

A Solvent-Free, $\text{SeCN}^-/(\text{SeCN})_3^-$ Based Ionic Liquid Electrolyte for High-Efficiency Dye-Sensitized Nanocrystalline Solar Cells

Peng Wang, Shaik M. Zakeeruddin, Jacques-E. Moser, Robin Humphry-Baker, and Michael Grätzel*

Laboratory for Photonics & Interfaces, Swiss Federal Institute of Technology, CH 1015 Lausanne, Switzerland

Received March 17, 2004; E-mail: michael.gratzel@epfl.ch

Nanocrystalline dye-sensitized solar cells (DSCs) are attracting considerable academic and industrial interest as low-cost, high-efficiency alternatives to the conventional solid p-n junction photovoltaic devices.¹ A record of 10.6% total power conversion efficiency has recently been reached using a liquid organic electrolyte based on the iodide/triiodide redox couple.² The recent achievement of long-term thermal stability by molecular-scale interface engineering has undoubtedly injected new momentum into this field.³ However, the sealing of volatile electrolytes in large scale modules still remains a critical issue in view of the practical application. Solid hole-transport materials⁴ and solvent-free polymer electrolytes⁵ incorporating iodide and triiodide have been introduced to replace the liquid electrolytes, but until now efficiencies of these devices are still relatively low. Another attractive option which is widely investigated currently is to employ room-temperature ionic liquids as nonvolatile electrolytes for DSCs.⁶

While considerable interest has been focused on the engineering of sensitizers and mesoporous semiconductor films, efforts to identify new electron mediators that could replace the iodide/triiodide couple have so far met only with modest success. Several polypyridyl cobalt(II/III) complexes⁷ have shown promise to rival the iodide/triiodide couple at low light intensity. However, under standard air mass (AM) 1.5 full sunlight the conversion efficiencies dropped below 4% due to mass transport limitations of the photocurrent. Oskam et al.⁸ tested the pseudohalides $\text{SCN}^-/(\text{SCN})_2$ and $\text{SeCN}^-/(\text{SeCN})_2$ as redox couples in acetonitrile by employing the standard N3 sensitizer. Their performance was found to be disappointing, the incident photon-to-current conversion efficiency (IPCE) being at most 20% compared to >80% for the iodide/triiodide-based system. This was attributed to the inefficient dye regeneration by the SeCN^- or SCN^- electron donor. Here we present results on the new and low-viscosity ionic liquid 1-ethyl-3-methylimidazolium selenocyanate (EMISeCN). When used in conjunction with a nanocrystalline TiO_2 film sensitized by an amphiphilic analogue of the N3 dye, unprecedented solar to electric power conversion efficiencies have been reached for solvent-free redox electrolytes.

EMISeCN was prepared according to the procedure published for 1-ethyl-3-methylimidazolium thiocyanate (EMISCN).⁹ The viscosity of pure EMISeCN was determined to be 25 cP at 21 °C, which is extraordinarily low for an ionic liquid. The most fluid imidazolium iodide-based analogue, i.e., 1-propyl-3-methylimidazolium iodide (PMII), has a 35 times higher viscosity, i.e., around 880 cP at room temperature. The specific conductivity of EMISeCN is 14.1 mS/cm compared to 0.5 mS/cm for PMII. Even at -30 °C it is still 1 mS/cm, whereas it becomes negligibly small for PMII. The higher conductivity of EMISeCN is mainly due to a decrease in cohesive energy, probably because the van der Waals energy associated with the highly polarizable iodide component has been removed.

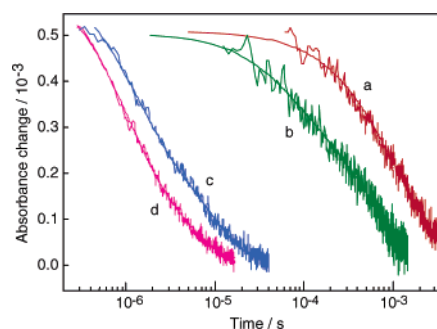


Figure 1. Transient absorbance decay kinetics of the oxidized state of Z-907 dye anchored on a nanocrystalline TiO_2 film in the presence of various pure ionic liquids (a, EMIDCN; b, EMISCN; c, PMII; d, EMISeCN). Absorbance changes were measured at a probe wavelength of 650 nm, employing 532 nm pulsed laser excitation (10 ns fwhm pulse duration, 40 $\mu\text{J}/\text{cm}^2$ pulse fluence).

