

Electronic Supplementary Information (ESI)

for

Successful demonstration of an efficient $I^-/(SeCN)_2$ redox mediator for dye-sensitized solar cells

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Experimental Section

a. Synthesis of tetrabutylammonium selenocyanate (TBASeCN)

All chemicals were used as received. Silver nitrate ($AgNO_3$; 2 g, 12 mmol; Sigma, 99%) dissolved in 30 ml distilled water reacted at ambient conditions with potassium selenocyanate ($KSeCN$; 1.7 g, 12 mmol; Sigma, 99%) in 20 ml distilled water, yielding solid-state silver selenocyanate ($AgSeCN$), filtered with excess distilled water. After dispersing $AgSeCN$ in 40 ml distilled water, the solution was stirred with tetrabutylammonium iodide (TBAI; 3.05 g, 8.25 mmol; Sigma, 99%) in 10 ml of methanol (MeOH) for 1 hr. Then, silver iodide (AgI) was removed by filtration and the solvents evaporated under vacuum. Adding diethyl ether (Et_2O) into the product, the solution was refrigerated for recrystallization. Yield: 73 %. 1H NMR ($CDCl_3$, δ/ppm relative to TMS): 0.95 (q, 3H), 1.41 (m, 2H), 1.60 (m, 2H), 3.17 (m, 2H). ATR-FTIR: 2961s [$\nu(CH_3)$], 2092s [$\nu(SeCN)$], 1481m [$\nu(CH_2)$], 1380m [$\nu(CH_3)$], 1707s, 884s [$\nu(CN)$].

[Reference: a) P. Bonhte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, 35, 1168-1178; b) J. M. Pringle, J. Golding, C. M. Forsyth, G. B. Deacon, M. Forsyth, D. R. MacFarlane, *J. Mater. Chem.* **2002**, 12, 3475-3480.]

b. Preparation of $I^-/(SeCN)_2$ redox couple

In preparation of $(SeCN)_2$, first $KSeCN$ (0.288 g, 2 mmol) reacted overnight with bromine (Br_2 ; 0.160 g, 1 mmol; Sigma, 99%) in a mixture of acetonitrile (AN) and ethylene carbonate (EC) (20 ml, 1:1, v/v) at sub-zero temperatures ($< 0^\circ C$) and under dark conditions, yielding $(SeCN)_2$ (0.21 g, 1 mmol) and potassium bromide (KBr) in an AN/EC solution (20 ml). The sedimented KBr was removed by filtration and subsequently the $(SeCN)_2$ solution was mixed with TBAI for the generation of an $I^-/(SeCN)_2$ redox couple. When TBAI was combined with the $(SeCN)_2$ solution, the color changed immediately from yellow to dark brown, which is quite similar to an I^-/I_3^- solution.

[Reference: a) G. A. Bowmaker, P. A. Kilmartin, G. A. Wright, *J. Solid State Electrochem.* **1999**, 3, 163-171; b) C. J. Burchell, P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2006**, 45, 710-716.]

c. Preparation of electrolyte

Both of 0.5 M 4-tert-butylpyridine (tBP) and 0.1 M guanidium thiocyanate (GTC) dissolved in AN/EC (1:1, v/v) were in common used and all electrolytes have different kinds of redox species. Electrolyte I contains 0.6 M TBAI, 0.05 M I_2 ; Electrolyte II 0.6 M TBASeCN, 0.05 M $(SeCN)_2$; Electrolyte III 0.6 M TBAI, 0.05 M $(SeCN)_2$; Electrolyte IV 0.6 M TBAI, 0.01 M $(SeCN)_2$; Electrolyte V 0.6 M TBAI, 0.025 M $(SeCN)_2$; Electrolytes A and C 0.6 M TBAI, 0.1 M I_2 ; Electrolytes B and D 0.6 M TBAI, 0.075 M I_2 , 0.025 M $(SeCN)_2$; Electrolyte E 0.6 M TBAI, 0.09 M I_2 , 0.01 M $(SeCN)_2$; Electrolyte F 0.6 M TBAI, 0.05 M I_2 , 0.05 M $(SeCN)_2$.

