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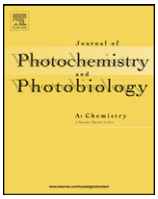

New functional triethoxysilanes as iodide sources for dye-sensitized solar cells

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ABSTRACT

Three new triethoxysilanes bearing quaternary ammonium alkyl iodides are reported, *N*,*N*,*N*-triethyl-3-(triethoxysilyl)propan-1-aminium iodide **1**, *N*,*N*,*N*-triheptyl-3-(triethoxysilyl)propan-1-aminium iodide **2** and *N*,*N*,*N*-tridodecyl-3-(triethoxysilyl)propan-1-aminium iodide **3**. ^{1}H and ^{13}C NMR spectroscopy and electrospray mass spectrometry were used to confirm the synthesis of pure products. Electrolytes based on these ionic liquids were developed and their performance in dye-sensitized solar cells (DSSCs) evaluated. The electrolytes incorporated **1** and **2** (in 30–60 wt%) as iodide sources together with I_2 (0.08 M), 0.1 M guanidinium thiocyanate and 0.5 M *tert*-butylpyridine in acetonitrile (AN); and I_2 (0.15 M) and *N*-methylbenzimidazole (0.5 M) for 2-methoxyproprionitrile (MPN) as co-solvent. Testing of DSSCs to analyze the influence of chain length (ethyl and heptyl) on cell efficiency revealed that, for silanes concentration of 1 M, electrolyte B (based on **2** in AN) and electrolyte C (based on **1** in MPN) gave the best cell efficiency at simulated full sunlight (AM 1.5, 1000 W m^{-2}) illumination (5.0–5.3%). At 0.1 Sunlight (AM 1.5, 100 W m^{-2}), electrolyte B gave the best performance of 8.0%. High open circuit voltages (V_{OC}) of 750–850 mV were achieved for a number of quite efficient cells (5–6%). For silane **2**, variation of the I^-/I_2 ratio and total silane content (1–2 M **2**) on DSSC efficiency gave a consistent efficiency of 8.0% at 0.1 Sunlight. At full sunlight, the cell efficiency decreased as the silane concentration increased from 1 M (5.0%) to 2 M (3.7%), largely due to a drop in short circuit current.

1. Introduction

The growing recognition that the world faces an energy crisis has seen greater emphasis being placed on finding cost-effective, efficient renewable energy sources, with much interest centered around the use of solar energy to generate electrical or chemical energy. The dye-sensitized solar cell (DSSC) represents a promising technology that has attracted significant attention since it was reported in 1991 [1], owing to their relatively high efficiency and low cost of production compared to Si-based photovoltaic devices. One important limitation to their commercialization is the volatility of the electrolyte containing the $I^-/I_3{}^-$ redox couple, which is filled between the nanocrystalline TiO_2 working electrode and the Pt counter electrode [2]. Attempts have been made to increase the stability of the electrolyte by using plastic crystals or room temperature ionic liquids well known for their outstanding ionic conductivity and thermal and chemical stabilities [3–6]. Research is now focused on finding new and versatile materials with low viscosity and high conductivity. Solidification of the electrolyte by addition of polymers, gelators or nanoparticles is now being widely studied as a means of improving the cell stability [7–9]. In an extension of previous approaches, a trimethoxysilane-derivatized ionic liquid has been used as a gel electrolyte in DSSCs, leading to an overall efficiency of 3% [10]. We report here the synthesis and characterization of a new series of ionic liquids consisting of 3-aminopropyltriethoxysilane chemically modified with quaternary ammonium iodides to be used as iodide source in electrolyte systems. These compounds, *N*,*N*,*N*-triethyl-3-(triethoxysilyl)propan-1-aminium iodide **1**, *N*,*N*,*N*-triheptyl-3-(triethoxysilyl)propan-1-aminium iodide **2** and *N*,*N*,*N*-tridodecyl-3-(triethoxysilyl)propan-1-aminium iodide **3**, are of interest as they can easily form a solid network by hydrolysis and condensation reactions or sol–gel process, leading therefore, to a new range of solid-state electrolytes. The performance of such functionalized alkoxysilanes was analyzed in common solvents in an effort to further understand the processes involved in the electron transfer and regeneration of the dye within the cells. The effect

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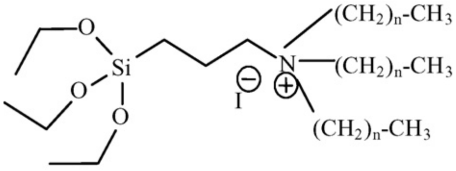
of the length of the alkyl chain attached to the quaternary nitrogen group on the photovoltaic properties was recorded with particularly good overall efficiencies at low light levels that allow high expectation for the silica-based electrolyte systems.