These trends are corroborated by the results from electrochemical measurements of the diffusion coefficients of SeCN^- and $(\text{SeCN})_3^-$. The composition of the ionic liquid employed was the same as that used in the photovoltaic experiments described further below. Apart from EMISeCN it contained 0.15 M $\text{K}(\text{SeCN})_3$,¹⁰ 0.1 M guanidinium thiocyanate, and 0.5 M *N*-methylbenzimidazole. The diffusion coefficients of SeCN^- and $(\text{SeCN})_3^-$ in this electrolyte, determined by ultramicroelectrode voltammetry^{6b} are 2.80×10^{-6} and 1.28×10^{-6} cm^2/s , respectively. These values are about 9 and 7 times higher than the respective values for iodide and triiodide in the pure PMII ionic liquid.^{6b}

These intriguing properties prompted us to investigate whether EMISeCN could replace iodide-based ionic liquids in dye-sensitized solar cells. Transparent nanocrystalline TiO_2 films of 8 μm thickness were deposited on glass and derivatized with $\text{Ru}(\text{H}_2\text{dcbpy})(\text{dnbpy})-(\text{NCS})_2$ dye,¹¹ where H_2dcbpy is 4,4'-dicarboxylic acid-2,2'-bipyridine and dnbpy is 4,4'-dinonyl-2,2'-bipyridine. This amphiphilic sensitizer, coded as Z-907, was adsorbed onto the TiO_2 film from a 300 μM solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) by overnight dipping. Charge injection from the excited state of Z-907 into the conduction band of TiO_2 occurs within the picosecond time scale.¹² In the absence of electrolyte the injected conduction band electrons are recaptured by the oxidized Z-907 dye molecules (S_{907}^+) in the microsecond–millisecond domain.¹¹ Time-resolved laser photolysis in conjunction with transient absorption spectroscopy was performed to examine whether SeCN^- could intercept the back electron-transfer reaction.

Shown in Figure 1 are results illustrating the temporal behavior of the 650 nm absorption of the S_{907}^+ in the presence of four imidazolium-based ionic liquids containing different anions. Curve A refers to an ionic liquid containing the redox-inactive dicyanamide (EMIDCN).¹³ Here the 650 nm absorption decay with $t_{1/2} = 1$ ms reflects the dynamics of recombination of injected conduction band

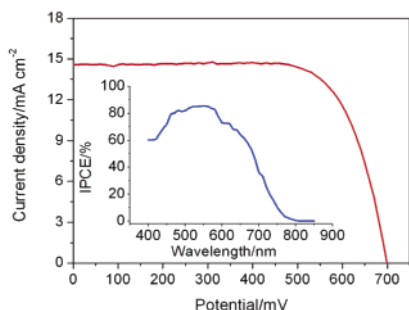


Figure 2. Current density–voltage characteristic under AM 1.5 illuminations of 99.7 mW/cm^2 . The inset is its photocurrent action spectrum. Cell active area tested with mask: 0.152 cm^2 .

electrons with S_{907}^+ . For EMISecN or PMII the disappearance of S_{907}^+ is greatly accelerated, the $t_{1/2}$ values being 1.5 and $3 \mu\text{s}$, respectively. This shows that, contrary to the results of Oskam et al.⁸ obtained with acetonitrile, the SeCN^- ions in the EMISecN ionic liquid intercept the back electron transfer very efficiently. Electron donation from the SeCN^- to the oxidized Z-907 dye is even faster than from iodide ions in the PMII ionic liquid, despite that the former has a more positive redox potential of 190 mV than the latter⁸ and hence is more difficult to be oxidized. However, for the EMISecN ionic liquid containing thiocyanate instead of selenocyanate anions, the S_{907}^+ decay has a much longer half-lifetime of $200 \mu\text{s}$ indicating inefficient interception of charge recombination. Insufficient thermodynamic driving force is the probable reason for slow electron donation from SCN^- to the S_{907}^+ as the replacement of selenium by sulfur results in a 270 mV increase of the standard redox potential,⁸ bringing it closer to that of the Z-907 sensitizer.¹⁴