d. Solar cell fabrication

Fluorine-doped tin oxide (FTO) glass (Pilkington, 15 $\Omega/square$) substrates were rinsed with a Helmanex solution, acetone and ethanol in this sequence in an ultrasonic bath for 15 min. To deposit a TiO_2 blocking layer on the FTO glass, the cleaned FTO glass substrates were treated with a 0.5 mM $TiCl_4$ solution for 20 min. at 70 $^\circ C$, followed by an annealing process for 30 min. at 450 $^\circ C$. Next, a 12 μm thick TiO_2 layer was coated with the shape of a square active area, 0.25 cm^2 , on the FTO glass by the doctor-blade technique with commercial TiO_2 paste (Dyesol, 18 NR-T). After annealing the TiO_2 -coated FTO glass, $TiCl_4$ treatment was repeated again with the method corresponding to the previous treatment. Then, the substrates were immersed into a dye solution composed of 0.5 mM N719 (Dyesol) dye dissolved in AN/tert-butanol

(*t*-BuOH) (1:1, v/v) for 18 hrs. After adsorption of dye to the TiO₂ layer, TiO₂ substrates were combined with counter substrates covered by sputtered platinum film through a hot-pressing process. The distance between the two substrates was maintained with Surlyn (Solaronix, 25 μm), a polyester material. The electrolyte was injected through the hole in counter substrates and the DSCs were sealed by sealants. For the fabrication of Devices C and D, 0.5 M CDCA (Solaronix) coadsorbent was additionally dissolved in a dye solution and a 4 μm thick scattering layer was deposited onto a 12 μm thick TiO₂ layer by the doctor-blade technique with commercial TiO₂ paste (Dyesol, WER 2-O).

UV-vis spectroscopy

UV-visible absorption spectra of the electrolytes were obtained by JASCO UV-vis spectrometer (Model V-670) with a 5 nm resolution. The spectra were fitted with Lorentz transformation for calculation of the absorption area in the range of 350 – 400 nm. Electrolytes I, II and III were diluted 5000 times by AN/EC (1:1, v/v).

Cyclic voltammetry (CV)

CV measurement was conducted at a scan rate of 50 mV/s with the help of a potentiostat/galvanostat (Autolab PGSTAT 302N) under ambient conditions. A conventional three-electrode cell with a platinum disc as a working electrode, a platinum foil as a counter electrode, and an Ag/AgCl (3 M saturated KCl solution) reference electrode was used with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Sigma, 99%) as a supporting electrolyte. The system was calibrated by a ferrocene/ferrocenium (Fc/Fc⁺) redox couple. For the estimation of $E_{F,redox}$, the solutions composed of 10 mM TBAI, 1 mM I₂ in AN/EC (1:1, v/v) and 10 mM TBAI, 1 mM (SeCN)₂ in AN/EC (1:1, v/v) were prepared, respectively. Because of the unknown composition of the redox species in TBAI/(SeCN)₂, we estimated the $E_{F,redox}$ from the formal potential (E_0') in the Nernst equation. The E_0' of TBAI/I₂ and TBAI/(SeCN)₂ was 0.23 V and 0.27 V (vs Ag/AgCl) or 0.42 V and 0.46 V (vs NHE, 25 °C) from the 1st cyclic voltammogram in Fig. S1 and Fig. 1d, respectively (for reference, the $E_{F,redox}$ of (SeCN)⁻/(SeCN)₂ redox couple was moved down by 0.19 V, compared to I/I₃⁻).

[Reference: G. Oskam, B. V. Bergeron, G. J. Meyer, P. C. Searson, *J. Phys. Chem. B* **2001**, *105*, 6867-6873]

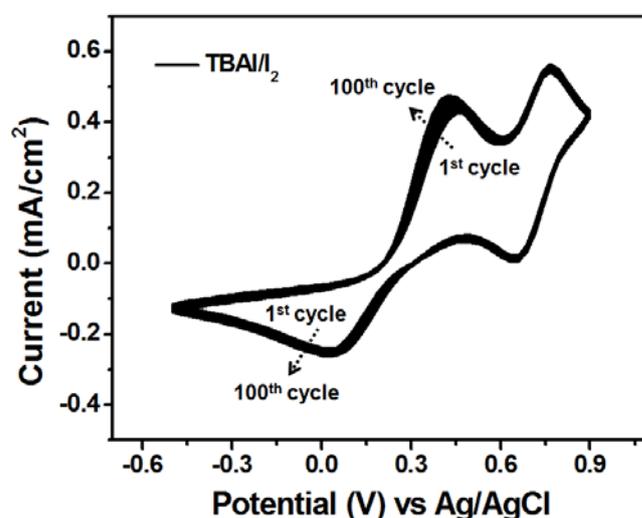


Fig. S1. Cyclic voltammograms (100 cycles) of TBAI/I₂.

