Electronic Supplementary Information (ESI) for

Hydroxyethyl and Ester Co-functionalized Imidazolium Iodide for Highly Efficient Solid-State Dye-Sensitized Solar Cells

Juan Li, Hong wang, Gang Zhou and Zhong-Sheng Wang*

Department of Chemistry, Lab of Advanced Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, PR China. Fax/Tel: +86-21-5163-0345; E-mail: zs.wang@fudan.edu.cn

Experimental

Materials and Reagents. Transparent conductive glass (F-doped SnO_2, FTO, 15 Ω per square, transmittance of 85%, Nippon Sheet Glass Co., Japan) was used as the substrate for the fabrication of TiO_2 thin film electrodes. LiI, I_2, 1-methylbenziimidazole (NMBI), and 1-methyl-3-propylimidazolium iodide (MPII) were obtained from Acros. The organic dye MK2 (Figure S7) was prepared according to the reported method.[1] 2-Iodoethanol, iodoethane, 1-methylimidazole were purchased from J&K Chemical Ltd, China. Organic solvents used in this work were purified using the standard process.

Synthesis of 1-(2-methoxy-2-oxoethyl)imidazole. Absolute dry methanol (50 mL) and sodium (2.3 g, 0.1 mol) were charged into a 100 mL three-necked flask equipped with a condensing tube and stirred at room temperature for 2 h. Then imidazole (6.8 g, 0.1 mol) was added to the above mixture, which was heated to 50 °C. After stirring for 1 h, methyl chloroacetate (21.7 g, 0.2 mmol) was added. The reaction was kept at 50 °C for additional 16 h. After filtration, the solvent was removed *via* rotary evaporation until yellow oil remained. Silica gel chromatography with CH_2Cl_2:CH_3OH (20:1, v:v) as eluent afforded the pure product as a white solid (yield, 67.0%). ^1H NMR (DMSO-d_6, 400 Hz, δ): 7.44 (s, 1H), 7.03 (s, 1H), 6.89 (s, 1H), 4.66 (s, 2H); 3.72 (s, 3H).

Synthesis of 3-(2-hydroxyethyl)-1-(2-methoxy-2-oxoethyl)imidazolium iodide (HEII). 1.5 equiv. 2-iodoethanol and 1-(2-methoxy-2-oxoethyl) imidazole (4 g, 0.029 mmol) were dissolved in 10 mL methanol and the mixture was stirred at room temperature for 48 h. Afterwards the solvent was removed by rotary evaporation until viscous oil remained. Silica gel chromatography with CH_2Cl_2:CH_3OH (20:1, v:v) as eluent afforded the pure product as a white solid (yield, 75%). ^1H NMR (DMSO-d_6, 400 Hz, δ): 9.09 (s, 1H), 7.77 (s, 1H), 7.72 (s, 1H), 5.25 (s, 2H), 5.19 (s, 1H), 4.27 (s, 2H), 3.72 (m, 5H). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_8H_{13}N_2O_3^+$, 185.0926; found, 185.0932.

Fabrication of ssDSSCs. TiO_2 films (11 μm) composed of a 5 μm nanoparticle (20 nm) layer in direct contact with the FTO substrate and a 6 μm light scattering particle (80% 20 nm TiO_2 + 20% 100 nm TiO_2) layer[2] were fabricated with a screen printing technique and used in this study. The films were calcined at 500 °C with a rising rate of 10 °C/min and treated with 0.05 M $TiCl_4$ aqueous solution for 30 min at 70 °C followed by heating at 450 °C for 30 min. Then the films were immersed in the dye solution (0.3 mM in toluene) when the film was about 120 °C for at least 16 h. The dye-sensitized TiO_2 as the working electrode and the Pt-coated FTO as the counter electrode were separated by a hot-melt Surlyn film (30 μm) and sealed together by pressing them under heat. The methanol solution of the solid electrolyte (ionic conductor:I_2:LiI:NMBI:MPII=12:1:3:10:0.5, molar ratio) was injected into the internal space of the cell from the two holes predrilled on the back of the counter electrode and dried on a hot plate with the temperature of 80 °C for at least 30 min to remove methanol, which was repeated 3 times to ensure that the TiO_2 porous film was filled with solid-state electrolyte. To remove the residual solvent, the cell was further dried at 50 °C under vacuum for one day. The complete removal of methanol can be confirmed by a weighting method. The cell was first filled with the electrolyte solution in methanol containing known weight of methanol. After drying the cell under vacuum conditions, the weight loss is almost equal to the weight of methanol in the electrolyte. Thus, we believe that the solvent in the electrolyte is removed completely. Finally, the back holes were sealed with a Surlyn film covered with a thin glass slide under heat.