(1) n = 1; (2) n = 6 and (3) n = 11

2. Experimental

2.1. Materials

3-Aminopropyltriethoxysilane (APTS) (>97%), ethyliodide (EI), heptyliodide (HI), dodecyliodide (DI), and guanidinium thiocyanate (GuNCS) were purchased from Aldrich and used without further purification but handled under inert atmosphere (N_2). *N*-Methylbenzimidazole (NMB) was purchased from Aldrich and recrystallized before use. Potassium carbonate was obtained from ABCR. 3-Methoxypropionitrile (MPN) and 4-*tert*-butylpyridine (TBP) from Fluka were distilled before use. Acetonitrile, *tert*-butanol, chloroform and dichloromethane (DCM) were of analytical grade and used as received but handled under a nitrogen atmosphere. The amphiphilic Z-907Na dye [*cis*-Ru(HNadcbpy)(dnbpy)$(NCS)_2$, where the ligands H_2dcbpy and dnbpy correspond to 4,4′-dicarboxylic acid-2,2′-bipyridine and 4,4′-dinonyl-2,2′-bipyridine, respectively] was synthesized as described in the literature [11a].

2.2. Characterization techniques

^{1}H and ^{13}C NMR spectra were recorded on an Advance DRX-400 MHz or 300 MHz Brüker spectrometer at $T = 298$ K. The samples were analyzed in deuterated chloroform ($CDCl_3$) and the chemical shifts δ reported in ppm (parts per million) in reference to tetramethylsilane (TMS) used as an internal standard. The abbreviations for the peak multiplicities are as follows: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Positive and negative ion electrospray mass spectra were measured on samples dissolved in $CHCl_3$ using a Micromass Platform mass spectrometer fitted with an electrospray source.

2.3. Synthesis of *N,N,N*-triethyl-3-(triethoxysilyl)propan-1-aminium iodide **1**, *N,N,N*-triheptyl-3-(triethoxysilyl)propan-1-aminium iodide **2** and *N,N,N*-tridodecyl-3-(triethoxysilyl)propan-1-aminium iodide **3**

3-Aminopropyltriethoxysilane (17 mmol, 4.0 mL) was chosen as a starting material in the synthetic route to **1**–**3** as described in Scheme 1. The reaction of the secondary amine of APTS with ethyl (55 mmol, 4.4 mL), heptyl (55 mmol, 9.0 mL) or dodecyliodide (57 mmol, 14.0 mL) was carried out at reflux (for 48 h) under nitrogen atmosphere in acetonitrile (170.0 mL) in the presence of potassium carbonate (72 mmol, 10 g). The base neutralized the protons liberated during the nucleophilic coupling. Aliquots of dichloromethane were added to the reaction mixture, which was then filtered under a nitrogen stream to remove solid K_2CO_3. The desired alkylammonium triethoxysilane iodides were obtained after evaporation of DCM and acetonitrile under vacuum for 48 h at 50 °C, leading to a waxy white compound for **1**, a dark and viscous yellow oil for **2** and an orange and viscous oil for **3** in good yields (>88%).

