Electronic Supplementary Information

Photo-excitation intensity dependent electron and hole injections from lead iodide perovskite to nanocrystalline TiO₂ and *spiro*-OMeTAD

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1. Materials

Dehydrated PbI₂ was obtained by our simple purification method or distillation,¹ and is now commercially available from Tokyo Chemical Industry, CO., LTD. (TCI). Dehydrated form of PbI₂ was essential to prepare CH₃NH₃PbI₃ perovskite layer by two-step solution method.¹⁻⁵ CH₃NH₃I was provided from TCI. The solvents *N*,*N*-dimethylformamide (DMF, super dehydrated, Wako Pure Chemical Industries Ltd., Japan), 2-propanol (super dehydrated, Wako Pure Chemical Industries Ltd., Japan), 2-propanol (super dehydrated, Wako Pure Chemical Industries Ltd., Japan), and chlorobenzene (special grade, Wako Pure Chemical Industries Ltd., Japan) were degassed by consecutive argon gas bubbling for 30 min, and dehydration with activated molecular sieves (3A; 24 h, H₂O < 8 ppm). 2,2',7,7'-Tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (*spiro*-OMeTAD) was purchased from Merck. Tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide] was prepared following the reported method.⁶ A nanocrystalline TiO₂ (anatase structure) paste was provided from JGC C&C. Al₂O₃ powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided from Evonik Degussa GmbH. Deuterated acetonitrile (acetonitrile-d3, 99.5 % pure) was purchased from Sigma-Aldrich Co. LLC., and used without further purification.

2. Experimental

2.1 Preparation of perovskite deposited nanocrystalline films with spiro-OMeTAD

Transparent TiO₂ nanocrystalline films (thickness: 2.8 µm) were prepared by the screen printing method with the TiO₂ paste on a glass slide. The film, after printing, was leveled for 15 min, heated up to 500 °C at 15.8 °C/min, and calcined at 500 °C for 1 h in an air flow oven. Al_2O_3 nanocrystalline films (thickness: 3.0 µm) were prepared by the same screen printer with the different printing mask, using a home-made Al₂O₃ paste, following the previously reported method.^{7, 8} The printed Al₂O₃ films were calcined at 500 °C for 1 h in an air flow oven. The thickness of these metal oxide nanoporous films was measured by a surface profiler (KLA-Tencor P-16+). A CH₃NH₃PbI₃ perovskite layer was deposited on the nanocrystalline TiO₂ (TiO₂-MAPbI₃) and Al₂O₃ (Al₂O₃-MAPbI₃) film inside a glove box, similar to the reported method.¹ In order to excite the perovskite layer homogeneously for the laser experiments, a thick metal oxide nanocrystalline film and a thin perovskite layer in the film was prepared. Low concentrated solution of PbI₂ (0.2 M) in dehydrated (H₂O < 8ppm) N,N-dimethylformamide (DMF) was introduced to coat on the surface of the TiO₂ or Al₂O₃ nanopore during the spincoating at 70 °C. After drying at 70 °C for 1 h, the film was dipped for 20 s in a 0.06 M solution of CH_3NH_3I in 2-propanol ($H_2O < 8ppm$), forming into a perovskite layer. The films were quickly rinsed with 2-propanol and dried at 70 °C for 30 min. For some films, the holetransporting layer was deposited on top of TiO₂-MAPbI₃ and Al₂O₃-MAPbI₃ by spin-coating a solution of *spiro*-OMeTAD in chlorobenzene (0.058 M, $H_2O < 8ppm$). The resultant films were denoted as TiO₂-MAPbI₃-OMeTAD and Al₂O₃-MAPbI₃-OMeTAD, respectively. The film was fixed in a vacuum chamber with optical windows, and was kept under vacuum ($\sim 10^{-3}$ Torr)

during steady state or transient optical measurements. For all optical experiments, the films were excited from a glass substrate side.