Characterizations. The structure of HEII was characterized by ^{1}H-NMR (Varian 400 MHz NMR spectrometer) and high resolution mass spectrum (HRMS, 6890GC/5973MS HP). Thermogravimetric (TG) analysis was performed on a TG-DTA 2000S system (Mac Sciences Co. Ltd., Yokohama, Japan) at a heating rate of 10 ^{o}C min^{-1}. Differential scanning calorimetry (DSC) was studied on a Shimadzu DSC-60A at a heating rate of 5 °C min^{-1}. Crystal structure of HEII was acquired with a Bruker SMART diffractometer equipped with an APEX(II)-CCD area detector using graphite-monochromatic Mo K_α (λ = 0.71073 Å) radiation. The collected data are listed in Table S1. Empirical absorption correction was made with multi-scan based on symmetry-related measurements. The structure was solved by a direct method (SHELXLT-97) and refined by full matrix least-squares techniques based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. All computations were carried out using the SHELXL-97 program package. The ionic conductivity of the ion conductor, which was sandwiched in a homemade symmetrical cell made of two identical Pt coated FTO substrates with an active area of 0.36 cm^2 and an inter-electrode distance of 30 μm, was determined by electrochemical impedance spectroscopy (EIS). The EIS spectra were recorded under dark at 0 V in a frequency range of 0.01 to 10^5 Hz. The current density-voltage (*J-V*) characteristics of ssDSSCS were measured by recording the *J-V* curves with a Keithley 2400 source meter (Oriel) under illumination simulated AM1.5G solar light coming from a solar simulator (Oriel-94043A equipped with a 450 W Xe lamp and an AM1.5G filter). The incident light intensity was calibrated using a standard Si solar cell (Newport 91150) equipped with a KG5 filter. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with an Oriel-74125 system (Oriel Instruments). The intensity of monochromatic light was measured with a Si detector (Oriel-71640). Four identical DSSCs (active layer size 5 mm × 5 mm = 0.25 cm^2) for each sample were measured with standard deviation error of efficiency below 0.1%. To eliminate the stray light, a black mask with an aperture area of 0.2304 cm^2, measured with a Nikon Digital Camera controlled by a computer using an objective micrometer ruler as a reference, was used to cover the devices during measurements. The TiO_2 film thickness was measured by a surface profiler (Dektak 150, Veeco, USA).