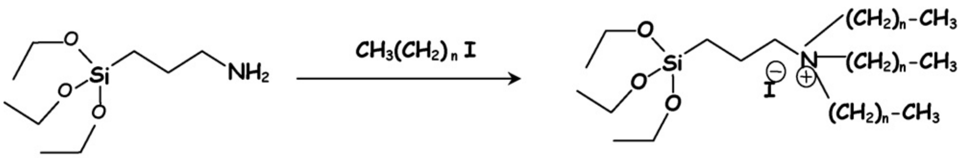
Characterization data—Compound **1**: $C_{15}H_{36}NISiO_3$. Yield: 91% (16 mmol, 6.8 g). ^{1}H NMR spectrum ($CDCl_3$), δ(ppm): 0.6 (t, 2H, Si–CH_2), 1.1 (t, 9H, O–CH_2–CH_3), 1.3 (t, 9H, N–CH_2–CH_3), 1.8 (m, 2H, CH_2–CH_2–CH_2), 3.2 (t, 2H, CH_2–CH_2–N), 3.4 (q, 6H, N–CH_2–CH_3), 3.7 (q, 6H, O–CH_2–CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ(ppm): 7.1 (Si–CH_2), 8.2 (N–CH_2–CH_3), 16.3 (CH_2–CH_2–CH_2), 18.4 (O–CH_2–CH_3), 47.1 (CH_2–CH_2–N), 54.1 (N–CH_2–CH_3), 58.8 (O–CH_2–CH_3). Electrospray mass spectrum (m/z) (positive ion): 306.4/307.4/308.4 $[M]^+$ (100%). Electrospray mass spectrum (m/z) (negative ion): 126.8 $[I]^-$ (100%).

Compound **2**: $C_{30}H_{66}NISiO_3$. Yield: 89% (15 mmol, 9.8 g). ^{1}H NMR spectrum ($CDCl_3$), δ(ppm): 0.7 (t, 2H, Si–CH_2), 0.8 (t, 9H, N–$(CH_2)_6$–CH_3), 1.16 (t, 9H, O–CH_2–CH_3), 1.22 (s, 18H, N–$(CH_2)_2$–$(CH_2)_3$–CH_2–CH_3), 1.3 (s, 2H, N–$(CH_2)_5$–CH_2–CH_3), 1.6–1.7 (m, 8H, CH_2–CH_2–N–CH_2–CH_2–$(CH_2)_4$–CH_3), 3.3 (m, 8H, CH_2–N–CH_2–$(CH_2)_5$–CH_3), 3.8 (q, 6H, O–CH_2–CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ(ppm): 7.0 (Si–CH_2), 13.9 (N–$(CH_2)_6$–CH_3), 16.5 (CH_2–CH_2–CH_2), 18.3 (O–CH_2–CH_3), 22.4 (N–CH_2–CH_2–$(CH_2)_4$–CH_3), 26.3 (N–$(CH_2)_4$–$(CH_2)_2$–CH_3), 28.7 (N–$(CH_2)_2$–CH_2–$(CH_2)_3$–CH_3), 31.5 (N–$(CH_2)_3$–CH_2–$(CH_2)_2$–CH_3), 58.7 (O–CH_2–CH_3), 59.5 (N–CH_2–$(CH_2)_5$–CH_3), 61 (CH_2–CH_2–N).

Compound **3**: $C_{45}H_{96}NISiO_3$. Yield: 98% (17 mmol, 14.4 g). ^{1}H NMR spectrum ($CDCl_3$), δ(ppm): 0.7 (t, 2H, Si–CH_2), 0.9 (t, 9H, N–$(CH_2)_{11}$–CH_3), 1.2 (t, 9H, O–CH_2–CH_3), 1.3 (m, 12H, N–CH_2–CH_2–$(CH_2)_3$–$(CH_2)_6$–CH_3), 1.4 (m, 6H, N–CH_2–CH_2–$(CH_2)_3$–$(CH_2)_6$–CH_3), 1.7 (m, 2H, CH_2–CH_2–CH_2), 1.8 (m, 2H, N–CH_2–CH_2–$(CH_2)_3$–$(CH_2)_6$–CH_3), 3.3 (m, 4H, CH_2–N–CH_2–$(CH_2)_{10}$–CH_3), 3.8 (q, 6H, O–CH_2–CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ(ppm): 7.2 (Si–CH_2), 14.1 (N–$(CH_2)_{11}$–CH_3), 18.3 (O–CH_2–CH_3), 22.2 (CH_2–CH_2–CH_2), 22.6 (N–$(CH_2)_{10}$–CH_2–CH_3), 26.0–30 (N–$(CH_2)_2$–$(CH_2)_7$–$(CH_2)_2$–CH_3), 31.9 (N–$(CH_2)_9$–CH_2–CH_2–CH_3), 33.6 (N–CH_2–CH_2–$(CH_2)_9$–CH_3), 58.7 (O–CH_2–CH_3), 59.8 (CH_2–N–CH_2–$(CH_2)_{10}$–CH_3). Electrospray mass spectrum (m/z) (positive ion): 726.7/727.7/728.7 $[M]^+$ (100%). Electrospray mass spectrum (m/z) (negative ion): 126.7 $[I]^-$ (100%).