The photovoltaic performance of an EMISecN-based ionic liquid was tested using state of the art mesoscopic titania films. The detailed fabrication procedure for the nanocrystalline photoanodes and the assembly of complete, hot-melt sealed cells have been described elsewhere.¹⁴ A thick film of 20 nm sized TiO_2 particles was first screen-printed on a fluorine-doped SnO_2 (FTO) conducting glass electrode and a second $4 \mu\text{m}$ thick second layer of 400 nm-sized light scattering anatase particles was subsequently coated onto the first one. The surface of the TiO_2 electrode was derivatized with the sensitizer by immersing it into the dye solution composed of $300 \mu\text{M}$ Z-907 and $300 \mu\text{M}$ 3-phenylpropionic acid as coadsorbent in acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) at room temperature for 12 h. A platinumized FTO conducting glass was used as counter electrode.

A typical photocurrent action spectrum obtained with the new ionic liquid electrolyte is shown in the inset of Figure 2. The incident photon to current conversion efficiency (IPCE) is very high, exceeding 80% in a spectral range from 470 to 580 nm and reaching its maximum of 85% at 550 nm. Considering the light absorption and scattering loss by the conducting glass, the conversion of photons to current is practically quantitative over this spectral range. Figure 2 presents the photocurrent–voltage curve measured under an air mass (AM) 1.5 illumination of 99.7 mW/cm^2 . The short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (ff) of the above device are 14.56 mA/cm^2 , 699 mV, and 0.735, respectively, yielding an overall conversion efficiency (η) of 7.5%. At the intermediate light levels of 9.5, 30, and 51.7 mW/cm^2 , the device efficiencies are 8.3%, 8.3%, and 8.1%, respectively. This is the first time such high efficiencies have been

reached for dye-sensitized solar cells with pure ionic liquid electrolytes. While detailed stability tests on this system are on going, we noticed that the efficiency of the cell under room light storage varied by less than 10% for eight weeks. Apart from the high efficiency, the high conductivity of EMISecN below 0°C allows for the realization of photovoltaic devices having a broader operational temperature than iodide-based ionic liquids. In addition, this new ionic liquid electrolyte has the advantage over the iodide/triiodide-based analogues of having considerably less light absorption in the visible region and thus reducing optical losses due to optical attenuation by the electrolyte.⁶

In summary, we have demonstrated that ionic liquids based on the $\text{SeCN}^-/(\text{SeCN})_3^-$ redox couple can be employed as mediators for high-efficiency dye-sensitized solar cells. For the first time an alternative redox couple has been identified that can rival and even exceed the performance of the iodide/triiodide couple even at full sunlight. Unprecedented 7.5–8.3% power conversion efficiencies under AM 1.5 sunlight have been achieved for photovoltaic devices with pure ionic liquid electrolytes. Work is in progress to further improve the performance of this promising system.

Acknowledgment. We are grateful to Marlene Rodlert (LTC, EPFL) for the viscosity measurement, P. Comte for the film fabrication, and CCIC (Japan) for a free sample of the 400 nm sized light scattering anatase particles. This work was supported by the Swiss Science Foundation, the Swiss Federal Office for Energy, and the European Office of the U.S. Air Force under Contract No. F61775-00-C0003.