Current-voltage (*J*-*V*) characteristics & Photocurrent response

The *J*-*V* performances of DSCs were measured under 1 sun conditions (AM 1.5G, 100 mW/cm²) shaded with a 0.25 cm² mask (the same as the active cell area) using a solar simulator (Newport) equipped with a 300 W Xenon lamp and a Keithley (Model 2,400) source meter, after calibrating with a silicon reference cell. Photocurrent response spectra were recorded for 5 seconds by the support of a solar simulator (Newport) and a potentiostat/galvanostat (Autolab, PGSTAT 302N). The *J*-*V* characteristics of Devices I, II, III, IV, V, A, B, C, D, E and F were carried out as changing the concentration of the oxidized species.

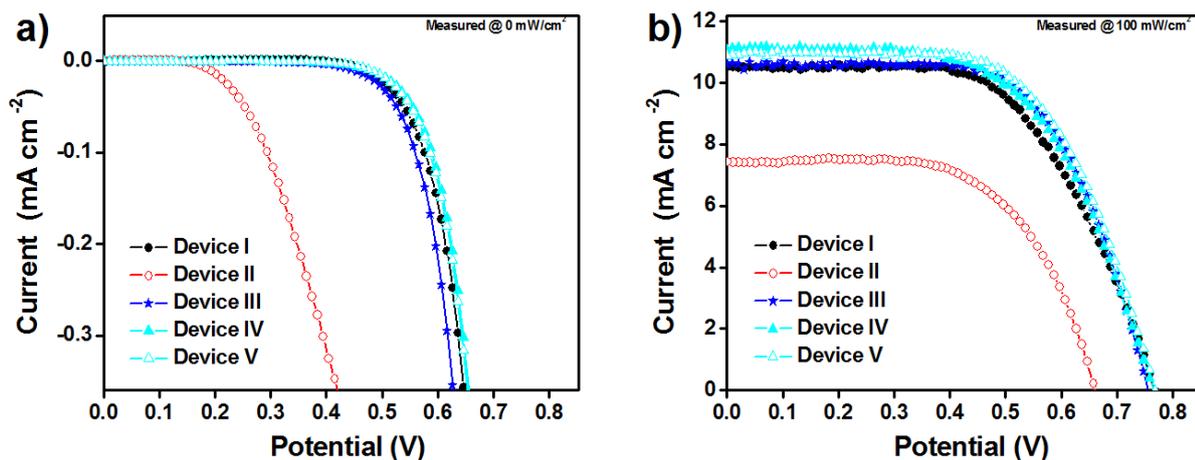


Fig. S2. J-V curves of Devices I, II, III, IV and V under (a) dark and (b) illumination conditions.

Table S1. J-V data of Devices IV, V, E and F.

| Devices ^[a] | Redox species | V_{oc} [V] | J_{sc} [mA/cm ²] | FF | η [%] |
|------------------------|--|--------------|--------------------------------|------|------------|
| IV | 0.6 M TBAI, 0.01 M (SeCN) ₂ | 0.77 | 11.1 | 0.59 | 5.0 |
| V | 0.6 M TBASeCN, 0.025 M (SeCN) ₂ | 0.77 | 10.9 | 0.62 | 5.2 |
| E | 0.6 M TBAI, 0.09 M I ₂ and 0.01 M (SeCN) ₂ | 0.75 | 11.3 | 0.68 | 5.7 |
| F | 0.6 M TBAI, 0.05 M I ₂ and 0.05 M (SeCN) ₂ | 0.73 | 11.1 | 0.72 | 5.8 |

[a] with the electrolyte containing 0.5 M tBP and 0.1 M GTC, and without a co-adsorbent and a scattering layer.

In the case of Devices C and D, a co-adsorbent (Solaronix, CDCA) and a scattering layer (Dyesol, WER 2-O) were adopted additionally in Devices A and B, respectively, for efficiency improvement.

