

Molten and Solid Trialkylsulfonium Iodides and Their Polyiodides as Electrolytes in Dye-Sensitized Nanocrystalline Solar Cells

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Potential new electrolytes for dye-sensitized nanocrystalline solar cells (DNSCs) of Grätzel type based on trialkylsulfonium iodides have been investigated. Room temperature molten salts of (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I, with iodine in low concentrations, revealed good conducting abilities. DNSCs using iodine-doped (Bu₂MeS)I as electrolyte achieved an overall light-to-electricity conversion efficiency of 3.7% in simulated AM 1.5 solar light at a light intensity of 0.1 Sun. The effects from varying the temperature during the I/V measurements were studied, as well as the effects of 4-*tert*-butylpyridine treatment of the electrodes.

Introduction

In photovoltaic systems, light energy is converted to electricity, and common applications today are for satellites, light-houses, and primary batteries. Because of the gigantic supply of energy from the sun, covering 0.1% of the Earth's surface with solar cells (with an efficiency of approximately 10%) would satisfy our present global needs.¹

Enormous research activity is dedicated to finding cost-effective solar cells. Photoelectrochemical (PEC) solar cells have been studied since the 1960s. In 1991, Grätzel and co-workers presented a PEC with a highly porous, nanocrystalline TiO₂ electrode sensitized with a ruthenium complex, by which high power conversion efficiencies were achieved.²

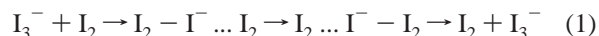
In dye-sensitized nanocrystalline photoelectrochemical solar cells (DNSCs), the function of light absorption is separated from the charge-carrier transport.³ The active electrode film consists of a monolayer of dye molecules, adsorbed on a nanostructured semiconductor film with a highly porous structure. The working electrode is connected to a counter electrode via an external circuit. Between the electrodes an electrolyte penetrates the pores in the nanostructured film and handles charge transport and dye regeneration in this type of solar cell. The advantages of nanocrystalline semiconductor films, as compared to single-crystal and polycrystalline films, are related to the large surface area and the high porosity, resulting in good electrical and optical properties.²

A redox couple, most commonly iodide/triiodide, in the electrolyte is the charge carrier between the electrodes. The I[−]/I₃[−] system is favorable due to its stability and reversibility, low visible light absorption, high diffusion constants, ability to provide fast regeneration of the oxidized dye, and very low dark current.^{4,5} Recently, some cobalt complexes of substituted polypyridine ligands were presented as possible alternative mediators to the I[−]/I₃[−] redox couple.⁶ An ideal regenerative PEC solar cell does not change the composition of the electrolyte during illumination.⁷ At any rate, the use of liquid electrolytes

containing conventional organic solvents may be sensitive to stability effects due to evaporation and reactions with water and/or oxygen. Alternative electrolytes of solid conducting materials have been studied, such as polymer electrolytes (conducting ions), and inorganic and also amorphous materials (conducting holes).^{8–10}

Room temperature molten salts have some qualities that would make them suitable as electrolytes, such as high conductivity, ionic mobility, and negligible volatility. Dialkyl-imidazolium salts are stable and good electrical conductors. Ionic liquids based on 1,3-dialkylimidazolium cations and hydrophobic anions (RR'Im⁺X[−]) have shown to be promising solvents for electrochemical and photovoltaic applications in studies performed by Grätzel and co-workers.¹¹ They used mixtures of hexyl-methyl-imidazolium iodide (HMImI) and organic solvents or ionic liquids such as butyl-methyl-imidazolium triflate as electrolytes in DNSCs.¹² Quasi-solid-state electrolytes of HMImI and iodine with addition of low-molecular-weight gelators have been investigated by Kubo and co-workers.^{13,14} Solid-state amorphous organic hole-transport materials have been successfully tested as mediators by Grätzel and co-workers.¹⁵ Modifications of these compounds have provided improved results in solar cell measurements.^{16–18}

Trialkylsulfonium polyiodides have been found to exhibit good electrical conductivity, 10^{−3} to 10^{−4} S/cm, which increases with larger contents of iodine.¹⁹ This is explained by a mechanism of electrical conduction in polyiodide chains via a Grotthuss mechanism, a relay mechanism, in which a net transport of charge is achieved without any net transport of mass. The effect is favored by a reduced distance between donors and acceptors.^{19–20}



To investigate and develop new electrolyte materials for the DNSCs, we have synthesized and studied trialkylsulfonium iodides, differing in chain-length of the alkyl groups. Cations with long-chained alkyl groups are more likely to form room temperature molten salts than their short-lengthened congeners because of less favorable packing in a crystalline lattice. In this work, the overall solar-to-electric energy conversion efficiencies

