacuum oven at 40 °C for 4 h giving orange powder. 6.71 g (80%).

TLC: R_f (methanol/dichloromethane 3/97) = 0.94; Mp (°C): 162-164

^{1}H NMR (200 MHz, $CDCl_3$)δ ppm: 8.17 (d, 1H, H_{Ar}), 7.97 (d, 2H, $2H_{Ar}$), 7.64 (d, 1H, $1H_{Ar}$), 7.56 (t, 1H, H_{Ar}), 7.39 (t, 1H, H_{Ar}), 5.35 (s, 1H, C-H), 4.85 (q, 2H, $-O-CH_2-CH_3$), 3.51 (s, 3H, $^+N-CH_3$), 1.82 (s, 6H, -2 CH_3), 1.47 (t, 3H, $-O-CH_2-CH_3$).

FTIR (KBr, cm^{-1}) ν: 3680-3150 (w), 2978 (w), 2932 (w), 1775 (w), 1712 (m), 1619 (s), 1537 (s), 1512 (m), 1416 (m), 1332 (m), 1297 (s), 1253 (s), 1212 (m), 1069 (m), 936 (w), 811 (w).

ESI-MS: m/z $C_{22}H_{21}NO_3$ calc. 347.41, found 348.53 $[M+1]^+$.

(E)-3-hydroxy-4-((1,1,3-trimethyl-1H-benzo[e]indol-2(3H)-ylidene)methyl)cyclobut-3-ene-1,2-dione (**3**).[16,17]

(E)-3-ethoxy-4-((1,1,3-trimethyl-1H-benzo[e]indol-2(3H)-ylidene)methyl)cyclobut-3-ene-1,2-dione **(2)** (6.71 g, 0.019 mol) was dissolved in 100 ml ethanol in a 250 ml round bottom flask and then 3.5 ml of a 40% NaOH solution was added. The orange mixture was refluxed under vigorously stirring for 10 minutes. After, it was concentrated and washed with 30 ml of cold ethanol. Solvent was removed from the yellow filtered solution and solid obtained was washed with acetonitrile and dried in vacuum oven at 40 °C for 6 h giving orange powder.
3 g (50%).

TLC: R_f (methanol/dichloromethane 3/97) = 0,68; Mp (°C): 185-188.

^{1}H NMR (200 MHz, DMSO)δ ppm: 7.99 (d, 1H, H_{Ar}), 7.76 (d, 2H, $2H_{Ar}$), 7.39 (d, 1H, $1H_{Ar}$), 7.32 (t, 1H, H_{Ar}), 7.15 (t, 1H, H_{Ar}), 5.30 (s, 1H, C-H), 3.23 (s, 3H, $^+N-CH_3$), 1.76 (s, 6H, -2 CH_3).

FTIR (KBr, cm^{-1}) ν: 3550-3200 (m), 3100-3000 (w), 1780 cm^{-1} (s), 1566 cm^{-1} (s).

ESI-MS: m/z $C_{20}H_{17}NO_3$ calc. 319.35, found 318.25 (M^+).

UV-VIS spectra and determination of molar absorption coefficient

UV-VIS spectra were recorded on a Shimadzu 1700 PharmaSpec Spectrophotometer using 1 cm quartz cells. A known amount of CT 1 dye (about 5 mg) was dissolved in 200 ml of acetonitrile in a volumetric flask (mother solution). Three solution were prepared from mother solution diluting 8.0, 4.0 and 3.3 ml to 10 ml of solvent (daughter solutions). All solutions were analyzed by UV-VIS spectroscopy and absorbance at the λ_{max} (388 nm, 419 nm and 434 nm) were recorded. The λ_{max} absorbances were plotted vs. dye concentrations and a linear fitting was performed. The slope of the plot correspond to the molar absorption coefficient (ε).

The determination of molar absorption coefficient was conducted, in duplicate, by preparing two concentrated dye mother solutions subjected to the same dilution and calculation procedures. The logε obtained from the two separate data set was compared with their average: if the difference is less or equal to 0.02, the data were considered acceptable. In this case the average become the true value. Otherwise, the same procedure was repeated until a difference not more then 0.02 was attained. A sole value for The CT 1 dye molar absorption coefficient was than obtained by calculating the average value of the molar extinction coefficients at the three wavelengths (388 nm, 419 nm and 434 nm).

Fluorescence emission measurements were acquired on a Horiba Jobin Yvon Fluorolog3 TCSPC spectrofluorimeter equipped with a 450 W Xenon Lamp and a Hamamatsu R928 photomultiplier. The emission spectra were performed in 1cm path-length Sigma Aldrich cell with slit set at 5.

A diluted solution of the CT 1 dye in acetonitrile was prepared so as to ensure that its absorbance at λ_{max} was lower of 0.1 unit of absorbance.

The sample was excited at 388 nm, 419 nm and 434 nm (corresponding at the absorbance peaks). The ranges for fluorescence emission recording respectively were 400-700 nm, 430-700 nm and 450-700 nm obtaining the same maximum emission value (480 nm).