2.4. Preparation of ionic liquid electrolytes

Electrolyte A was prepared by dissolving 43.3 mg of **1** (1 M), 2.0 mg of I_2 (0.08 M), 1.2 mg of guanidinium thiocyanate (0.1 M) and 6.8 mg of 4-*t*-butylpyridine (0.5 M) in 0.1 mL of acetonitrile to



(1) n = 1; (2) n = 6 and (3) n = 11

Scheme 1. Synthetic route to *N,N,N*-triethyl-3-(triethoxysilyl)alkyl-1-aminium iodides **1**–**3**.

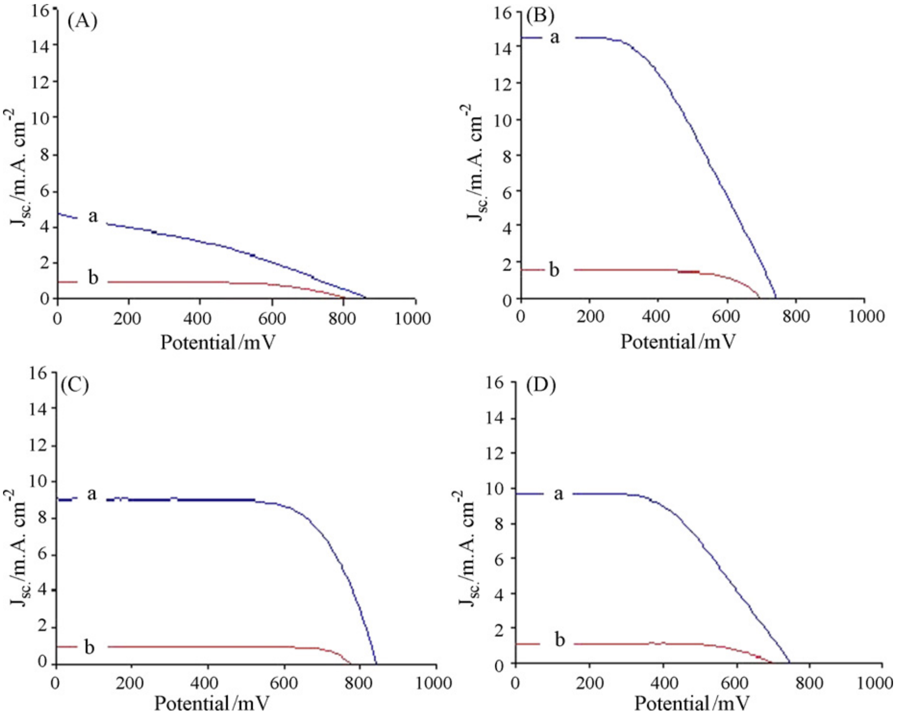


Fig. 1. Photovoltaic *I–V* curves of cells containing electrolytes A–D under an illumination of (a) AM 1.5 full sunlight (1000 W/m^2) and (b) 0.1 Sunlight (100 W/m^2). (The active area of the devices with a mask is 0.158 cm^2.)

give an electrolyte solution with the concentrations indicated in brackets. Electrolyte B consisted of 64.4 mg of **2** (1 M), 2.0 mg of I_2 (0.08 M), 1.2 mg of guanidinium thiocyanate (0.1 M) and 6.8 mg of 4-*t*-butylpyridine (0.5 M) in 0.1 mL of acetonitrile. For electrolytes A and B, the loading of silane was 33 weight percent (wt%) of **1** and 42 wt% of **2**, respectively. The MPN-based electrolytes, C and D, were prepared by mixing 43.3 mg of **1** and 64.4 mg of **2** (1 M), respectively with 3.8 mg of iodine (0.15 M), 6.6 mg of *N*-methylbenzimidazole (0.5 M) and 0.1 mL of MPN (93.8 mg). The silane loading in electrolytes C and D was 29 wt% and 38 wt%, respectively. Two further acetonitrile-based electrolytes were prepared, which contained an increased loading of silane. Electrolyte E consisted of 96.6 mg of **2** (1.5 M), 2.0 mg of I_2 (0.08 M), 1.2 mg of guanidinium thiocyanate (0.1 M) and 6.8 mg of 4-*t*-butylpyridine (0.5 M) in 0.1 mL of acetonitrile, while for electrolyte F, 129 mg of silane **2** (2 M) were used. The viscosity of the AN-based electrolytes was much lower in comparison to those based on 3-methoxypropionitrile.

