Electronic and charge transfer properties of bio-inspired flavylium ions for applications to TiO₂-based dye-sensitized solar cells.

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Electronic Supplementary Information (ESI)

EXPERIMENTAL DETAILS

Instruments and measurements

All solvents and chemicals employed for synthesis and for preparation of samples were of reagent or spectrophotometric grade and were used as received. NMR spectra were run on a Bruker AMX 400 instrument operating at 400.13 MHz (¹H) or 100.00 MHz (¹³C). Elemental analyses (EA) were performed on a Thermofinnigan Flash EA 112 Series. The absorption spectra of the photo-electrodes were recorded by a Perkin Elmer L20 spectrophotometer UV-Vis (range 180 nm-1100 nm). Emission spectra were collected on an Edinburgh FLS 920 spectrofluorimeter equipped with a double emission monochromator.

Electrochemical measurements. Cyclic voltammetry was carried out in a single compartment three electrode electrochemical cell under nitrogen atmosphere using glassy carbon, platinum and a Hg/HgSO₄ electrode as working, counter and reference electrodes respectively. Unless otherwise stated the scan rate was 100 mV/s. Since compounds **1-4** were found poorly soluble in pure acetonitrile (ACN), the electrolyte used for the cyclic voltammetry measurements was either 0.1 M TBAPF₆ in acetonitrile/tert-butanol 1:1 (ACN/tBuOH) or 0.1 M LiClO₄ in acidified ethanol obtained by addition of a few drops of concentrated HClO₄ in ca. 100 ml of electrolyte. In both electrolytes a similar voltammetric response by the dyes under investigation was recorded. Electrochemical Impedance Spectroscopy (EIS) was carried out on the sandwich DSSCs under illumination at their open circuit photovoltage (Voc). Typically, a sinusoidal perturbation having a 10 mV amplitude in the range between 10^5 Hz and 10^{-2} Hz was applied. All electrochemical measurements were performed on an Ecochemie Autolab PGSTAT 302/N equipped with a FRA2 frequency response analyzed and run under GPES and Nova 1.10.

Photoelectrochemical Measurements Current-Voltage curves were recorded by a digital Keithley 236 multimeter connected to a PC and controlled by a homemade program. Simulated sunlight irradiation was provided by a LOT-Oriel solar simulator (Model LS0100-1000, 300 W Xe Arc lamp powered by LSN251 power supply equipped with AM 1.5 filter, 100 mW/cm²). Incident irradiance was measured with a Si-based pyranometer. Incident photon-to-current conversion efficiency (IPCE) and relative photoaction spectra of sealed DSSCs were measured by a IPCE station. The IPCE station was composed by a 150 Xenon Light Source (model ASB-XE, Spectral Products), a Monochromator (model CM110, Spectral Products) equipped with a slit set, a Si calibrated detector (model 818-UV, Newport), a Picoamperometer (model 6487, Keithley) and a IPCE Solarena Software. The thickness of the oxide film deposited on the photoanodes was measured by using a DektakXT profilometer (Bruker) equipped with a diamond-tipped stylus (radius of 2µm) and selecting a vertical scan range of 65 µm with 8.0 nm resolution, a programmed scan length of 6000 µm and a stylus force of 1 mg. Each measure was verified by acquiring different runs, starting from different positions set by rotating or translating the sample.

Transient Absorption and Emission Spectroscopy. Emission lifetimes were obtained with a PicoQuant Picoharp 300 Time-correlated Single Photon Counting (TCSPC) apparatus by exciting at 460 nm with a nanoled driven by a PDL 800 B pulsing unit at 10 MHz. The fluorescence decay was deconvolved from the excitation profile according to a monoexponential function by using the dedicated program Fluofit. Nanosecond transient differential absorption spectra (TAS) of the flavylium dyes **1-4** dissolved in acidic ethanolic solution (EtOH + HClO₄) were acquired by excitation into their lowest energy absorption band using the second harmonic (532 nm) generated by a Continuum Surelite II Nd-Yag laser (FWHM 7 ns). The oscillographic traces used to construct the TAS were averaged over at least 10 shots and were acquired on a 600 MHz Lecroy 9360 oscilloscope having an additional input resistance of 350 Ohm. Although in this condition a slower response of the spectral apparatus (τ =R×C = 30 ns,) is introduced, a substantial improvement of the S/N ratio is gained, which was necessary to obtain acceptable traces, in spite of the generally weak spectroscopic signature of the excited states of these flavylium moieties.