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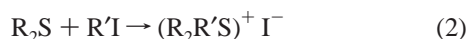
TABLE 1: Synthesized Trialkylsulfonium Iodides, (R₂R'S)I and Their Melting Points

| | Me ₂ S | Et ₂ S | Pr ₂ S | Bu ₂ S | DodMeS |
|--------|----------------------|----------------------|-----------------------|----------------------|---------------------|
| MeI | white solid (187 °C) | yellow liquid | white solid (96 °C) | orange liquid | white solid (68 °C) |
| EtI | white solid (30 °C) | white solid (120 °C) | yellow solid (112 °C) | yellow liquid | white solid (46 °C) |
| 1-PrI | white solid (172 °C) | white solid (133 °C) | white solid (70 °C) | white solid (80 °C) | |
| 1-BuI | white solid (160 °C) | yellow liquid | white solid (85 °C) | yellow solid (77 °C) | |
| 1-PeI | white solid (87 °C) | yellow liquid | | yellow liquid | |
| 1-HxI | white solid (162 °C) | | | | |
| 1-DodI | white solid (68 °C) | | | | |

in solar simulators, and also the incident monochromatic photon-to-current-efficiencies (IPCE), have been measured for a selection of molten salt electrolytes to reveal their possible use as electrolytes in DNSCs.

Experimental Section

Synthesis. Trialkylsulfonium iodides, (R₂R'S)I, were synthesized from dialkylsulfides (Me₂S, Et₂S, Pr₂S, Bu₂S, DodMeS) and alkyl iodides (MeI, EtI, 1-PrI, 1-BuI, 1-PeI, 1-HxI, 1-DodI). This involves a nucleophilic attack by the sulfide on the alkyl iodide in a reaction such as:



About 5 or 10 g of the alkylsulfide was dissolved in 10–20 mL of acetone (dried) in a round bottle covered with aluminum foil, since some of the reactants are light-sensitive. An equimolar amount of the corresponding alkyl iodide was added. The reaction atmosphere was protected from oxygen and water by a continuous flow of dry nitrogen gas. The reaction mixture was left for several days at ambient conditions. Addition of diethyl ether resulted in two different kinds of product phases: crystalline solid precipitates or liquid, molten products with higher viscosity and density than the acetone/diethyl ether solvent. The products were separated from the solvent followed by thorough washing and recrystallizations in acetone and diethyl ether. The final products were dried, and possible remaining traces of solvent were slowly evaporated under dynamic vacuum. The syntheses of the (R₂R'S)I salts were performed at room temperature. Higher reaction temperatures were also tested, resulting in decreased yields of the products. Most of the 22 compounds synthesized, all presented in Table 1, are white solids at room temperature. Some products from syntheses with Et₂S and Bu₂S are yellow, viscous liquids (molten salts). All pure products were stored in a freezer to ensure that pure and noncontaminated electrolytes are studied.

By addition of iodine to the (R₂R'S)I salts the viscosities were decreased and the colors turned to different shades of purple-red. Polyiodides were prepared from the trialkylsulfonium iodides, without any additional solvents, by addition of iodine in the following iodide-to-iodine ratios (100:1), (50:1), (10:1), and (1:1). The reactants were heated to the melting point of the appropriate trialkylsulfonium iodide. After slow cooling the polyiodides obtained were stored in a freezer to ensure purity.

Structural Characterization and Physical Properties. The melting points of the (R₂R'S)I salts synthesized were determined to confirm the degree of purity and also to verify the absence of contaminants such as reactants. The (R₂R'S)I salts were structurally characterized by Raman and nuclear magnetic resonance (NMR) spectroscopy. For Raman spectroscopy, two kinds of equipments were used: Raman Bio Rad FTS 6000 equipped with an Nd:YAG laser (1064 nm), quartz beam splitter and a liquid nitrogen Ge-detector, as well as a Renishaw Ramascope with a diode laser (780 nm) and CCD detector (the

TABLE 2: Results from the Elemental Analyses

| | (Me ₂ DodS)I | | | (Et ₂ MeS)I | | | (Bu ₂ MeS)I | | |
|-------------------|-------------------------|-----|-----|------------------------|-----|------|------------------------|-----|------|
| | C | H | S | C | H | S | C | H | S |
| theor result (%): | 46.9 | 8.7 | 8.9 | 25.9 | 5.6 | 13.8 | 37.5 | 7.3 | 11.1 |
| exp result (%): | 46.7 | 8.7 | 9.0 | 25.0 | 5.7 | 13.2 | 36.5 | 7.3 | 10.9 |

Ramascope was only used for solid crystals). Addition of iodine resulted in two new peaks in the Raman spectra, 113 and 152 cm⁻¹, which indicate the presence of polyiodide ions.^{19–20} ¹H and ¹³C NMR spectroscopy was routinely used to check the purity of the products. All NMR spectra were recorded on a Bruker DMX 500 MHz spectrometer. Elemental analyses (C, H, S) were performed for three selected products: (Bu₂MeS)I, (Et₂MeS)I, and (Me₂DodS)I. The experimental results correspond very well to the theoretical values, see Table 2.