2.5. Solar cell construction

The preparation of double layer structured mesoscopic TiO_2 films, the fabrication of devices and measurement of cell efficiency were carried out as reported earlier [12–14]. The working electrodes (film thickness of 12–14 μm) were sintered in air at 500 °C for 20 min and cooled down to ca 80 °C before dye adsorption was done by immersing these electrodes in a 3×10^{-4} M solution of Z-907Na in acetonitrile:*tert*-butyl alcohol (1:1, v/v) at room temperature overnight. A standard procedure, using a 0.05 M hexachloroplatinic acid solution, was applied in the preparation of the counter electrodes, which were heated at 400 °C for 10 min prior to device assembly. The devices were then filled with the electrolyte solution containing the alkoxysilanes as the iodide source via vacuum backfilling and sealed up using a 35 μm-thick hot-melt ring Bynel (DuPont, USA) and a thin glass cover.

2.6. Photocurrent–voltage measurements

The current–voltage curves were obtained by measuring the photocurrent of the cells using a Keithley model 2400 digital source meter (Keithley, USA) under an applied external potential. The irradiation source for the photocurrent–voltage (*I–V*) measurement was a 450 W xenon light source (Osram XBO 450, USA), which simulates the solar light. The incident light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the cell under test (illuminated area of 0.158 cm^2). Light intensity was varied from 100 mW cm^{-2}, the equivalent of 1 Sunlight at AM 1.5, to 0.1 Sunlight with neutral wire mesh attenuators in front of the light source. The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent (J_{SC}), the open-circuit photovoltage (V_{OC}), the fill factor of the cell (ff) and the intensity of the incident light [13].

3. Results and discussion

3.1. Synthesis of alkylammonium silane ionic liquids

The new ionic liquids consisting of alkoxysilanes bearing trialkylammonium iodide moieties were synthesized following the procedure described in Section 2 and illustrated in Scheme 1. Commercially available 3-aminopropyltriethoxysilane has been chosen as a precursor of choice as it has been applied in surface modification of inorganic materials and hybrid membranes preparation, using sol–gel chemistry [15,16]. The quaternarization reaction of the $-NH_2$ functionality was conducted in acetonitrile under an inert atmosphere by reaction with three alkyliodides, viz., ethyliodide,

Table 1

Comparison of the photovoltaic performance of solar cells containing electrolytes A–D, measured at AM 1.5 full sunlight (1000 W/m^2) and 0.1 Sunlight (100 W/m^2) irradiations (the active area of the devices with a mask is 0.158 cm^2)[a]

	Electrolyte							
	A: **1** in AN		B: **2** in AN		C: **1** in MPN		D: **2** in MPN	
	Sun 0.1	Sun 1	Sun 0.1	Sun 1	Sun 0.1	Sun 1	Sun 0.1	Sun 1
J_{SC} (mA cm^{-2})	1.04	4.9	1.53	14.5	0.95	9.1	1.12	9.5
V_{OC} (mV)	814	870	695	740	774	844	721	775
ff	0.64	0.33	0.72	0.47	0.80	0.70	0.69	0.52
η (%)	5.7	1.4	8.0	5.0	6.2	5.3	5.9	3.9

[a] Electrolytes A and B are based on 1 M **1** and **2**, respectively, 0.08 M I_2, 0.1 M GuNCS and 0.5 M TBP in AN, while electrolytes C and D are composed of 1 M **1** and **2**, respectively, 0.15 M I_2 and 0.5 M NMB in MPN.

heptyliodide and dodecyliodide. The products were obtained in very high yields (89–98%).