Cyclic voltammetry

All the electrochemical measurements were carried out at room temperature in nitrogen-saturated solutions. The solvent system was dimethylformamide (DMF, dehydrated before use) and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte; concentration of 6.3 mM CT1 was investigated. Electrochemical measurements were performed using an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat in a conventional three-electrode cell configuration with glassy carbon (GC) (3 mm in diameter) as working electrode, a SCE (saturated KCl) as reference electrode and a platinum wire as counter electrode. All the voltammetric potentials are reported with respect to NHE reference, scan rate employed was 0.05 V s^{-1}. The dye exhibit a redox stability showing voltammetric scans super imposable for more then 10 times.

III. DSCs FABRICATION

Fluorine-doped tin oxide (FTO) covered glasses (7 Ω/sq, Solaronix), 2 cm x 2 cm x 0.22 cm, were immersed in acetone in an ultrasonic bath for 10 min, rinsed with ethanol and dried under nitrogen flow. The substrates were then cleaned for 10 minutes in a 3:1 (Sulfuric Acid: Hydrogen Peroxide) “piranha” solution in order to remove organic residues, abundantly rinsed with deionized water and dried with N_2 stream. Glasses were heated at 100 °C for 2 minutes to remove humidity from the surface; afterward a TiO_2 layer (Ti-Nanoxide D37 paste, Solaronix) with a circular shape was deposited onto FTO by tape casting technique. Printed substrates were dried at room temperature for 30 minutes, then at 50 °C for 10 minutes on a hot plate and finally a sintering process at 450 °C for 30 minutes allowed the interconnection among TiO_2 nanoparticle network with a final film thickness of 7.5 μm, as measured by profilometer (P.10 KLA-Tencor Profiler).

The sensitizing solution was prepared dissolving the hemi-squaraine dye in an acetonitrile solution with the concentration of 0.25 mM, adding different amounts of chenodeoxycholic acid (CDCA) (0 mM, 1 mM and 10 mM, corresponding to 0, 4:1 and 40:1 concentration ratios between the CDCA and the dye, respectively). For the standard cell, prepared for comparison, a 0.3 mM ethanolic solution of cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) dye (N719, Ruthenizer535bis-TBA, Solaronix) was prepared as well. The N719-sensitized reference photoelectrode was prepared soaking overnight the TiO_2 film in ethanolic N719 dye solution at room temperature, while the hemi-squaraine-sensitized photoelectrodes were incubated at room temperature for 5 h. The films were then rinsed (in ethanol and acetonitrile for N719 and hemi-squaraine dye, respectively) to remove the unspecific adsorbed molecules.

The photoelectrochemical devices were assembled using a microfluidic architecture. The preparation and assembling of FTO/Pt counter electrodes, polydimethylsiloxane (PDMS) membranes and polymethylmetacrylate (PMMA) clamping system are described elsewhere[18]. The electrolyte (Iodolyte AN 50, Solaronix) filling was performed by connecting a syringe to the housing ports. Inlet/outlet connections were closed during cell operation using cap made of LDPE tubes filled with cross-linked PDMS to avoid spontaneous inlet of air and water vapor inside the microfluidic chamber. Copper foils (50 μm thick, area 0.5 x 3 cm^2) were used as electric contacts with FTO, dielectrically insulated each other by the PDMS membrane. The active area of the cells was 0.78 cm^2 and the measurements were performed with a 0.22 cm^2 rigid black mask.

IV. OPTICAL AND ELECTRICAL CHARACTERIZATION

The absorption spectra of the hemi-squaraine sensitizing solution (without CDCA) and of the photoanodes were obtained through UV-visible spectroscopy measurements using a spectrophotometer (Cary 5000, Varian) equipped with an integrating sphere for diffuse and specular reflectance. The absorbance spectra of the dye on the photoanodes were obtained from the measurements performed before and after the dye impregnation.

The cells were characterized through I-V measurements under AM1.5G (1000 W/m^2) illumination using a class A solar simulator (91195A, Newport) and a Keithley 2440 source measure unit. Incident Photon-to-electron Conversion Efficiency (IPCE) spectra were measured in DC mode using a 100 W QTH lamp (Newport) as light source and a 150 mm Czerny Turner monochromator (Omni-λ 150, Lot-Oriel). Electrochemical impedance spectra (EIS) were collected under illumination using an electrochemical workstation (760D, CH Instruments) in the frequency range 10^{-1} – 10^{5} Hz, at cell open circuit voltage; the amplitude of the AC signal was 10 mV. Experimental data of EIS were fitted using an equivalent circuit in order to obtain information about the transport and the recombination of the charges. In the circuit[19], the interface between the electrolyte and the counter electrode was modeled through the parallel $R_1//Q_1$ and the interface between the oxide and the electrolyte through the parallel $R_2//Q_2$; in both cases R_i is a resistance and Q_i is a constant phase element (CPE). The resistance R_s represents all the series resistances and a Warburg impedance W describes the charge diffusion within the electrolyte.

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