Conductivity measurements were performed at room temperature in the frequency interval 1–10 000 Hz using a EG&G PAR model 263 A potentiostat/galvanostat with impedance capability and a conductivity cell with platinum electrodes. The inner area of the cell was 2.75 × 5.9 mm² with an electrode distance of 2 mm, which gave a cell constant of 1.23 cm⁻¹. The electric conductivities of the molten salts (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I were determined before and after the addition of iodine. For the solid salt (Pr₂MeS)I measurements were feasible only after iodine addition. The results are given in the Supporting Information, Table S1.

Current vs. Potential Characteristics. The photoelectric conversion efficiency was experimentally obtained by measuring the current–voltage characteristics of the solar cells at room temperature. I/V diagrams were monitored and recorded using a computerized Keithley model 2400 source measure unit. Two different kinds of solar simulators were employed. A microwave-powered sulfur plasma lamp, Light Drive 1000 provided an AM 1.5 spectrum with a light intensity of 100–1000 W/m² (0.1–1 Sun). To investigate the possibility of applications for indoor power supplies, the solar cells were also illuminated by fluorescent light including UV wavelengths (170–200 Lux).

Two-electrode measurements were performed in air using an open sandwich-type solar cell, which had not been sealed, with a working electrode of dye-sensitized TiO₂ and a counter electrode of platinized conducting glass. The active electrode area was typically about 0.8–1 cm². The electrodes were prepared following almost the same procedure first presented by Nazeeruddin and co-workers in 1993.^{21–23} The nanostructured, porous film covering the working electrode was prepared from a colloidal dispersion of TiO₂ powder (Degussa P25 from Solaronix S.A., Switzerland) deposited on a transparent, conducting glass sheet (fluorine-doped SnO₂). Treatment with a newly developed press technique followed, not demanding any thermal supply.^{23,24} Dye-sensitized electrodes were provided by immersing the TiO₂ electrodes, heated at 450 °C for 5–10 min and then cooled to about 80 °C, into an 0.5 mM ethanolic dye solution for at least 2 h. The dye used was N719, or Ru(dcbpy)₂-(CNS)₂·2TBA, with the full name cis-bis(isothiocyanato)-bis-(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)-bis-tetrabu-

TABLE 3: Best Results Obtained from I/V Measurements of DNSCs Using Different Light Sources as Solar Simulators

| electrolyte | prop | AM 1.5 (100 W m ⁻²) | | | | fluorescent light (incl. UV) (170–200 Lux) | | | |
|---|-------|---------------------------------|--------|--------------|---------------------------------|--|--------|--------------|---------------------------------------|
| | | η (%) | FF (%) | V_{OC} (V) | J_{SC} (mA cm ⁻²) | η (%) | FF (%) | V_{OC} (V) | J_{SC} (μ A cm ⁻²) |
| (Et ₂ MeS)I | | 2.0 | 58 | 0.57 | 0.6 | 0.5 | 47 | 0.38 | 20 |
| (Et ₂ MeS)I:I ₂ | 100:1 | 2.8 | 60 | 0.49 | 1.0 | 0.1 | 31 | 0.23 | 10 |
| (Bu ₂ MeS)I | | 1.5 | 59 | 0.63 | 0.4 | 1.7 | 44 | 0.48 | 54 ^a |
| (Bu ₂ MeS)I:I ₂ | 100:1 | 3.7 | 62 | 0.60 | 1.0 | 0.6 | 55 | 0.40 | 20 |
| HMIml:I ₂ ^b | 10:1 | 5.0 | 66 | 0.64 | 11.8 | | | | |
| standard results for a liquid electrolyte ^c | | 5–6 | 60–70 | 0.6–0.7 | 1.0 | | 50–60 | 0.45–0.55 | 15 |

^a In irradiation of 176 Lux. ^b HMIml stands for 1-hexyl-3-methylimidazolium iodide. The irradiated area was 0.27 cm² and the results can be found in ref 14. ^c Results obtained from using an electrolyte of 0.5 M LiI, 50 mM I₂ and 0.5 M 4-*tert*-butylpyridine in 3-metoxipropionitrile, at the Dept. of Physical Chemistry, Uppsala University.

tyl- ammonium, provided by Solaronix S.A., Switzerland. 4-*tert*-Butylpyridine was added to the electrodes and a silver conductive paint applied on the part not covered with TiO₂. The counter electrode was composed of conducting glass, thermally platinized and prepared from 5 mM H₂PtCl₆ in dry 2-propanol heated at 380 °C for 10 min.²³ The electrolyte was applied to the solar cell assembly by using glass capillaries and then spread throughout the porous electrode structure. No complicated injection techniques were required, since only open systems were used.