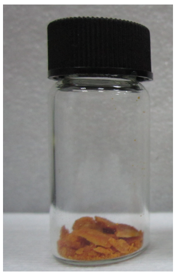

Figure S1. Photograph of HEII

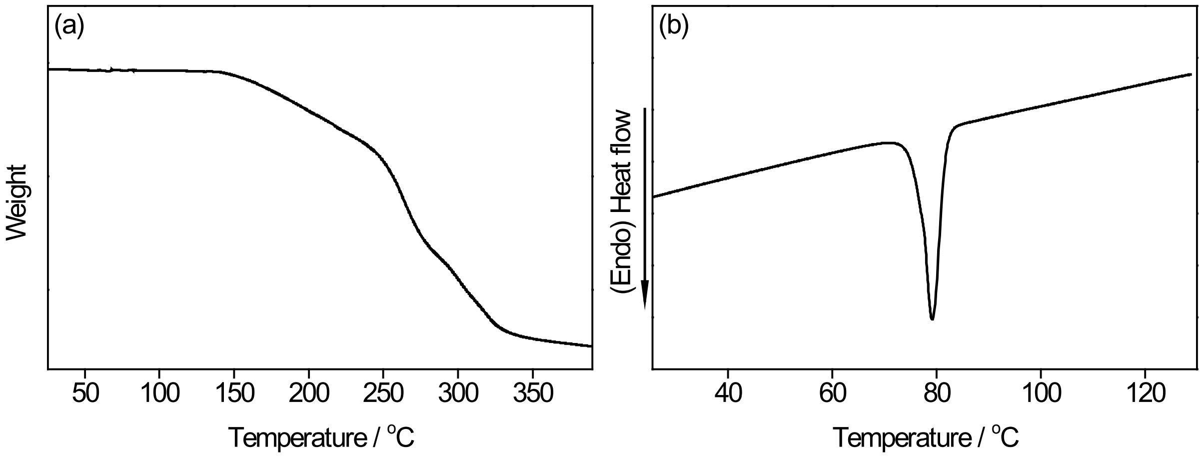

Figure S2. The TG and DSC curves for HEII.

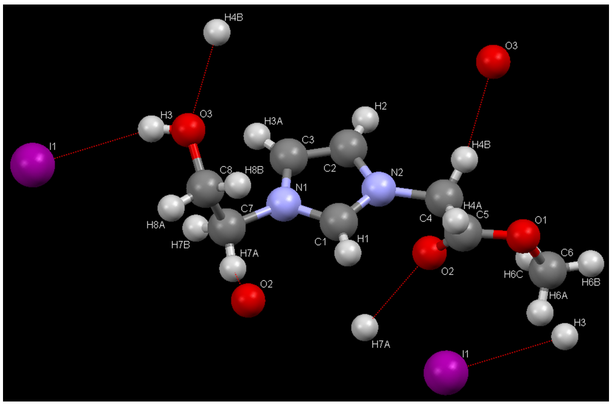

Figure S3. Hydrogen bonds in the crystal structure of HEII. I (purple), O (red), N (blue), C (gray), H (white); the same below.

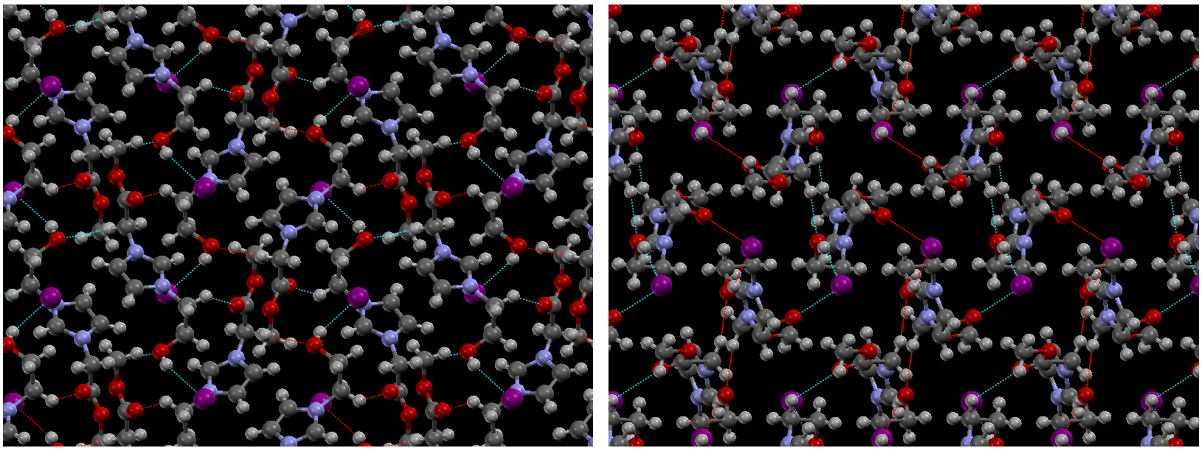

Figure S4. Packing structures of HEII viewed down the *a* (left) and *c* (right) axis.