2.2 Fabrication of solar cells

Perovskite solar cells were fabricated by the reported method.¹ A fluorine doped tin oxide (FTO, 25 mm \times 25 mm) glass plate was etched with Zn powder and 2 M HCl aqueous solution. The patterned substrate was covered with a compact TiO₂ layer by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) in ethanol (0.05 M) at 450 °C. Subsequent spin-coating of an ethanol suspension of a TiO₂ paste (PST–18NR, TiO₂ paste:ethanol = 1:3.5 wt ratio) resulted in the deposition of ca. 200 nm-thick mesoporous films of TiO₂ nanoparticles (particle diameter = ca. 20 nm). In an Ar-filled glovebox, a perovskite layer and a *spiro*-OMeTAD containing 4-tertbutylpyridine (0.19 M), lithium bis(trifluoromethylsulphonyl)imide (0.031 M) and tris[2-(1Hpyrazol-1-yl)-4-tert butylpyridine]cobalt(III)tris[bis(trifluoromethylsulfonyl)imide] (5.6 \times 10⁻³ M) were coated with the method described above. For the back contact, a gold layer (80 nm) was deposited thermally on top of the device. The performance of the solar cells was measured using a 2 mm square mask in air without sealing.

2.3 Optical measurements

2.3.1 Steady state absorption and photoluminescence measurements

Absorption spectra of perovskite deposited films were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Photoluminescence spectra of the film were collected using a PTI UV-Vis fluorometer (Photon Technology International, Inc.) with slit widths of 1.6 mm (6.4 nm resolution) at room temperature. The spectra were observed using a photomultiplier

detector in a wavelength range between 400 and 800 nm, and corrected for the spectral response of the grating in the emission monochromator and the detector.

2.3.2 Nanosecond transient emission measurements

Nanosecond transient emission spectroscopy (ns-TES) was employed to monitor perovskite excited state decay dynamics. An electron or hole injection from the perovskite excited state to the TiO₂ or to spiro-OMeTAD was also measured by following the emission quenching dynamics compared to the excited state decays observed for Al₂O₃-MAPbI₃. Data were obtained by a home-built transient emission spectrometer with a N2 laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The excitation wavelength was 625 nm, not to excite TiO₂ (by ~400 nm)⁹ and PbI₂ (by ~550 nm),¹⁰ if PbI₂ remains in the perovskite layer. The excitation laser pulse was irradiated from the substrate (the metal oxide film) side. Emission from a perovskite layer was collected through a monochromator (Acton, Princeton Instruments), and detected by a nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM)) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate. The emission decay profile was synchronized with the excitation pulse and the detection system using a laser trigger detector.

2.3.3 Microsecond-millisecond visible transient absorption measurements

Microsecond-millisecond visible transient absorption spectroscopy (mms-Vis-TAS) was employed to monitor charge separated states at the perovskite interfaces. The measurements were conducted by a home-built transient absorption spectrometer with a N_2 laser (OBB, OL-4300) pumped dye laser (OBB, OL-401, 800 ps pulse duration) as a pump source, a 100 W halogen lamp (Olympus) as a probe source, a Si photodiode-based detection system (Costronics Electronics, probe wavelength range: 400~1,100 nm, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (JASCO, M10). Transient data were collected with 625 nm excitation with a repetition rate of 2 Hz at 22 °C. The pulse excitation intensity was adjusted to 120 μ J/cm² to correlate with a control data using the TiO₂ film (thickness: 2.8 µm) sensitized by *cis*bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), N3 (Solaronix). No change in steady state absorption spectra prior to and after the transient measurements was observed, when the perovskite film was fixed in the optical vacuum chamber during the laser measurements, indicating that the samples were stable during the experiments. Note that we have observed gradual degradation of the perovskite film, when the sample was left in an ambient atmosphere in air during the laser spectroscopy measurements.