The ^{1}H and ^{13}C NMR spectra of the starting materials (APTS and the corresponding alkyliodides) were used as reference in the assignment of signals of **1**–**3**. New signals below 3.5 ppm were representative of the presence of alkyl chains on the terminal N, and the integration for each signal confirmed the full conversion of the amino group to alkylammonium derivative (see Section 2). The ^{13}C and ^{1}H NMR spectra indicated no change in the $Si(O–CH_2–CH_3)_3$ moieties during synthesis. ESI mass spectrometry, conducted in the negative ion mode confirmed the presence of the iodide ion, while major signals corresponding to the cations and exhibiting the expected isotope distribution for molecules containing Si were observed in the positive ion mode spectrum.

3.2. Electrolyte preparation

The new ionic liquid alkoxysilanes were used to prepare a series of electrolytes, which consisted of the alkoxysilane mixed with iodine to convert some iodide to triiodide, an important component of the redox couple, and different additives, which have been found to improve DSSC performance. Compound **3** was found to be insoluble or immiscible in the solvent typically used in DSSCs. Our solar cell testing was therefore conducted on compounds **1** and **2**. Four electrolytes containing 1 M concentration of either **1** and **2** in acetonitrile (electrolytes A and B) or **1** and **2** in MPN (electrolytes C and D) were prepared and tested in DSSCs. Two further electrolytes E and F were also developed containing the components of B and **2** in the higher concentrations of 1.5 M and 2 M, respectively.

3.3. Silane and solvent dependence of DSCC performance

The *I*–*V* characteristics for DSSCs constructed with electrolytes A–D, measured at two light intensities, are summarized in Fig. 1 and Table 1. Significant variations in performance are evident. The open circuit potential (V_{OC}) for cells incorporating electrolytes A and C, based on silane **1**, are higher than those constructed with electrolytes B and D, based on silane **2**. The difference is higher at 1 Sunlight (>100 mV) but is still substantial at 0.1 Sunlight (50–100 mV). This indicates that the silanes have the potential to slightly increase the band gap energy of the semiconductor or to slightly reduce the potential of the I^-/I_3^- redox couple. Comparison of the two acetonitrile based electrolytes A and B shows that electrolyte B gives an excellent performance at 0.1 Sunlight, viz. a high current, and fill factor gives rise to an overall efficiency of 8.0% and a respectable performance of 5.0% at 1 Sunlight. The drop in performance for B, while increasing the light intensity to 1 Sunlight, is due exclusively to a drop in fill factor from 0.72 (0.1 Sunlight) to 0.47 (1 Sunlight), which compensates for an almost constant current and a 50 mV increase in V_{OC}. For electrolyte A, the performance at 1 Sunlight is much lower (η of only 1.4%) due to an even lower ff value of 0.33 and a significant lower current of 4.9 mA cm^{-2}.

Devices with electrolyte C (MPN) exhibited a slightly better performance at 0.1 Sunlight than those with electrolyte A (AN), largely due to a better ff (0.80 for C vs. 0.64 for A). The difference in performance is much greater at 1 Sunlight, where the efficiency drops to 1.4% for electrolyte A but only decreases slightly to 5.3% for electrolyte C, due to compensating effects of an increase in V_{OC} coupled with a decrease in ff and a slight decrease in J_{SC}. Electrolyte C offers much better prospect for higher light intensity applications than electrolyte A. A comparison of devices with electrolytes B and D, which are based on silane **2**, reveals poorer overall performance for the latter largely due to the lower short circuit currents, measured at both 0.1 and 1 Sunlight, which more than compensate for the increases in V_{OC}. Lower current appears to be a feature of the MPN based electrolytes, which may be related to the rate of charge transport through the more viscous electrolyte. Devices with electrolytes C and D show a similar performance at 0.1 Sunlight, those with electrolyte C being slightly more efficient. While both electrolytes lead to lower efficiencies at 1 Sunlight, the drop in performance is much greater for electrolyte D, largely due to a much poorer fill factor. Overall, the cells show good performance at 0.1 Sunlight (5.7–8%) but poorer performance at 1 Sunlight (1.4–5.3%). In general, significant drops in fill factor, observed in going from 0.1 to 1 Sunlight irradiation, contributed to the poor performances of the cells under 1 Sunlight illumination. This may be explained in terms of a mass transport problem encountered at the counter electrode [17]. Devices with electrolyte C showed the smallest drop in ff of the four electrolytes tested and produced cells with the highest efficiency at full sunlight. The *I*–*V* curve obtained with electrolyte A reveals the photocurrent was limited by mass transfer and/or space