Supporting Information Available: Synthetic procedure and data on additional conductivity, voltammetric, I – V , and UV–vis measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Grätzel, M. *Nature* **2001**, *414*, 338.
- Grätzel, M. J. *Photochem. Photobiol. C: Photochem. Rev.* **2003**, *4*, 145.
- Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Moser, J. E.; Grätzel, M. *Adv. Mater.* **2003**, *15*, 2101.
- For example: (a) O'Regan, B.; Lenzmann, F.; Muis, R.; Wienke, J. *Chem. Mater.* **2002**, *14*, 5023. (b) Kumara, G. R. A.; Kaneko, S.; Okuya, M.; Tennakone, K. *Langmuir* **2002**, *18*, 10493. (c) Krüger, J.; Plass, R.; Grätzel, M.; Matthieu, H.-J. *Appl. Phys. Lett.* **2002**, *81*, 367. (d) Taguchi, T.; Zhang, X.; Sutanto, I.; Tokuhiko, K.; Rao, T. N.; Watanabe, H.; Nakamori, T.; Uragami M.; Fujishima, A. *Chem. Commun.* **2003**, 2480.
- For example: (a) Nogueira, A. F.; Durrant, J. R.; De Paoli, M. A. *Adv. Mater.* **2001**, *13*, 826. (b) Stergiopoulos, T.; Arabatzis, I. M.; Katsaros, G.; Falaras, P. *Nano Lett.* **2002**, *2*, 1259.
- For example: (a) Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *Chem. Commun.* **2002**, 374. (b) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166. (c) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 13280.
- For example: (a) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. *J. Phys. Chem. B* **2001**, *105*, 10461. (b) Sapp, S. A.; Elliott, M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 11215. (c) Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. *Chem. Eur. J.* **2003**, *9*, 3756.
- Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C. *J. Phys. Chem. B* **2001**, *105*, 6867.
- Pringle, J. M.; Golding, J. Forsyth, C. M.; Deacon, G. B.; Forsyth, M.; MacFarlane, D. R. *J. Mater. Chem.* **2002**, *12*, 3475.
- (a) Hauge S. *Acta Chem. Scand.* **1971**, *25*, 3081. (b) Bowmaker, G. A.; Kilmartin, P. A.; Wright, G. A. *J. Solid State Electrochem.* **1999**, *3*, 163.
- Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi T.; Grätzel, M. *Nat. Mater.* **2003**, *2*, 402.
- Benkő, G.; Kallioinen, J.; Myllyperkiö, P.; Trif, F.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundström, V. *J. Phys. Chem. B* **2004**, *108*, 2862.
- MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. *Chem. Commun.* **2001**, 1430.
- Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry-Baker, R.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 14336.

JA048472R

Supporting information:

Synthesis of EMISECN. Silver selenocyanate was precipitated by mixing 30 ml aqueous solution of silver nitrate (2 g, 12 mmol) and 20 ml aqueous solution of potassium selenocyanate (1.7 g, 12 mmol) and then washed thoroughly with water to remove any unreacted reagents. A 20 ml aqueous solution of 1-ethyl-3-methylimidazolium iodide (2.07 g, 8.25 mmol) was added to the slurry of the excess silver selenocyanate (12 mmol) in 40 ml water and the solution was heated gently with stirring for 1 h. Silver iodide was removed by filtration and the water removed from the filtrate under vacuum at 55 °C. Dichloromethane (20 ml) was added to the product and the solution was cooled in a refrigerator overnight before filtration and removal of the solvent. The ionic liquid of EMISECN was dried under vacuum at 55 °C for 6 h before use. Yield: 65%. ¹H NMR (CD₃OD, δ ppm relative to TMS): 1.58 (t, 3H), 3.98 (s, 3H), 4.29 (q, 2H), 7.65 (d, 2H), 8.98 (s, 1H). ATR-FTIR: 3435m (br), 3144m [ν (CH₃)], 3092m [ν (CH)], 2981m [ν (CH)], 2057s [ν (SeCN)], 1567s, 1448m, 1385w, 1335m, 1165s, 1087w, 1026w, 958w.

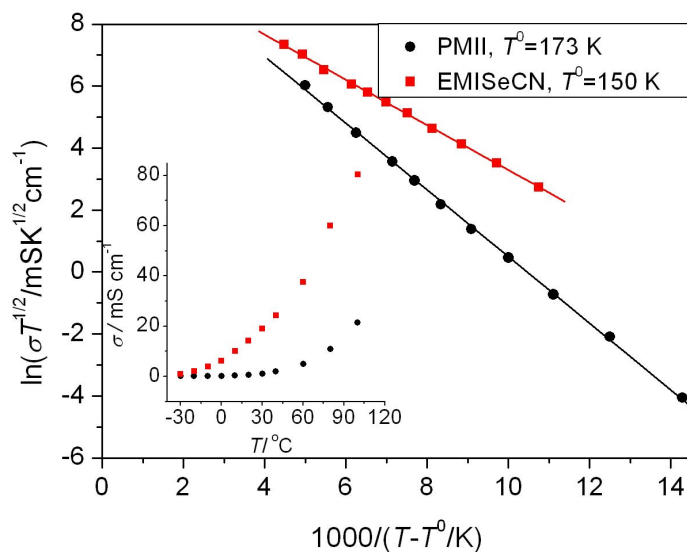


Figure S1. Plots of conductivity–temperature data of pure EMISecN and PMII in the Vogel-Fulcher-Tammann (VFT) coordinates. T^0 is the Kauzmann temperature. The inset is the relationship between conductivity and temperature.