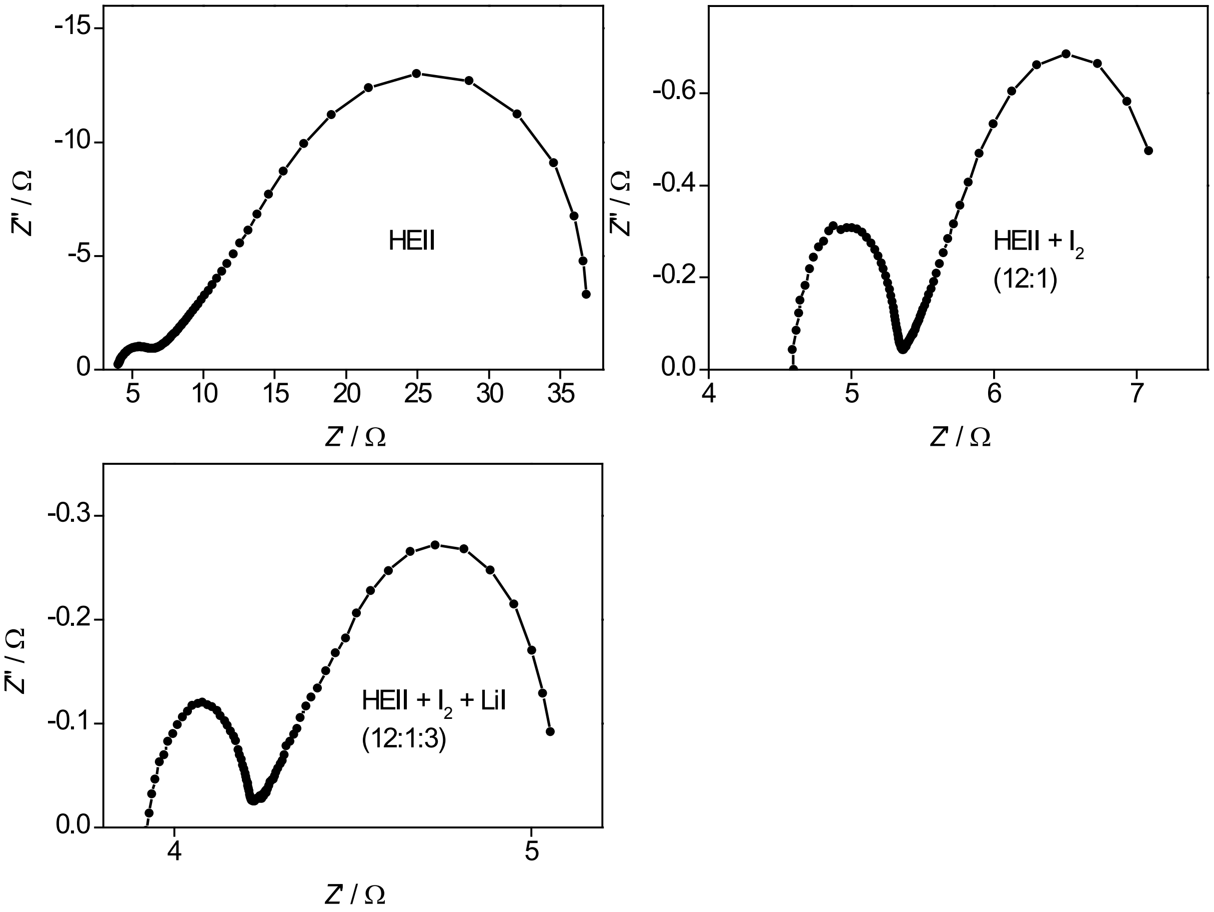

Figure S5. Impedance spectra for pure HEII, HEII + I_2 (12:1) and HEII + I_2 + LiI (12:1:3) measured at 0 V bias under dark. The solid electrolyte layer is 30 μm thick with an active area of 0.36 cm^2. The high-frequency semicircle (left) is attributed to the charge-transfer from the electrode to I_3^- while the low-frequency semicircle (right) is attributed to the ionic movement or charge transfer in the bulk electrolyte. The resistance (R) of the electrolyte is estimated by the diameter of the low-frequency semicircle. The conductivity (σ) is calculated with the expression of $\sigma = d/(R \times A)$, where d is the electrolyte layer thickness and A is the active area.

