Supporting Information

Solid State p-Type Dye-Sensitized Solar Cells: Concept, Experiment and Mechanism

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Experimental Section

General methodology. PCBM (99%) was purchased from Solenne b.v.. P1 dye is provided by Dynamo AB. All other chemicals were purchased from Sigma-Aldrich (Sweden) and used without further purification. *J-V* characteristics were measured using a Keithley source/meter under AM 1.5 G simulated sunlight of 100 mW·cm⁻² light intensity from a Newport 300 W solar simulator. Incident photon-to-current conversion efficiencies (IPCE) were obtained using monochromatic light from a system consisting of a xenon lamp, a monochromator and transmittance filters. Light filters were used for calibration of light intensities. Both systems were calibrated versus a certified reference solar cell. UV-vis spectra were recorded on a Lambda 750 UV-Vis spectrophotometer. All solar cells were illuminated from the glass side with an aperture area of 0.20 cm² (0.4×0.5 cm²). The thickness of film was determined by Scanning Electron Microscope and or DekTak profilometer.

Device Fabrication: Fluorine-doped tin-oxide (FTO) coated glass substrates were patterned by etching with zinc powder and 8 M hydrochloric acid. A compact NiO blocking layer (BL NiO) was first deposited onto the surface of a pre-cleaned FTO substrate by spray pyrolysis on a hotplate at 450 °C using an airbrush.¹ The solution used in the spray pyrolysis was 20 mM Nickel(II) acetylacetonate (Ni(acac)₂) in acetonitrile. 30 spray cycles were used to control the thickness of CL-NiO to ca. 200 nm. Mesoporous NiO films (700 nm) were coated on the compact NiO layer by spin-coating 100 mg NiO paste on each electrode (1.5 cm×2.5 cm), which is prepared by diluting the 2.8 g reported NiO paste with 14 g terpinol, 7 ml 10% wt cellulose ethanol solution and 10 mL ethanol, and then removing the ethanol. After sintering the NiO film (1.5 cm*2.5 cm) on a hotplate at 450 °C for 30 min, the film was cooled to room temperature and then was further immersed into 0.2 mM P1 acetonitrile to

complete the sensitization process. Subsequently, 100 μ l **PCBM** (4 mg) chloroform solution was placed on the top of dyad NiO film and allowed the solution to penetrate for 10 s. Then, the samples were spin-coated at 1000 rpm for 3 s and then 3000 rpm for 30 s and were further treated at 100 °C for 5 mins. Finally, a layer of ca.100 nm Al was rapidly deposited as back contact by thermal evaporation in a vacuum chamber (Leica EM MED020) with a base pressure of about 10⁻⁵ mbar, to complete the device fabrication.

Nanosecond Transient Absorption Spectrometer: The sample was excited by a Q-switched YAG-laser/OPO combination (Spectra Physics) that delivered ca. 8 ns pulses at 10 Hz repetition frequency. The pulses were attenuated to ~10 mJ/pulse over ca. 0.3 cm². The spectrometer (Edinburgh Instruments) was coupled to a probe light from a pulsed Xe-lamp at a 90 degree angle with the laser excitation, while the sample was placed at 45 degrees with respect to both beams for sensitized NiO films. Kinetic traces were recorded using a PMT and NIR traces using an InGaAs PIN photodiode and a digital oscilloscope. Transient spectra were detected with a CCD (ANDOR).

Ultrafast Transient Absorption Spectrometer: Femtosecond time-resolved measurements were done by means of transient absorption. A detailed description can be found in Petersson et al². Briefly, the output from a Coherent Legend Ti:Sapphire amplifier (1 kHz, $\lambda = 800$ nm, FWHM 100 fs) was split into pump and probe light. The desired pump wavelength was obtained with a TOPAS, and with neutral density filters the pump energy was kept around 500 nJ/pulse. The white light continuum probe was obtained by focusing part of the 800 nm light on a moving CaF2 plate. Polarization of the pump was set at magic angle, relative to the probe. Instrumental response time depends on pump and probe wavelengths, but is typically about 150 fs.

	$\tau_1(ps)$	$\tau_2(ps)$	τ_3 (ps)	$\tau_4(ps)$
ACN	0.098 ± 0.013	1.83 ± 0.24	9.74 ± 0.03	34.1 ± 0.3
DBM	0.325 ± 0.047	1.55 ± 0.02	98.9 ± 0.9	1330 ± 37

Table S1 Time constants obtained from global analysis of P1 in ACN and DBM.

Data analysis are done in MATLAB (The MathWorks, Inc.), a robust trust-region reflective Newton nonlinear-least-squares method are used for the fits of time traces. Traces (ΔA vs. t) are fitted to a sum of exponentials convolved with a Gaussian shaped response. Also included in the fits is an artifact signal that is due to cross phase modulation during pump and probe overlap³. All spectra are corrected for chirp in the white light probe, time

zero is set at maximum pump-probe temporal overlap. The region around pump wavelength is removed due to scatter of pump light.

Table S2 Time constants obtained from multi-exponential fit of solid state film samples (probed at 480 nm). Relative amplitudes (%) at 480 nm are given (cf. Figure 6), where positive values indicate signal decay and negative absorption increase/bleach recovery. Note that different species are probed at different times and between different samples, thus charge separation yields cannot simply be estimated from the relative amplitudes.