2.3.4 Microsecond-millisecond near infrared transient absorption measurements

Microsecond-millisecond near infrared transient absorption spectroscopy (mms-NIR-TAS) was employed to monitor charge separated states and charge recombination dynamics at the perovskite interfaces. The measurements were conducted by a home-built transient absorption spectrometer with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as a pump source, a 100 W halogen lamp (Olympus) as a probe source, InGaAs photodiode-based detection systems (Unisoku Co., Ltd., TSP-1000-NIR25, probe wavelength range: 900~2,500 nm, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (Acton, Princeton Instruments). Transient data were collected with 625 nm excitation with a repetition rate of 1 or 2 Hz at 22 °C. The

excitation intensity was adjusted to $120 \ \mu J/cm^2$ to correlate with a control data using the N3 sensitised TiO₂ film (thickness: 2.8 µm), as discussed above. The data were normalized considering the absorbance at 625 nm excitation, i.e. the number of absorbed photons is identical for both TiO₂ and Al₂O₃ films. The perovskite film was maintained in vacuum during the laser experiments, as mentioned above.

2.3.5 Analysis of transient emission data and charge injection yield

The increase of the excitation intensity results in acceleration of the photoluminescence decay dynamics. These decay kinetics, comparing between Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ and between Al₂O₃-MAPbI₃ and Al₂O₃-MAPbI₃ and Al₂O₃-MAPbI₃ -OMeTAD, were analyzed by a rate equation including a first order recombination via carrier trap states, second order non geminate free carrier (electron and hole) recombination and charge transfer processes, as shown in Equation S1.

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_{e-inj} n + k_{h-inj} n$$
(S1)

where *n* is the photo-excited charge carrier density, k_1 is the rate constant of trap state mediated recombination, k_2 is the rate constant of electron-hole recombination, k_{e-inj} is the injection rate of the electron from perovskite to TiO₂ conduction bands, k_{h-inj} is the injection rate of the hole from a perovskite valence band to *spiro*-OMeTAD, and *t* is the time. Here, we do not include three body Auger recombination, since the excitation intensity is relatively small.¹¹

For analysis of the perovskite excited state, i.e. data for Al₂O₃-MAPbI₃, Equation S1 is simplified to,^{2, 11}

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 \tag{S2}$$

For analysis of the electron injection dynamics, i.e. data for TiO₂-MAPbI₃, Equation S1 is simplified to,

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_{e-inj} n$$
(S3)

For analysis of the hole injection dynamics, i.e. data for Al₂O₃-MAPbI₃-OMeTAD, Equation S1 is simplified to,

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_{h-inj} n$$
(S4)

Charge injection yields were estimated by comparing lifetimes of the observed photoluminescence decays. Since the excited state decay has two components, i.e. first and second order components, it is not simple to evaluate the lifetime. Here, we define an effective lifetime, $\tau_{1/e}$,²

$$I_{PL}(\tau_{1/e}) = \frac{I_{PL}(0)}{e}$$
(S5)

where $I_{PL}(\tau_{1/e})$ is the intensity of photoluminescence at time τ after the excitation. Charge injection yields were evaluated using the following equations, and the electron and hole injection yield was estimated using Equation S8 and S10, respectively.

$$\frac{1}{\tau_{Al_20_3}} = \frac{1}{\tau_{1/e(Al_20_3)}}$$
(S6)

$$\frac{1}{\tau_{TiO_2}} = \frac{1}{\tau_{1/e(Al_2O_3)}} + \frac{1}{\tau_{e-inj}} = \frac{1}{\tau_{1/e(TiO_2)}}$$
(S7)

$$\Phi_{e-inj} = \frac{\tau_{TiO_2}}{\tau_{e-inj}} = 1 - \frac{\tau_{TiO_2}}{\tau_{Al_2O_3}}$$
(S8)

$$\frac{1}{\tau_{OMeTAD}} = \frac{1}{\tau_{1/e(Al_2O_3)}} + \frac{1}{\tau_{h-inj}} = \frac{1}{\tau_{1/e(OMeTAD)}}$$
(S9)