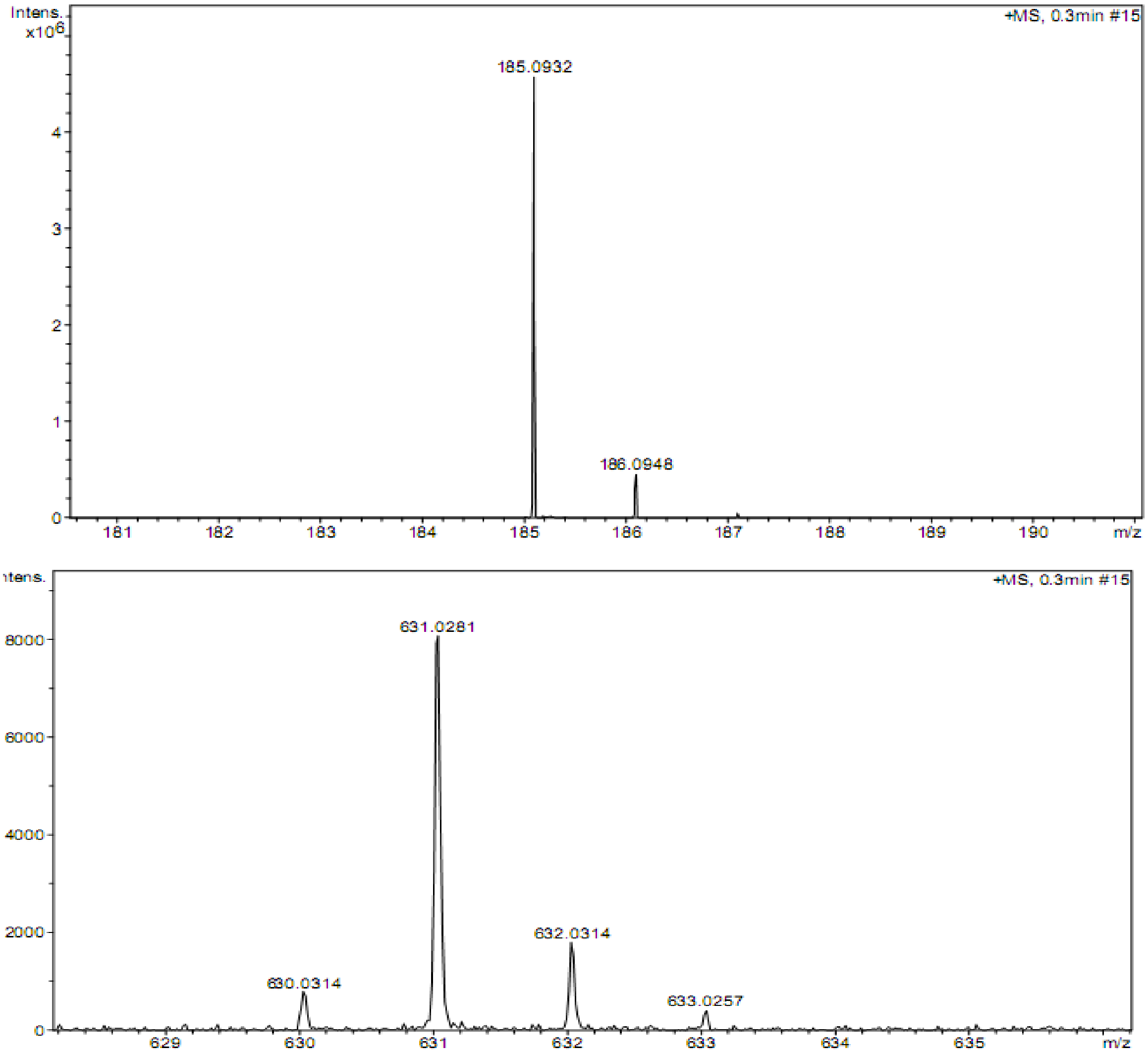

Figure S6. HRMS for HEII (top) and the HEII-LiI mixture (bottom).