From I/V diagrams the short-circuit current (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and overall energy conversion efficiency (η) could be determined using the definitions:

$$FF = \frac{(JV)_{MAX}}{J_{SC}V_{OC}} \quad (3)$$

$$\eta = \frac{J_{SC}V_{OC}FF}{I_s} \quad (4)$$

where I_s is the intensity of the incident light (W m⁻²).⁵ The effects of pyridine treatment were studied for some selected electrolytes. To investigate the influences of temperature, a furnace was constructed to which the solar cells were attached. The furnace contained heating elements (power resistors) and a Pt-100 sensor, which were regulated by a PID thermostat. The studies were performed from ambient conditions up to 80 °C, using electrodes not treated with 4-*tert*-butylpyridine.

IPCE Measurements. Photocurrent yields can be analyzed by the expression of the incident monochromatic photon-to-current conversion efficiency (IPCE) based on:²⁵

$$IPCE = \frac{hcJ_{ph}}{e\lambda I_s} = \frac{1240J_{ph}}{\lambda I_s} \quad (5)$$

where J_{ph} is the photocurrent density (Am⁻²), λ is the wavelength of the monochromatic light (nm), and I_s is the light power density (W m⁻²). 1240 is the product of the constants h , c , and e , thus Planck's constant, the speed of light in vacuum, and the elementary charge, respectively. IPCE was measured as a function of illumination wavelength for a two-electrode solar cell using a computer-controlled potentiostat. The light source was a 300 W xenon arc lamp, whose beam passed through an 80 mm water filter (to avoid IR light) into a high-intensity monochromator proceeded by a UV cutoff filter and a focusing quartz lens. The two-electrode cell was illuminated through the substrate (F:SnO₂)/electrode interface (SE), since this has provided higher efficiencies than through the electrolyte/electrode interface (EE).²⁵ The effects from 4-*tert*-butylpyridine treatment were also studied.

Results and Discussion

Current vs Potential Characteristics. The performance of the dye-sensitized solar cells is highly dependent on the structure and the viscosity of the electrolytes used. The conducting abilities of the (R₂R'S)I compounds are also of importance. The room-temperature molten salts (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I showed good conductivities: about 6.8 mS/cm for (Et₂MeS)I and 0.4 mS/cm for (Bu₂MeS)I and (Bu₂EtS)I, respectively (Supporting Information, Table S1). They also provided the best efficiency results obtained from the DNSC measurements, with good short-circuit currents, photovoltages, and fill factors. By using electrolytes of these ionic liquids in DNSCs, overall energy conversion efficiencies of 2.0, 1.5, and 2.1% were achieved for (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I, respectively (Table 3). It should be mentioned that all iodide liquids contain a very small proportion of iodine, which guarantees the presence of the iodide/triiodide redox couple in the electrolytes.

Addition of iodine in small proportions (100:1) made a negligible impact on the conducting abilities. However, further addition resulted in considerably improved conductivities, about 20–40 mS/cm for iodine proportions of (1:3). This could theoretically be explained by enhancing the so-called Grotthuss effect, describing the mechanism of electrical conductivity in polyiodide chains. The charge-carrier transfer mechanism influences the overall transport with increasing iodine concentrations.¹⁹ The connection between higher contents of iodine in the electrolyte and enhanced conducting abilities was found to be highly correlated with high conversion efficiencies in the solar cell measurements.

From the I/V studies an addition of iodine to the salts, in small proportions (100:1), resulted in enhanced conversion efficiencies. For (Bu₂MeS)I, the overall conversion efficiency of the solar cell increased from 1.5% (pure salt) to 3.7% with J_{SC} 1.0 mA/cm², V_{OC} 0.60 V, and FF 62% (see Figure 1). Regarding (Et₂MeS)I an increase from 2.0% (pure salt) to 2.8% with J_{SC} 1.0 mA/cm², V_{OC} 0.49 V, and an FF of 61% was obtained. The improvement from iodine-doping of (Bu₂EtS)I was less noticeable, since the efficiency stabilized just above 2%. The improved efficiencies were related to an increase in the current, whereas the FFs and the photopotentials were almost unchanged. The iodine-containing electrolytes of (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I showed high efficiencies until the proportion (10:1) was exceeded. Higher concentrations, up to equimolar amounts, resulted in decreasing efficiencies. This is in contrast to the conductivity results, which are greatly improved at higher contents of iodine. An explanation could be that iodine lowers the photoresponse at all wavelengths, thus disturbing the light-absorbing ability of the dye-sensitized film. Also, recombination losses of photogenerated electrons to