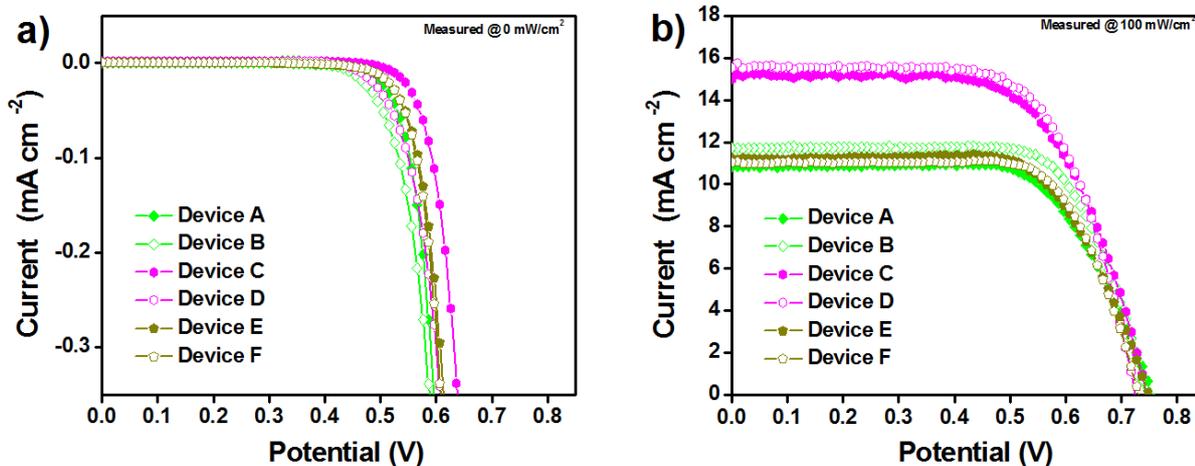


Fig. S3. J-V curves of Devices A, B, C, D, E and F under (a) dark and (b) illumination conditions.

Charge extraction (CE) & Open-circuit voltage decay (OCVD)

The combination of CE and OCVD methods is an effective way to determine an average lifetime for electrons in a TiO₂ layer.

For the measurement of CE, Zahner CIMPS system was applied to measure the amount of charge stored in a TiO₂ layer, depending on V_{OC} . Initially, DSCs were illuminated with a red LED light for 5 seconds at open-circuit conditions and then the light was immediately switched off automatically. After a delay time of milliseconds or seconds, *i.e.* voltage decay time, the circuit condition of DSCs was altered to short-circuit condition and the simultaneously extracted charge (Q_{ex}) and the V_{OC} were measured.

For the measurement of OCVD, a solar simulator (Newport) and a potentiostat/galvanostat (Autolab, PGSTAT 302N) were used. The electron lifetimes (τ_e) were calculated according to equation S1:

$$\tau_e = \frac{k_B T}{q} \left(\frac{dV_{OC}(t)}{dt} \right)^{-1} \quad (S1).$$

where k_B is the Boltzmann constant, T the absolute temperature, and q the elementary charge. After combining two relations from CE and OCVD methods, τ_e can be expressed by Q_{ex} as shown in Fig. 2.

[Reference: a) B. C. O'Regan, J. R. Durrant, *Accounts Chem. Res.* **2009**, *42*, 1799-1808; b) N. Kopidakis, N. R. Neale, A. J. Frank, *J. Phys. Chem. B* **2006**, *110*, 12485-12489; c) J. Bisquert, F. Fabregat-Santiago, I. Mora-Seró, G. Garcia-Belmonte, S. Giménez, *J. Phys. Chem. C* **2009**, *113*, 17278-17290.]

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was supported by a potentiostat/galvanostat (Autolab PGSTAT 302N).

a. Ionic conductivity

To obtain the information about the ionic conductivities of Electrolytes I, II and III, we equipped a lab-made four-probe conductivity cell suggested in the reference. After obtaining the data of electrolyte resistances (R_s), the conductivities were calculated by the following equation S2:

$$\sigma = \frac{l}{R_s \times S} \quad (S2)$$

where σ is the conductivity (S/cm) of electrolyte, l the length (cm) of electrolyte, R_s the solution resistance (Ω or S^{-1}) and S the surface area of electrode (cm^2).

[Reference: J. H. Kim, M.-S. Kang, Y. J. Kim, J. Won, Y. S. Kang, *Solid State Ionics* **2005**, *176*, 579–584]

b. Impedance parameters & Lifetime

The impedance spectra of Devices I, II and III were measured varying the frequency from 1 MHz to 10 mHz with the direct current (DC) voltage at their respective V_{OC} of the cells and the alternating current (AC) voltage at 20 mV were obtained under 1 sun illumination conditions. The data from the Nyquist plots (Fig. 4) were simulated with Z-View software (Solartron Analytical) to estimate all parameters including the resistance.

Table S2. Impedance parameters of Devices I, II and III.^[a]

| Devices | R_{Pt} [Ω] | R_D [Ω] | R_{rec} [Ω] |
|---------|--------------------------|-----------------------|---------------------------|
| I | 13.5 | 7.2 | 15.9 |
| II | 7.9 | 2.9 | 9.0 |
| III | 10.3 | 6.6 | 12.9 |

[a] R_{Pt} : charge transfer resistance at cathode,

R_D : diffusion resistance in electrolyte,
 R_{rec} : recombination resistance at photoanode.