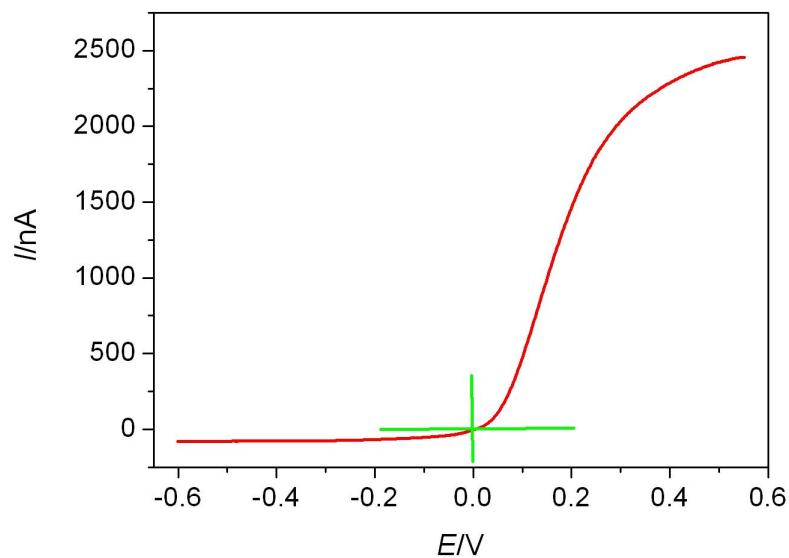


Figure S2. Steady-state voltammogram of a 5 μm radius Pt ultramicroelectrode in the new ionic liquid electrolyte. A two-electrode system with Pt foil as counter electrode was used. Scan rate: 20 mV/s.

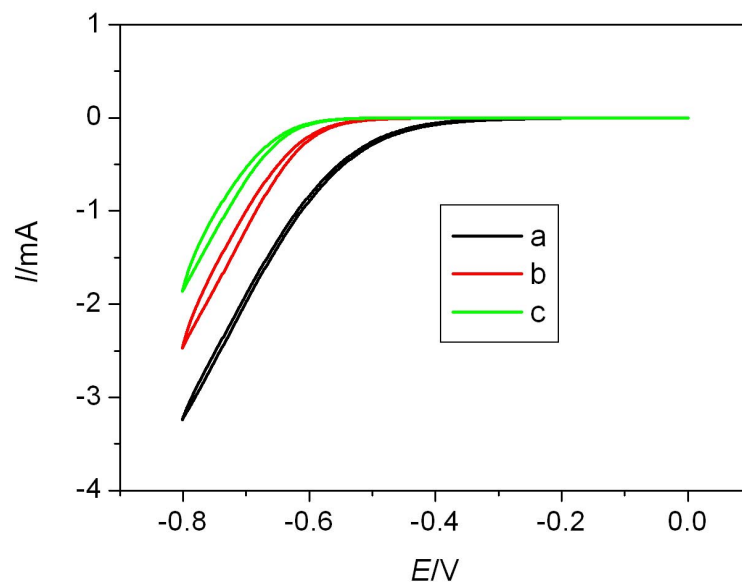


Figure S3. Cyclic voltammograms of the new ionic liquid electrolyte in thin-layer electrochemical cells with (a) conducting glass electrode (F-doped SnO_2), (b) double-layer nanocrystalline TiO_2 electrode, and (c) Z-907 dye coated TiO_2 electrode as working electrode. Counter electrode: platinumized conducting glass. Scan rate: 20 mV/s.