Table 2

Comparison of the photovoltaic performance of DSSCs containing electrolytes B, E and F, measured at AM 1.5 full sunlight (1000 W/m^2) and 0.1 Sunlight (100 W/m^2) irradiations[a]

Electrolyte	Silane **2** loading (wt%)	J_{SC} (mA cm^{-2})		V_{OC} (mV)		ff		η (%)	
		0.1 Sun	1 Sun	0.1 Sun	1 Sun	0.1 Sun	1 Sun	0.1 Sun	1 Sun
B	42	1.53	14.5	695	740	0.72	0.47	8.0	5.0
E	52	1.45	13.5	719	769	0.74	0.42	8.1	4.4
F	59	1.48	10.0	713	765	0.73	0.48	8.1	3.7

[a] Electrolytes B, E and F are based on **2** at 1 M, 1.5 M and 2 M, respectively, 0.08 M I_2, 0.1 M GuNCS and 0.5 M TBP in AN.

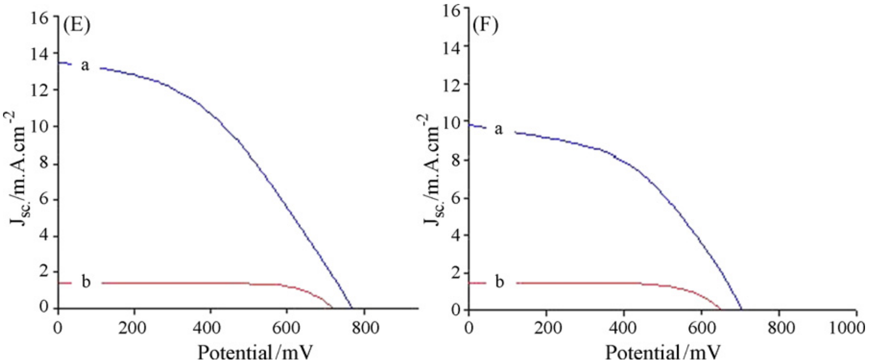


Fig. 2. Photovoltaic *I–V* curves of cells containing electrolytes E and F (1.5 M and 2 M in AN, respectively, 0.08 M I_2, 0.1 M GuNCS and 0.5 M TBP) under an illumination of (a) 1 Sunlight and (b) 0.1 Sunlight.

charge effects, in addition to a possible photo-current reduction by photo-induced shunt at full sunlight. The presence of these features in a low viscosity, high dielectric constant solvent like acetonitrile is unusual and needs to be further investigated.

For the devices with AN-based electrolytes, the decrease of efficiency for the cells containing **1** (A) compared with those containing **2** (B) may be due to the different length of the alkyl chain of the quaternary ammonium functionality. The presence of heptyl chains in **2** could create a specific pathway induced by hydrophobic interactions in favor of the I^-/I_3^- species transportation, which would not be as noticeable for shorter ethyl groups in **1**. This could lead to a higher conductivity. In the case of MPN solvent, electrolytes C and D result in similar performance at 0.1 Sunlight, but the drop in performance at 1 Sunlight is not significantly lower, largely due to smaller decrease in the fill factor. This could be due to a charge diffusion limitation in MPN as the viscosity of the corresponding electrolyte is becoming more important with the light intensity increase.

An efficiency of 7.6% at 0.1 Sunlight has been reported for a device filled with an organic solvent-based electrolyte containing an ionic liquid 1-methyl-3-propylimidazolium iodide (MPII) as iodide source and MPN as solvent, comparable to the present results [11b]. High photovoltage values without a big loss of photocurrent were obtained even at low light intensity, which is of great interest for indoor applications but also promising for quasi solid-state or solid-state electrolyte preparation.