The electron lifetime (τ_e) of Devices I, II and III was 0.011, 0.0011 and 0.0072 (s), respectively, according to the following equation S3:

$$\tau_e = \frac{1}{2\pi f_{max}} \quad (S3)$$

where f_{max} is the frequency at the mid-frequency peak in Bode plot. The τ_e values obtained from the EIS method showed the same trend with those from the combination of CE and OCVD methods as shown in Fig. 2. It seems that the EIS method caused the difference in the τ_e value between Devices I and II to be 10 times at a given V_{oc} for each cell measured at 1 sun conditions. However, the degree of difference will be varied depending on position of reference points (e.g. 0.4 V vs 0.6 V) and kind of variables at x-axis (voltage or charge density or *etc.*) because the electron recombination kinetics of Devices I and II is different, in this case, from each other.

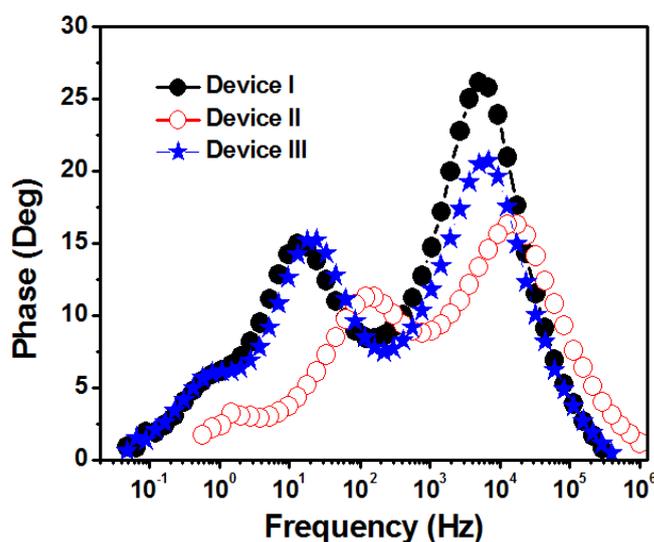


Fig. S4. Bode plots of Devices I, II and III.

c. Conduction band (CB) edge movement

For recording the stored charge (Q_s) in a broad range, the DC voltage was altered periodically from 0 V to their respective V_{OC} of the cells under dark conditions and the quasi-femi level, $E_{F,n}$ was obtained from the relation, $V_{OC} = |E_{F,n} - E_{redox}|$ as shown in Fig. S5. A noticeable variation of the CB edge position between Devices I and II was observed, whereas there was little offset between Devices I and III.

[Reference: H. Tian, Z. Yu, A. Hagfeldt, L. Kloo, L. Sun, *J. Am. Chem. Soc.*, **2011**, *133*, 9413–9422.]

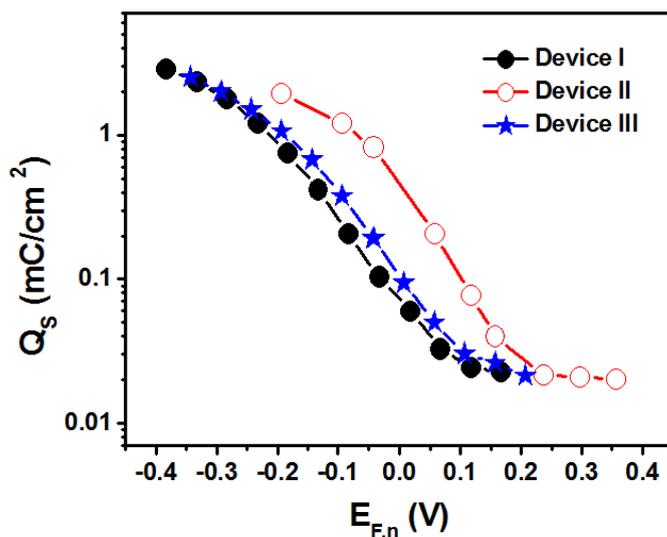


Fig. S5. Stored charge (Q_s) as a function of quasi-Fermi level ($E_{F,n}$) of Devices I, II and III.