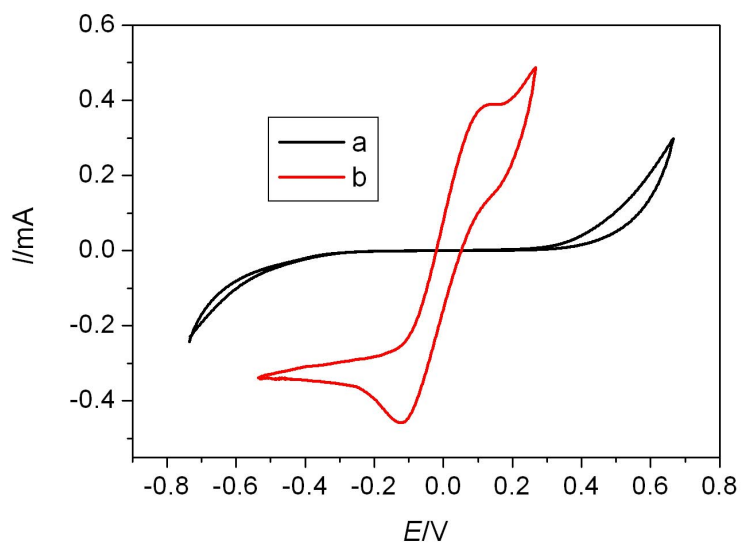


Figure S4. Cyclic voltammograms of (a) naked and (b) platinumized conductive glass electrodes (F-doped SnO_2) in the acetonitrile solution with 5 mM EMISECN and 5 mM $\text{K}(\text{SeCN})_3$. A two-electrode system with Pt foil as counter electrode was used. Supporting electrolyte: 0.2 M tetra-*n*-butylammonium hexafluorophosphate. Scan rate: 20 mV/s.

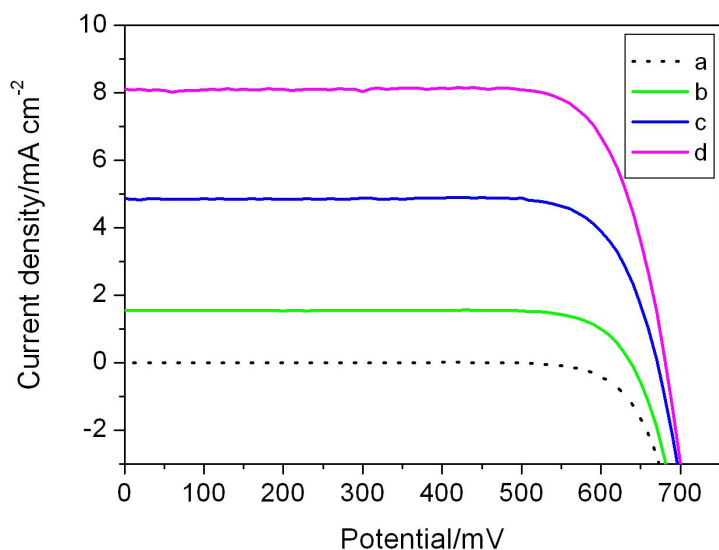


Figure S5. Current density-voltage characteristics under dark (curve a) and at AM 1.5 illuminations (light intensities for curves b to d: 9.5, 30, and 51.7 mW/cm², respectively). Cell active area tested with mask: 0.152 cm².

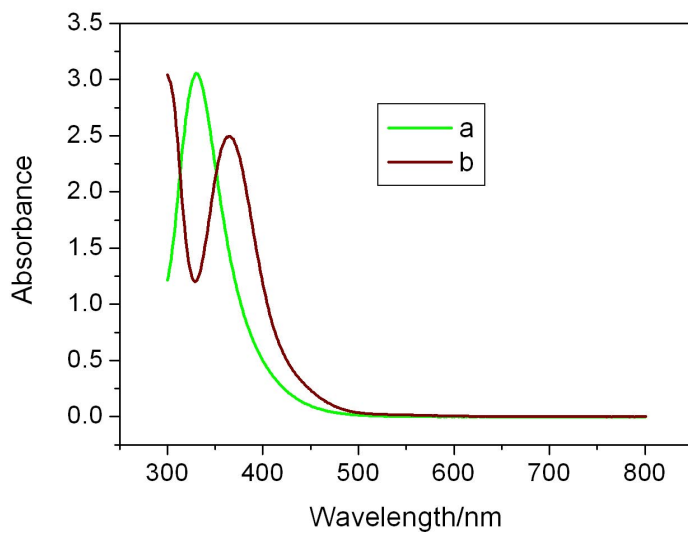


Figure S6. UV-vis spectra of (a) the electrolyte used in this paper and (b) the reference electrolyte (0.15 M I₂, 0.1 M guanidinium thiocyanate, and 0.5 M *N*-methyl-benzimidazole in PMII) which have been 10 times diluted by acetonitrile. Optical length: 25 μm.