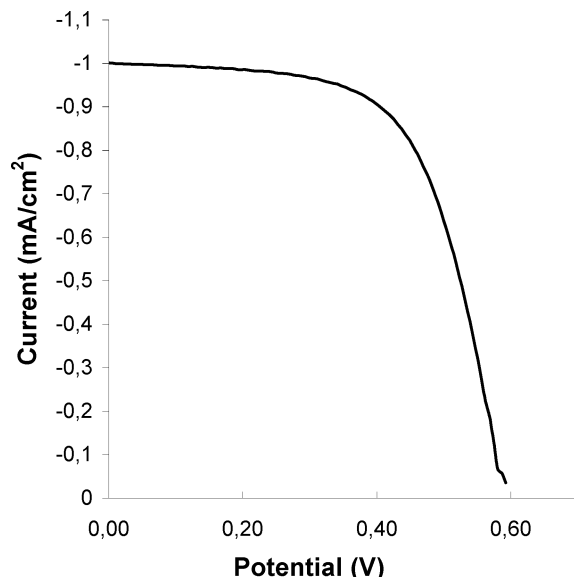


Figure 1. I/V diagram from using iodine-doped (Bu_2MeS)I as electrolyte in DNSCs, providing an efficiency of 3.7% (in irradiation AM 1.5, 100 W m^{-2}).

electron scavengers such as triiodide ions will become more prominent the higher the content of iodine is in the electrolytes.²²

The cell performance of DNSCs with molten salt electrolytes consisting of 1-alkyl-3-methylimidazolium iodides ($\text{C}_1\text{--C}_9$) and 1/10 molarity of iodine has been reported by Kubo and co-workers.¹⁴ The highest overall conversion efficiency, 5%, was obtained by using 1-hexyl-3-methylimidazolium iodide (HMIImI). In Table 3, these results are presented together with the best results recorded for the molten sulfonium iodide salts in this work.

($\text{R}_2\text{R}'\text{S}$)I salts that are solids at room temperature were difficult to apply, which complicated the measurements, thus resulting in poor performance. By addition of iodine the melting points were decreased, but the efficiencies at room temperature were almost unchanged. DNSCs with electrolytes of the solid salt (Me_2EtS)I with iodine added in the proportion (100:1) achieved an overall conversion efficiency of 1.5%. Using iodine-containing electrolytes of (Et_2BuS)I and (Pr_2MeS)I provided overall efficiencies of 0.5–0.8%, and for (Me_2DodS)I, (Bu_2PrS)I, and (DodEtMeS)I about 0.1%. I/V measurements of DNSCs with electrolytes of the rest of the solid salts were unfortunately impossible to obtain under the prevailing conditions, mainly because of too high melting points. More complete data from the I/V measurements can be found in Supporting Information, Table S2.

Using fluorescent light as solar simulator resulted in overall decreased values, regarding efficiencies, J_{SC} , V_{OC} , and FFs, in comparison with the AM 1.5 results; see Table 3. However, this negative effect excluded (Bu_2MeS)I, which also provided the best result with J_{SC} $54 \mu\text{A/cm}^2$, V_{OC} 0.48 V and FF 44% in an illumination of 176 Lux. Electrolytes of (Me_2EtS)I, (Et_2MeS)I, (Pr_2MeS)I, and (Bu_2MeS)I achieved the best results while applied as pure salts, whereas an addition of iodine resulted in decreased current values, which was opposite to the results obtained from the I/V measurements at AM 1.5 and also the conductivity results. The explanation could be related to the absorption spectrum of triiodide ions formed in the iodine-doped electrolytes. From UV/vis spectroscopy investigations it has been reported that the triiodide ion has absorption bands both at 290 and 367 nm.²⁰ In fluorescent light illumination the

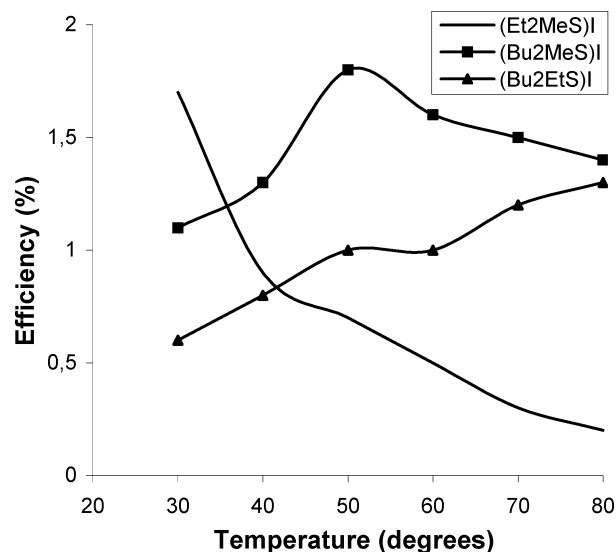


Figure 2. Best conversion efficiency results obtained from temperature-dependent I/V measurements of DNSCs using electrodes not treated with 4-*tert*-butylpyridine (in irradiation AM 1.5, 100 W m^{-2}).

absorption of the dye is therefore inhibited in the presence of polyiodide ions and thus lower overall conversion efficiencies achieved.