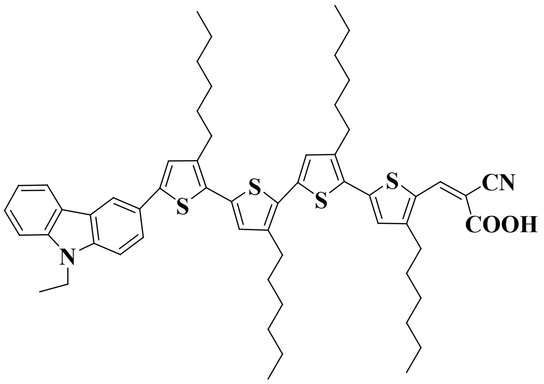

Figure S7. Chemical structure of the metal-free organic dye (MK2) used in this work.

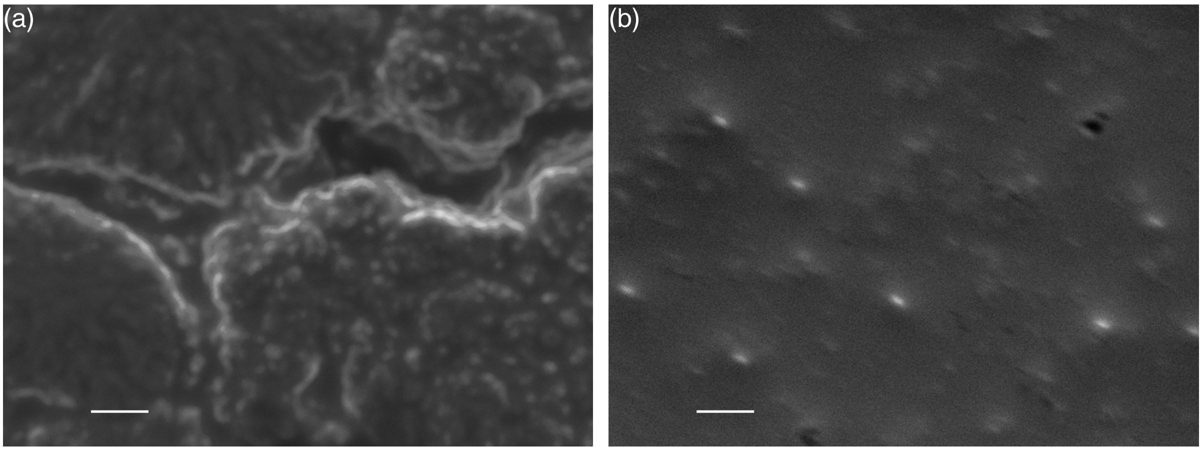

Figure S8. SEM images of dye-loaded TiO_2 films deposited with HEII based solid electrolyte: (a) without and (b) with small amount of MPII. The scale bar is 20 μm.

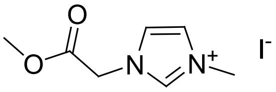

Figure S9. Chemical structure of the ester-methyl-substituted imidazolium iodide.

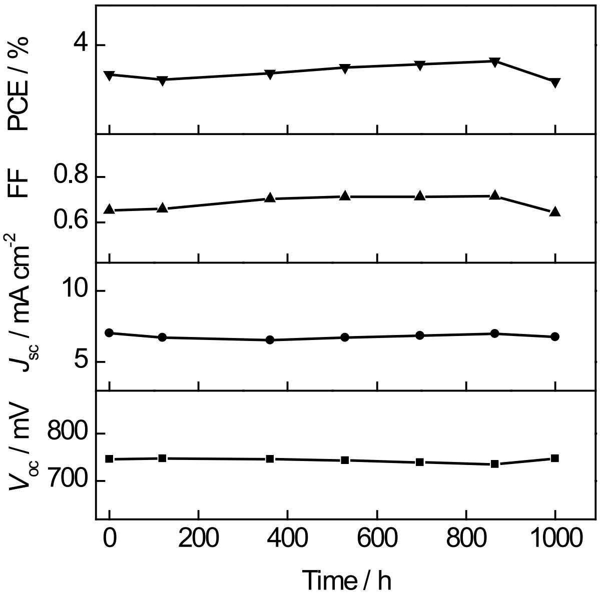

Figure S10. Evolutions of photovoltaic performance parameters for the ssDSSC under one sun soaking.