480 nm	τ_1/ps	τ_2/ps	τ₃/ps	τ ₄ /ps	$ au_{inf}$
NiO-P1	0.166/-38%	1.32/-39%	19.7/-22%		-1%
NiO-P1/PCBM	0.298/-34%	1.93/-18%	46.7/-22%	123.2/+15%	+11%
NiO/PCBM	0.294/-17%	15.5/+30%	393/+39%		-14%



Figure S1. Transient absorption results after fs-excitation of P1 in (A) $CH_3CN ACN$, (B) CH_2Br_2 (DBM); (C) ns transient absorption of P1 in DBM and (D) steady-state photo emission spectrum of P1 in ACN and DBM. Inset is probed kinetics of 550 nm in ACN, 560 nm in DBM and 485 nm by ns photolysis in degassed DBM, which shows 1.9 µs triplet lifetime. fs measurement excited at 525 nm, 500 nJ/pulse and ns measurement excited at 532 nm, 10 mJ/pulse.

The electron transfer mechanism of the dye in solution and on NiO films were investigated by femtosecond and nanosecond transient absorption spectroscopies. The solution phase of P1 was studied in both acetonitrile (ACN) and dibromomethane (DBM) solvents. The result of P1 in ACN agrees with previously published results⁴, although our interpretation is different. The initially formed singlet excited state (S₁) of P1 shows a strong absorption band around 600 nm and a weak one around 410 nm, in addition to ground state bleach around 450 nm. Importantly, stimulated emission is seen to shift from around 620 nm to > 680 nm during the first few ps, presumably due to solvent relaxation. At 300 ps essentially all signals are gone, and from a global sum-of-exponentials fit to the data we determine the S₁ lifetime to about 32 ps (Table S1). We see no evidence for intermolecular electron transfer in P1 aggregates, as was suggested in ref. 4; the absorption band at 410 nm is too weak compared to the 600 nm to be consistent with the P1^{•-} anion spectrum absorption determined bv spectroelectrochemistry.²³ In the less polar DBM solvent, the S₁ lifetime is much longer (\approx 1.3 ns) and the stimulated emission shows less dynamic shift. After decay of the S1 state a different species is apparent, with a much longer lifetime of 2 µs, as determined by ns transient absorption spectroscopy. This is assigned to the triplet excited state of P1 formed by intersystem crossing from S1 due to the heavy atom solvent.



Figure S2. ns transient absorption spectra of NiO/PCBM and Glass/PCBM at 50 ns time delay. Excitation at 532 nm, 10 mJ/pulse.

Singlet excited state PCBM on glass formed after excitation at 532 nm. The 550 nm band shows absorption of ^{1*}PCBM, with a ground state absorption bleach component of PCBM at 700 nm. For PCBM on NiO, after 50 ns delay, the 550 nm peak is smaller due to hole injection from ^{1*}PCBM to NiO, and the spectrum is similar to that after 2 ns in the fs data (Figure 5c). This shows slow components of NiO⁺/ PCBM[•]- recombination on the ns scale.



Figure S3. fs transient absorption result of P1/PCBM on glass (A) and exponential fitted kinetics traces probed at 450 nm (black square and green line) and 600 nm (black cycle and blue line). Excitation at 525 nm, 500 nJ/pulse.



Figure S4. ns transient absorption spectra of P1/PCBM on glass (A) and TiO₂-P1 (B) at 50 ns time delay. Excitation at 532 nm, 10 mJ/pulse.

Figure S3 present the fs results of P1/PCBM on glass by spin coating. Figure S4 shows ns data for the same sample (panel A) and for a sample where P1 was attched to a mesoporous TiO₂ film (panel B). Both spectra are much too long-lived to be the ^{1*}P1 state. They are also significantly redshifted, but with much weaker absorption in the red part, compared to those of both the ^{1*}P1 and ^{3*}P1 states. Formation of P1^{•-} by electron abstraction from PCBM or TiO2 is energetically not feasibly, and again the spectrum is too weak around 600 nm. Thus, we assign it to the P1 cation radical (P1^{•+}), fromed by electron transfer to PCBM and TiO₂, respectively. The ns data for the two samples show strong similarities, indicating formation of the P1 cation radical (P1^{•+}) in both cases, with absorption bands around 425 and 610 nm. In

Figure 4A the PCBM bleach is clear at 710 nm, while bleach of the PCBM also weakens the 610 nm band P1 $^{\bullet+}$ compared to the case on TiO₂.

The fs data in Figure S3 follows the formation of the P1 $^{+}/PCBM$ $^{-}$ state; the initial ^{1*}P1 state looks similar to the P1 $^{+}/PCBM$ $^{-}$ but both the 420 nm and 590 nm bands red-shift and broaden upon charge separation, and the stimulated emission around 660 nm disappears. Figure S3B shows traces, where 450 nm is a particualrly useful wavelength to probe charge separation: the signal is initially close to an isosbest, but grows in as the P1 $^{+}/PCBM$ $^{-}$ state is formed.



Figure S5. Decay associate spectra (left) and recalculated species associated spectra (right) of each system. The top is NiO-P1, middle is NiO-P1/PCBM and bottom is NiO/PCBM.

Species Associated Spectra (SAS) were recalculated from the amplitudes of the decay associated spectra (DAS). Amplitudes of the resulting spectra depend on the reaction scheme and the individual reaction rates. While DAS reflect changes in absorbance associated with each time constant, the recalculated species associated spectra give the "pure" absorbance of each component and allows for a more straight and direct observation.



Figure S6. NIR kinetics traces of NiO/PCBM at 1000 nm (top) and P1/PCBM on glass at 950 nm (bottom). Excitation at 532 nm, 10 mJ/pulse.



Figure S7. The first derivative of absorption of P1 on NiO

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