Increased Light Intensities. On a regular basis, the photoelectrochemical I/V measurements were performed in AM 1.5 illumination and at a light intensity of 100 W m^{-2} . For comparison, also higher light intensities within the interval of $100\text{--}1000 \text{ W m}^{-2}$ were used; see Supporting Information, Figure S1 and Table S3. The overall conversion efficiency of the solar cells, while using the molten salt electrolytes, decreased with increasing intensities, due to impaired FFs. It should be noted that the decrease was less prominent in comparison with standard electrolytes based on organic solvents. However, the J_{SC} and V_{OC} values were both improved at higher light intensities, but low efficiencies result because of overloading.

Temperature-Dependent Measurements. Since the working temperature of DNSCs is expected to be considerably higher than room temperature, also the performance at higher temperatures was investigated. The effects of temperature variation were studied in DNSCs from ambient conditions up to 80°C using electrodes not treated with 4-*tert*-butylpyridine. The results obtained are presented in Supporting Information, Table S4. The changes noticed regarding the overall efficiency, J_{SC} , V_{OC} , and FF with temperature were just moderate and different trends probably depending on the structures and the viscosities of the electrolytes measured. DNSCs with electrolytes of the liquid, molten salts (Et_2MeS)I, (Bu_2MeS)I, and (Bu_2EtS)I showed good overall conversion efficiencies within the temperature interval studied, but their individual trends were quite different (Figure 2). While using (Et_2MeS)I, with and without iodine, the highest values of efficiency, V_{OC} and J_{SC} were achieved at room temperature, followed by decreasing values with increasing temperatures. More viscous electrolytes based on (Bu_2MeS)I and (Bu_2EtS)I showed different trends in the changes of potential and current where increased temperatures resulted in enhanced currents (J_{SC}), though the potentials (V_{OC}) were unchanged or slightly decreased. The highest overall efficiencies were achieved at different temperatures, for (Bu_2MeS)I 1.8% at 50°C and for (Bu_2EtS)I 1.3% at 80°C . The iodine-containing electrolytes of (Bu_2MeS)I and (Bu_2EtS)I, with lower viscosities than the pure salts, achieved the highest conversion efficiencies at room temperature. However, the iodine-doped (Bu_2EtS)I provided

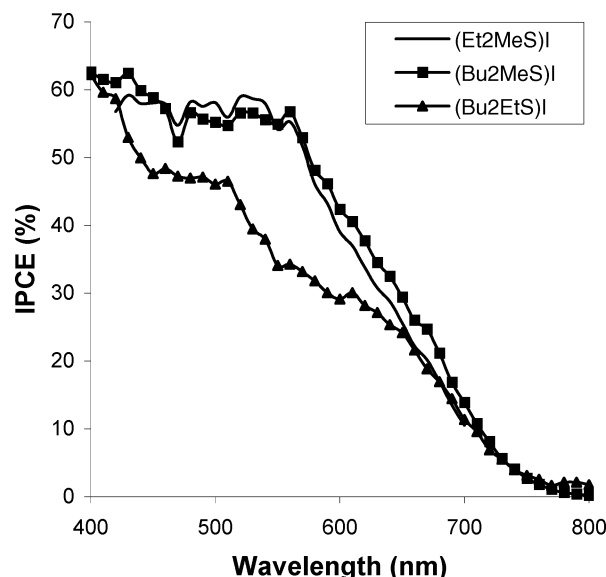


Figure 3. IPCE action spectra for DNSCs from using (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I electrolytes.

almost as high efficiencies also at 70–80 °C, because of the increase in currents with higher temperatures.

Among the compounds that are solids at room temperature (Me₂EtS)I provided the best results, as the iodine-doped (Me₂-EtS)I in the proportion (100:1) achieved an overall conversion efficiency of 0.8% at about 40 °C. Higher temperatures gave lower efficiency values. Some electrolytes provided negligible currents; however, their open-circuit potentials were fairly good: 0.5–0.6 V for (Pr₂MeS)I, and 0.2–0.5 V for (Me₂PrS)I, (Me₂DodS)I, (Pr₂EtS)I, (Pr₂BuS)I, (Bu₂PrS)I, and (DodEtMeS)I. I/V measurements of DNSCs with electrolytes of the remaining room-temperature solids were unfortunately impossible to fulfill, mainly due to their high melting points.