Table S1. Crystallographic data (CCDC 889350) and structural refinement for HEII

Empirical formula	$C_8H_{13}IN_2O_3$
Formula weight	312.10
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a=8.7155(17)Å; b=13.9002(27)Å; c=10.2532(20)Å; α=90°; β=111.210(2)°; γ= 90°
Volume	1158.0(4) $Å^3$
Z, Calculated density	4, 1.790 g/cm^3
Absorption coefficient	2.752 mm^{-1}
F(000)	608
Crystal size	0.22 x 0.20 x 0.15 mm
Theta range for data collection	2.59 to 27.90 °
Limiting indices	-11<=h<=9, -18<=k<=17, -8<=l<=13
Reflections collected / unique	6279 / 2520 [R(int) = 0.0251]
Completeness to □ = 25.49°	90.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on *F*2
Data / restraints / parameters	2520 / 0 / 129
Goodness-of-fit on *F*2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0626
R indices (all data)	R1 = 0.0334, wR2 = 0.0673
Largest diff. peak and hole	0.552 and -0.753 e.$Å^{-3}$

Table S2. Conductivity of HEII, HEII + I_2 (12:1) and HEII + I_2 + LiI (12:1:3)

Electrolyte	σ/[mS cm^{-1}	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	PCE/%
HEII	0.27	-	-	-	-
HEII+I_2 (12:1)	3.97	0.32	563	0.448	0.081
HEII+I_2+LiI (12:1:3)	6.94	9.33	564	0.673	3.54
HEII+I_2+LiI+NMBI (12:1:3:10)	6.92	13.81	687	0.661	6.27
HEII+I_2+LiI +NMBI+MPII (12:1:3:10:0.5)	7.06	14.66	733	0.693	7.45

The solar cell performance was roughly optimized by varying the composition with various ratios using the TiO_2 films with same thickness and the same dye. The photovoltaic data was summarized in Table S3-S6.

Table S3. Photovoltaic parameters for ssDSSCs with HEII and iodine

HEII/I_2	J_{sc} / mA cm^{-2}	V_{oc} / mV	FF	PCE/%
2:1	0.20	268	0.430	0.023
5:1	0.30	0.557	0.482	0.081
12:1	0.32	0.563	0.448	0.081

Table S4. Photovoltaic parameters for ssDSSCs with HEII, I_2 and LiI at HEII/I_2 = 5:1

HEII/I_2/LiI	J_{sc} / mA cm^{-2}	V_{oc} / mV	FF	PCE/%
5:1:0	0.30	0.557	0.482	0.081
5:1:0.83	1.26	402	0.540	0.27
5:1:1.25	6.87	564	0.680	2.63
5:1:2.5	5.47	525	0.670	1.92
5:1:5	2.09	474	0.552	0.55

Table S5. Photovoltaic parameters for ssDSSCs with HEII, I_2 and LiI at HEII/LiI = 4:1

HEII/I_2/LiI	J_{sc} / mA cm^{-2}	V_{oc} / mV	FF	PCE/%
5:1:1.25	6.87	564	0.680	2.63
12:1:3	9.33	564	0.673	3.54
20:1:5	5.86	536	0.679	2.13

Table S6. Photovoltaic parameters for ssDSSCs with HEII, I_2, LiI and NMBI at HEII/I_2/LiI = 12:1:3

HEII/I_2/LiI/NMBI	J_{sc} / mA cm^{-2}	V_{oc} / mV	FF	PCE/%
12:1:3:0	9.33	564	0.673	3.54
12:1:3:6	9.36	604	0.737	4.17
12:1:3:10	11.98	622	0.658	4.90
12:1:3:12	8.65	635	0.728	4.00

References

1. Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* 2008, **20**, 3993.

2. Z.-S. Wang, H. Kawauchi, T. Kashima and H. Arakawa, *Coord. Chem. Rev.*, 2004, **248**, 1381.