3.4. Silane concentration dependence of DSCC performance

In order to investigate whether the efficiency of DSSCs was affected by the concentration of silane ionic liquid, two further electrolytes E and F were prepared for which the concentrations of **2** in AN were 1.5 M and 2 M, respectively, while keeping the I_2, GuNCS and TBP concentrations constant. The increase in silane concentration changes the ratio of I^- to I_2 and, consequently, allows us to probe whether this was important in achieving high efficiency. It also significantly changes the wt% loading of silane, from 42% at 1 M to 59% at 2 M, which results in a more viscous electrolyte. The photovoltaic performance of the corresponding cells is reported in Table 2.

Increasing the concentration of **2** in acetonitrile to 1.5 M and 2 M in electrolytes E and F, respectively, results in a constant overall efficiency of 8.0% at 0.1 Sunlight. The minor changes in photocurrent and open circuit voltage are self-compensatory and the fill factors constant. This result is impressive when it is considered that the loading of silane ionic liquid increases dramatically in going from electrolyte B to F and that acetonitrile is becoming an increasingly minor component. At 1 Sunlight, in contrast to the results obtained at 0.1 Sunlight, the efficiency of the cells was found to decrease significantly and systematically as the ionic liquid silane concentration increased. For all the three electrolytes, higher V_{OC} values were observed for testing at 1 Sunlight (50 mV higher relative to 0.1 Sunlight) and the fill factors were quite constant. The major difference in performance is the systematic decrease in J_{SC} to 10.0 mA cm^{-2} for the electrolyte containing **2** at 2 M. The highest photocurrents and lowest V_{OC} were recorded for the solution B consisting of 1 M **2**. It should be noted that reliable ff values could only be obtained when the cells are illuminated at 10% light intensity, as depicted by the shapes of the *I–V* curves of the corresponding cells in Fig. 2. The *I–V* curves show normal behavior at 10% Sun and all the photovoltaic performance parameters show good values. The overall conversion efficiency obtained (close to 8%) is impressive for the Z907 sensitizer employed. However, at full sun the *I–V* curves show lower fill factors, non-linear current response to light intensity and a V_{OC} increment <60 mV for a 10-fold increase in light intensity. These effects are attributed to the high viscosity of the electrolytes, adding to the mass transfer limitations of the photocurrent. In addition the cell appears to be shunted at the higher light levels leading to loss of V_{OC} and the observed slope in the *I–V* curve. As the concentration of I_2 remains constant in the electrolyte systems E and F, a decrease of the number of I_3^- species is expected since the concentration of the I^- counter ion in the alkylammonium silane increases. This phenomenon could explain the observation that no significant changes occurred at higher alkoxysilane concentration, the I^- anion probably strengthening ion-pairing in the system and therefore decreasing charge screening and ionic diffusion. It would be interesting to increase the concentration of iodine in these electrolytes to maintain the I^-/I_2 ratio constant and observe the changes in performance.

4. Conclusion

Three new alkoxysilanes were synthesized and characterized, which contain appended quaternary ammonium iodide salts bearing ethyl, heptyl and dodecyl chains. Two of these silanes are liquids at room temperature and therefore can be classified as ionic liquids while the third is a waxy solid. These new ionic liquid silanes have been applied as iodide sources in DSSC electrolytes and efficiencies of up to 8.0% achieved at 0.1 Sunlight (100 W/m^2) intensity, which is promising from the point of view of low light or indoor application. The performance of the cells was reduced at higher light intensity (1 Sunlight) but efficiencies ≥5.0% were achieved for some electrolytes. The MPN-based electrolytes performed well at 1 Sunlight intensity, exhibiting smaller decreases in performance than the AN-based electrolytes, but did show lower overall short circuit currents.

The best photovoltaic performances were recorded for the electrolytes based on *N*,*N*,*N*-triheptyl-3-(triethoxysilyl)propan-1-aminium iodide **2** in acetonitrile. An efficiency of over 8.0% was achieved at 0.1 Sunlight for electrolytes containing 1–2 M concentration of this silane, which reduced to 3.7–5.0% at 1 Sunlight irradiation. The long hydrophobic heptyl chains may create specific pathways for ion transport in the devices and the size of the cation could reduce ion pairing, enabling a faster ion transfer rate. Thus, these alkylammonium functionalized alkoxysilanes can be used as iodide sources in DSSCs at low light intensity. An initial study of their performance as electrolytes following grafting on silica nanoparticles highlights their potential as quasi-solid-state electrolytes [18].

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