In summary, low viscosities are correlated to higher efficiencies. It is a well-known fact that doping causes melting-point suppression. This is of particular importance for systems, like the sulfonium iodides in this study, where the properties are studied close to the melting point. This is also the reason for the observed increase in efficiency with temperature for electrolytes with high viscosities (melting points) at room temperature.

IPCE Measurements. IPCE studies were performed for DNSCs at wavelengths from 400 to 800 nm using the molten electrolytes (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I, with and without addition of iodine. It should be mentioned that our results have not been corrected for possible reflection and absorption losses due to the conducting glass substrate.

The IPCE results of (Et₂MeS)I and (Bu₂MeS)I are stable above 55% from 400 to 550 nm and then decrease on the red side of the spectra; see Figure 3. A threshold appeared at

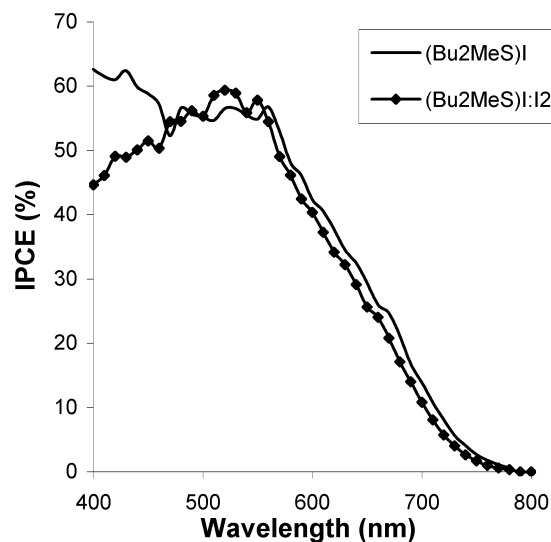


Figure 4. IPCE action spectra for DNSCs from using electrolytes of (Bu₂MeS)I with and without iodine.

wavelengths of 520–540 nm, which coincides with the peak at 530 nm present in the spectra of the dye.⁴

Addition of iodine to (Bu₂MeS)I and (Bu₂EtS)I indicate increasing IPCE values at 520–540 nm; from 55 to 60% and 38 to 46%, respectively; see Figure 4. This prevailed until the proportion (50:1) with respect to iodine was exceeded. These results correlate very well with the results from the I/V measurements and also the conductivity determinations. The best IPCE results obtained, just above 60% at 520–540 nm, are compatible with results from earlier studies where solution electrolytes have been used.⁴

No shifts of the highest peaks at 520–530 nm could be noticed in the IPCE spectra following the effects of iodine-doping of the electrolytes. However, a noticeable decrease appeared on the blue side of the spectra, at wavelengths below 530 nm. This also correlates well with the results obtained from the fluorescent light measurements, where iodine-doping of the electrolytes caused a decrease in conversion efficiencies. Addition of iodine in the proportions (100:1) to the electrolytes of (Et₂MeS)I resulted in decreased IPCE values at 520–540 nm, from 55 to 48%, which is an anomaly according to the I/V results. This decrease was even enhanced with higher proportions of iodine.

4-*tert*-Butylpyridine Treatment. The effects from applying 4-*tert*-butylpyridine as an additive to the working electrode were studied. From the I/V studies addition of 4-*tert*-butylpyridine resulted in an increase in conversion efficiencies, thus indicating enhanced currents, see Table 4. The greatest improvement was noticed for iodine-containing (Bu₂MeS)I in the proportion (100:1), where the efficiency increased from 2.0 to 3.7% in the presence of 4-*tert*-butylpyridine. The improvement, caused by

TABLE 4: Best Results Obtained from I/V Measurements of DNSCs Using Working Electrodes that Were Treated or Not with 4-*tert*-Butylpyridine^a

| electrolyte | prop | addition of 4- <i>tert</i> -butylpyridine | | | | no addition of 4- <i>tert</i> -butylpyridine | | | |
|---------------------------------------|-------|---|--------|--------------|---------------------------------|--|--------|--------------|---------------------------------|
| | | η (%) | FF (%) | V_{oc} (V) | J_{sc} (mA cm ⁻²) | η (%) | FF (%) | V_{oc} (V) | J_{sc} (mA cm ⁻²) |
| (Et ₂ MeS)I | | 2.0 | 58 | 0.57 | 0.6 | 1.7 | 65 | 0.69 | 0.4 |
| (Et ₂ MeS)I:I ₂ | 100:1 | 2.8 | 60 | 0.49 | 1.0 | 1.8 | 54 | 0.42 | 0.8 |
| (Bu ₂ MeS)I | | 1.5 | 59 | 0.63 | 0.4 | 1.4 | 67 | 0.59 | 0.3 |
| (Bu ₂ MeS)I:I ₂ | 100:1 | 3.7 | 62 | 0.60 | 1.0 | 2.0 | 42 | 0.53 | 0.9 |
| (Bu ₂ EtS)I | | 2.1 | 56 | 0.61 | 0.6 | 0.6 | 55 | 0.74 | 0.2 |
| (Bu ₂ EtS)I:I ₂ | 100:1 | 2.2 | 62 | 0.52 | 0.7 | 1.2 | 55 | 0.68 | 0.3 |