$$\Phi_{h-inj} = \frac{\tau_{OMeTAD}}{\tau_{h-inj}} = 1 - \frac{\tau_{OMeTAD}}{\tau_{Al_2O_3}}$$
(S10)

where $\tau_{Al_2O_3}$ is the lifetime of the observed photoluminescence decay for Al₂O₃-MAPbI₃, τ_{TiO_2} is the lifetime of the observed photoluminescence decay for TiO₂-MAPbI₃, τ_{OMeTAD} is the lifetime of the observed photoluminescence decay for Al₂O₃-MAPbI₃-OMeTAD, τ_{e-inj} is the electron injection rate, τ_{h-inj} is the hole injection rate, Φ_{e-inj} is the electron injection yield, and Φ_{h-inj} is the hole injection yield.

2.4 Spectroelectrochemical measuremnts

Spectroelectrochemical technique was employed to observe a spectrum of absorption by electrons in the TiO₂ conduction band under an application of negative bias into the bare TiO₂ electrode. The measurements were conducted with the similar method reported previously.^{8, 12} The experiments were performed in a three-electrode electrochemical cell with a quartz optical window using a potentiostat (Ivium Technologies B.V., Compact Stat). The TiO₂ nanocrystalline film was prepared on the FTO substrate, and used as a working electrode, attached to the cell window. A platinum wire electrode and a Ag/AgCl electrode were used as a counter and reference electrode, respectively. The photoelectrochemical cell was placed in a UV-VIS-NIR absorption spectrometer (JASCO, V670). Absorption difference spectra were measured by monitoring intensity change of the probe light passing through the TiO₂ film electrode in the cell containing 0.1 M lithium perchlorate (supporting electrolyte) in deuterated acetonitrile, after the bias application into the TiO₂ film electrode for approximately 5 min. The bias was applied from 0 V with +0.1 V steps, following the measurement of the reference line after 15 min stabilization at 0 V vs. Ag/AgCl.

2.5 Electron microscopy measurements and XRD measurements

Electron microscopy images of Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ were obtained by JEOL JEM-6500F scanning electron microscopy (SEM) operated at 10 kV at Institute of Advanced Energy, Kyoto University.

X-ray diffraction patterns were obtained by Rigaku RINT2500 at Institute for Chemical Research, Kyoto University. Data was collected at room temperature using Cu K α radiation (λ = 1.54178 A) with a potential of 60 kV and a current of 300 mA.

3. Results

3.1 Solar cell performance

Fig. S1 shows current density – voltage (J - V) curves and an IPCE spectrum of the fabricated solar cell. With the forward bias scan, the short circuit photocurrent, *J*sc, is 20.1 mAcm⁻², the open circuit voltage, *V*oc, is 1.01 V, and the fill factor, *FF*, is 0.71, resulting in an energy conversion efficiency of 14.4 %, while an energy conversion efficiency of 14.7 % was achieved with *J*sc of 19.7 mAcm⁻², *V*oc of 1.01 V and *FF* of 0.74 by scanning the bias voltage to the reverse direction. This observation has reproduced the result reported recently.¹³



Fig. S1. (a) J - V curve and (b) IPCE spectrum of the perovskite solar cell. The J - V measurements were performed under AM1.5G solar simulated light, 100 mW cm⁻² at 25 ± 2 °C or without light irradiation (in dark). The voltage was applied to forward and reverse directions. The IPCE spectrum is not corrected for reflection at the glass surface and at the interfaces.

3.2 Electron microscopy measurements and XRD measurements

Scanning electron microscope images of Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ are shown in Figs. S2a and S2b. In both cases, MAPbI₃ crystals are formed on top of nanocrystalline metal oxide film. The number of crystals seems higher for Al₂O₃-MAPbI₃, however the crystal size appears to be similar (several hundred nm), being relatively large from the preparation with low PbI₂ concentration (0.2 M). The similar low concentration crystal growth was previously observed by Park et al.¹⁴ By comparing the surface of these films microscopically, the surface morphology is essentially indistinguishable.