Incident photon-to-current conversion efficiency (IPCE)

IPCE spectra of DSCs were recorded in the range of 300 nm and 800 nm, with an interval of 10 nm, using a monochromatic halogen light and additional illuminating white bias light source in the device (PV Measurements Inc., QEX7), after calibration by a silicon reference cell. Because the illuminated area onto DSCs by monochromatic halogen light was a little larger than the active area (0.25 cm²) of DSCs, the integrated IPCE values slightly were lower than the J_{SC} measured from solar simulator.

Intensity-modulated photocurrent spectroscopy (IMPS)

IMPS measurement was carried out to obtain electron transport time in a TiO₂ layer on a Zahner CIMPS system. The red LED light with a maximum wavelength at 670 nm was exposed on DSCs. The intensity of AC light is kept at 10 % of the intensity of DC light and the DSCs were maintained at short-circuit conditions during the measurement. The transport time constant (τ_{tr}) was regarded as the IMPS time constant (τ_{IMPS}) and is calculated by the following relationship S4:

$$\tau_{tr} \approx \tau_{IMPS} = \frac{1}{2\pi f_{min}} \quad (S4)$$

where f_{min} (Hz) is the frequency at the minimum point of an imaginary part.

The τ_{tr} values measured from the IMPS were not very different among the three devices

[Reference: H. Paulsson, L. Kloo, A. Hagfeldt, G. Boschloo, *J. Electroanal Chem.*, **2006**, 586, 56–61]

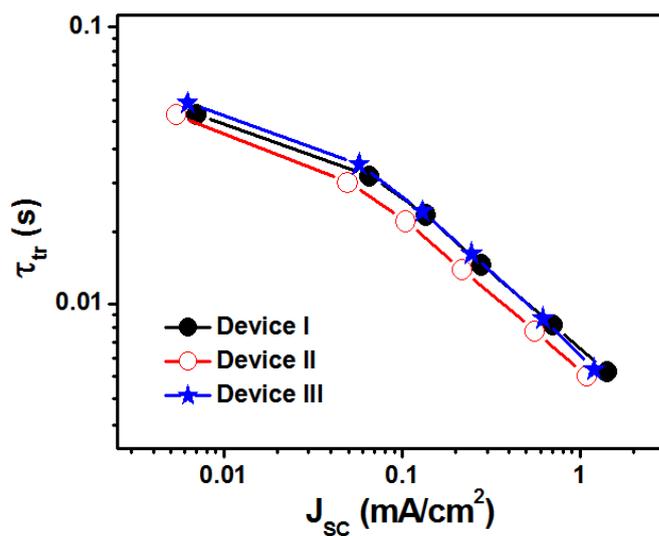


Fig. S6. Electron transport time (τ_{tr}) as a function of J_{sc} of Devices I, II, and III.

Long-term stability test

The stability result of Device III implies that the initial efficiency almost maintained over 700 h at ambient conditions.

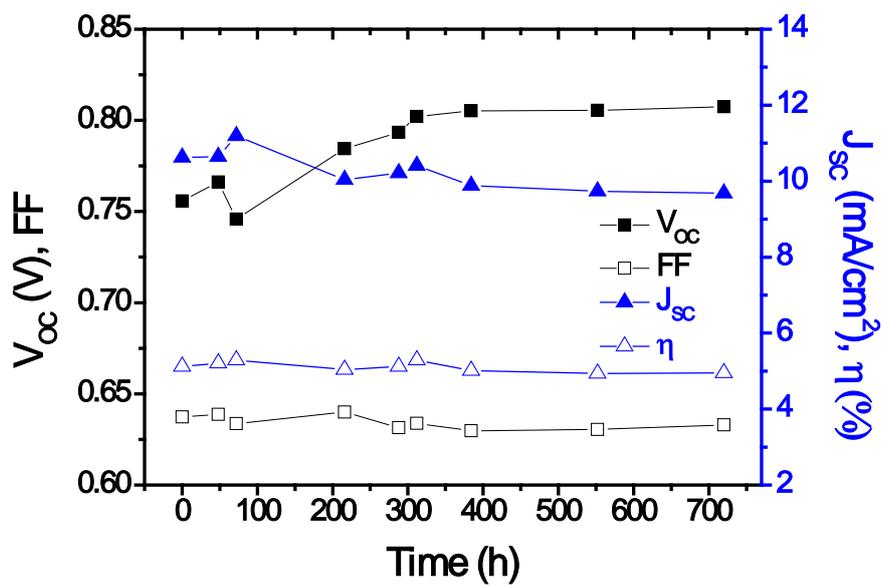


Fig. S7. Stability test of Device III.