TAS spectra of 1-4 sensitized TiO_2 films were recorded under lowered laser excitation energies (ca. 3 mJ/cm²/pulse) obtained by defocusing the laser beam (ca. 1 cm² illuminated area on the sample) with a plano-concave lens and by further attenuating the defocused excitation pulse with a 25% T neutral density filter. The probe beam generated by a pulsed 150 W Xe lamp was also attenuated by a 400 nm cut off filter (to avoid direct excitation of the TiO₂ band gap) and by a 50% T neutral density filter. A 532 nm notch filter prevented laser stray light to reach the photomultiplier (Hamamatsu R3896). The oscillographic traces, acquired through

the 350 Ohm input resistance of the oscilloscope were averaged over 20 shots.

Synthesis strategy

For the preparation of dyes we used the synthetic route schematized below:



Scheme S1 - Synthetic route for preparation of 4.

TABLES & FIGURES



Table S1-Frontier Orbital Composition Analysis



Table S1B- composition calculation analysis



Table S2 - Computed spectra (300-800 nm) and excitation energies with their main single particle contribution in the Kohn Sham basis calculated in ethanol at the B3lyp 6311G d,p level.







Fig. S1 - HOMO and LUMO of flavylium 1 attached to a Ti_2O_8H fragment cut out from the optimized slab.



Fig. S2 - Optimized equilibrium geometry of 1 interacting in semi-quinonic form with the TiO_2 surface. This equilibrium geometry was the result of an initial geometry in which both OH groups were coordinated to the same Ti(IV) center.



Fig. S3 - Normalized emission spectra of 1-4 in ACN/tBuOH 1/1.



Figure S4. Instrumental response of the nanosecond laser spectrometer with the input resistance of 350 Ohm. Signal acquired by observing the 532 nm laser scattering by an opaque film



Figure S5. Transient absorption (left) and emission (right) of dye 2 in ACN/TbuOH 50/50, following 532 nm laser excitation taken within the first 100 ns.



Figure S6. Transient absorption (left) and emission (right) of dye 3 in ACN/TbuOH 50/50, following 532 nm laser excitation taken within the first 100 ns.



Figure S7. Long lived (> 420 ns) excited state absorption in Dye 2 in the 550-620 nm region taken with a higher resolution (150 lines/mm) monochromator. Note similar spectral features in both cases (i.e. two absorption shoulders around 560 and 575 nm)



Fig. S8 - Transient emission spectra of 4 loaded on transparent TiO₂ in the presence of 0.1 M Li⁺.



Fig. S9 Cyclic voltammetry of the ACN/tBuOH 1/1 + 0.1 M TBAPF₆ supporting electrolyte used for measurements reported in Figure 11.



Table S3. Cyclic voltammetry of compound 1-4 in $EtOH/HClO_4$ in + 0.1 M $LiClO_4$ as supporting electrolyte. $GC/Pt/HgSO_4$, scan rate 100 mV/s.



Figure S10. Cyclic voltammetry of **3** (anodic region) recorded at 0.5 and at 1 V/s in ACN/TbuOH 50/50.



Figure S11. Cyclic voltammetry of 3 (cathodic region) recorded at 1 V/s in ACN/TbuOH 50/50.

Dye	Anodic 1 (V) (backwave)(V)	Anodic 2 (V)	Cathodic (V)
1	0.39	/	-0.82
2	0.48 (0.20)	0.69	-0.92
3	0.43 (0.19)	0.64	-1.05
4	0.42 (0.28)	/	-1.03

Table S4. Peak potentials of the main redox processes observed in CV mode in EtOH/HClO₄ +0.1 M LiClO₄. Potentials are referred to the Hg/HgSO₄ electrode.

Table S5. I_V parameters (cell maximum power, fill factor, short circuit current, open circuit voltage) of DSSC under stability test (during 32h, alternating dark /light condition).

Time	mW	FF	Isc	Voc
			(mA)	(V)
start	0.49	0.47	2.56	0.404
After 8h light	0.52	0.50	2.55	0.407
After 8dark	0.49	0.49	2.49	0.399
After 8 light	0.48	0.50	2.42	0.399
After 8 dark	0.54	0.57	2.30	0.413