X-ray diffraction patterns were observed for Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ with reference to their respective metal oxide nanoporous film alone. The results are shown in Figs. S2c and S2c. The diffraction pattern obtained for the nanocrystalline Al₂O₃ film can be mainly indexed to the orthorhombic γ-AlOOH (boehmite) phase (JCPDS No. 21-1307)¹⁵⁻¹⁷ in addition to cubic γ-Al₂O₃ phase.^{15, 17, 18} The pattern for the nanocrystalline TiO₂ film typically indicates anatase structure.¹⁹ The diffraction patterns of both Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ indicate a tetragonal MAPbI₃ phase in addition to γ-AlOOH/γ-Al₂O₃ phase and anatase structure, respectively, in agreement with the previous reports.^{10, 13} Note that we do not see any sign of PbI₂ crystal formation for both Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃, suggesting complete conversion to perovskite.¹³ These observations suggest that the morphology and crystal structure of MAPbI₃ are not influenced by the type of metal oxide nanostructure.



Fig. S2. SEM images of Al_2O_3 -MAPbI₃ (a) and TiO_2 -MAPbI₃ (b) observed at 10 kV. X-ray diffraction patterns of a nanocrystalline Al_2O_3 film and Al_2O_3 -MAPbI₃ (c) and a nanocrystalline TiO_2 film and TiO_2 -MAPbI₃ (d). Peaks from MAPbI₃ are shown as asterisks.

3.3 Steady state photoluminescence measurements

Steady state photoluminescence spectra were measured for Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ to estimate the upper limit of an electron injection yield (from the excited perovskite to the TiO₂ conduction band). The results are compared in Fig. S3a. TiO₂-MAPbI₃ shows clear emission quench, compared to Al₂O₃-MAPbI₃. The photoluminescence was integrated, and the amount of detected photons were compared between Al₂O₃-MAPbI₃ and TiO₂-MAPbI₃ to estimate an electron injection yield as photoluminescence quenching efficiency. The estimated injection yield is 85 %, indicating that the rate is approximately one order of magnitude faster than the excited state lifetime.



Fig. S3. (a) Photoluminescence spectra of Al_2O_3 -MAPbI₃ and TiO_2 -MAPbI₃ with 625 nm excitation. (b) Photoluminescence spectra of Al_2O_3 -MAPbI₃ and Al_2O_3 -MAPbI₃-OMeTAD with 625 nm excitation. The photoluminescence spectra were normalized with the number of absorbed photons at the excitation wavelength.

A hole injection yield was estimated in the similar manner using the data from Al₂O₃-MAPbI₃ and Al₂O₃-MAPbI₃-OMeTAD. In this case, only a hole transfer reaction from the perovskite valence band to the OMeTAD is expected, while no electron injection occurs. The result is shown in Fig. S3b. By coating an OMeTAD layer on top of the perovskite layer, photoluminescence was remarkably quenched, indicating 96 % hole injection yield.

3.4 Transient emission measurements

Transient photoluminescence spectroscopy was employed to assess dynamics of an electron injection process (from the perovskite to the TiO₂ conduction band), since this spectroscopy is sensitive to detect change in low photoluminescence intensity at the low excitation intensity (typically $0.01 \sim 1 \ \mu J/cm^2$). A wide range of excitation intensities ($0.01 \sim 50 \ \mu J/cm^2$) was introduced to monitor their influence on the dynamics. Excitation intensity dependence of photoluminescence dynamics for TiO₂-MAPbI₃ was observed. The results are shown in Fig. S4a. Similar to the decays obtained for Al₂O₃-MAPbI₃ (Fig. 2a), the increase of the excitation intensity results in acceleration of the photoluminescence decay dynamics. These decay kinetics were analyzed using Equation S3 above.