^a In irradiation AM 1.5, 100 W m⁻².

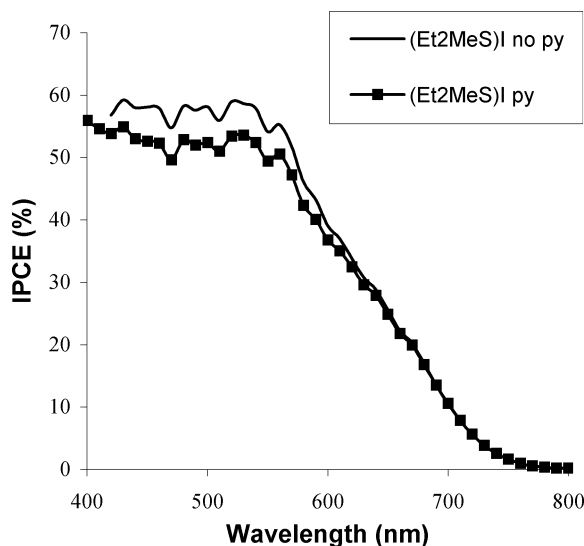


Figure 5. IPCE action spectra for DNSCs from using electrolytes of (Et₂MeS)I and electrodes that were treated or not with 4-*tert*-butylpyridine.

iodine-doping the electrolytes of (Et₂MeS)I and (Bu₂MeS)I, was more apparent while using electrodes treated with 4-*tert*-butylpyridine. From literature, treatment of the TiO₂ surface with 4-*tert*-butylpyridine may increase the voltage output of the solar cell, whereas the current may decrease. Also, the rate constant of the triiodide reduction is reduced, by preventing the loss of conduction-band electrons to the electrolyte.^{4,22} From our I/V studies, it was noticed that the *J*_{SC} was consequently increased in the presence of 4-*tert*-butylpyridine and thus caused improved conversion efficiencies. The photovoltages were almost indifferent to the addition of 4-*tert*-butylpyridine to the electrodes. Good *V*_{OC}'s of about 0.5–0.7 V were achieved with as well as without 4-*tert*-butylpyridine present in the solar cells.

The IPCE measurements revealed another impact from the presence of 4-*tert*-butylpyridine in the solar cells, which resulted in decreased IPCE values and overall impaired currents (Figure 5). This is opposed to the results obtained from the I/V measurements, where the current values were instead consequently increased by the addition of 4-*tert*-butylpyridine. The reason for these different trends has not been verified, but could be related to the very high sensitivity of the IPCE measurements. Also from other studies of DNSCs using liquid electrolytes the same pattern with decreased IPCE values upon the addition of 4-*tert*-butylpyridine has been observed.⁴

Conclusions

The room temperature molten salts of (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I showed good conducting abilities at ambient conditions. They also provided good light-to-electricity conversion efficiencies while used as electrolytes in DNSCs. Iodine-doped electrolytes of (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I provided overall conversion efficiencies of 2.8, 3.7, and 2.2%, respectively. The liquid electrolytes of (Et₂MeS)I provided the highest conversion efficiencies at room temperature. By heating treatment the viscosities of (Bu₂MeS)I and (Bu₂EtS)I were decreased and thus higher overall efficiencies were obtained above room temperature. The effects from 4-*tert*-butylpyridine addition to the electrodes were difficult to interpret. From the I/V studies the impact was positive providing increased ef-

ficiencies, photocurrents, and potentials, whereas the IPCE results were moderately decreased. Concludingly, since the molten salts provided promising capabilities as electrolytes in DNSCs further investigations and optimizations of performance will be pursued.

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Supporting Information Available: Results for DNSCs using (Bu₂MeS)I electrolytes measured at different light intensities (Figure S1); results from conductivity measurements of iodine-doped (Et₂MeS)I, (Bu₂MeS)I, and (Bu₂EtS)I (Table S1); results from IV measurements of DNSCs while using different solar simulators (Table S2); results from IV measurements performed at different light intensities (Table S3); results from temperature-dependent I/V measurements of DNSCs (Table S4).

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