Fig. S4. (a) Excitation intensity dependence of transient emission (perovskite excited state) decays obtained for TiO_2 -MAPbI₃ with 625 nm excitation. The number in the figure presents excitation intensity (unit: μ J/cm²), and the line shows a result of fitting with Equation S3. (b) Comparison of transient emission decays of Al₂O₃-MAPbI₃ (dark red dots: data, line: fitted result) and TiO₂-MAPbI₃ (dark blue dots: data, line: fitted result). The solid line indicates results of fitting with Equation 1 and S3, respectively.

The photoluminescence decay dynamics were compared with those for Al_2O_3 -MAPbI₃. As shown in Fig. S4b, a clear acceleration of the photoluminescence decay is observed for TiO₂-MAPbI₃ with 50 nJ/cm² excitation. This acceleration is owing to an electron injection process from the excited perovskite to the TiO₂ conduction band. Even with the higher excitation intensity (2.3 μ J/cm²), slight acceleration of photoluminescence decays was observed. These data suggest that the electron injection process is one of the major paths to quench the photoluminescence. The electron injection yield (Φ_{inj}) was estimated using Equation S8. With the excitation intensity of 50 nJ/cm², the calculated electron injection yield is 90 %. In contrast, the excitation intensity of 2.3 μ J/cm² decreased the electron injection yield to 37 %. This result suggests that the increase in the excitation intensity decreases an electron injection yield.

3.5 Transient absorption measurements of N3 sensitized TiO₂ films

The same TiO₂ film was employed to monitor charge recombination dynamics at N3 dye/TiO₂ interface. An absorption spectrum of the N3 sensitised TiO₂ film is shown in Fig. S5a. A transient absorption spectrum of this film was obtained at 2 μ s after 625 nm excitation (Fig. S5b). This spectrum essentially indicates charge separated states. Following the previous report, the absorption around 800 nm is assigned to N3 dye oxidized state, while the absorption at a 1,200–2,500 nm range was resulting from absorption by the injected electrons in the TiO₂ conduction band or surface states.²⁰ A transient absorption decay is shown in Fig. S5c. Slightly accelerated dynamics was observed for charge recombination between a dye oxidized state and an electron in the TiO₂ with the half lifetime of approximately 150 μ s (stretched parameter, α , = 0.36), compared to the reported data.²⁰ The difference probably originates from the thinner TiO₂ film thickness: 2.8 μ m) we employed here, as the increased number of the injected electrons in the TiO₂ results in faster charge recombination dynamics.^{21, 22} Here we employ this decay dynamics to compare charge recombination dynamics observed for TiO₂-MAPbI₃.



Fig. S5. (a) Absorption spectrum, (b) transient absorption spectrum, and (c) transient absorption decay of N3 dye sensitized TiO_2 films. The fitted line using a stretched exponential function is shown as a black line in Fig. S5c. The transient absorption spectrum and decay were obtained at 2 µs and at 1,600 nm (probe wavelength), respectively, after 700 ps pulse excitation at 625 nm.

3.6 Spectrochemical and spectroelectrochemical measurements of *spiro*-OMeTAD oxidized states and electrons in TiO₂ conduction band spectra

The oxidized state of *spiro*-OMeTAD was prepared by adding tris[2-(*1H*-pyrazol-1-yl)-4-tertbutylpyridine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide]⁶ into *spiro*-OMeTAD solution (CH₂Cl₂). The results are shown in Fig. S6. The spectrum of absorption by electrons accumulated in the TiO₂ conduction band was created spectroelectrochemically by applying electrical bias into the TiO₂ electrode. The absorption difference spectrum from the spectra between -0.9 and -1.0 V is shown in Fig. S6. The addition of these two spectra between 1,100 and 2,500 nm is also shown in Fig. S6. The amplitude increase around 2,500 nm was clearly observed, compared to the OMeTAD oxidized state spectrum.



Fig. S6. Absorption spectra of *spiro*-OMeTAD oxidized state and electrons in the TiO_2 conduction band. The addition of these spectra between 1,100 and 2,500 nm is also shown (black line). The spikes at 2,250 and 2,380 nm originate from absorption by the solvent or the electrolyte.

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