# Highly Stable Dye-Sensitized Solar Cells Based on Novel 1,2,3-Triazolium Ionic Liquids

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ABSTRACT: We describe the design and synthesis of novel low viscosity bicyclic 1,2,3-triazolium ionic liquids. These new salts are applied as nonvolatile electrolytes in dye-sensitized solar cells, affording efficiencies up to 7.07% at low light intensities, and 6.00% when illuminated at 100 mW cm^{-2}. The devices are highly stable, retaining ca. 90% of their initial performance even after 1000 h of sun testing at 60 °C. The results obtained with these new ionic liquids compare very favorably to benchmark ionic liquid-based devices and illustrate the potential of the triazolium family of salts to compete with their imidazolium counterparts.

HIGHLY STABLE
DYE-SENSITIZED SOLAR CELLS

η = 6.00 %

WORK

KEYWORDS: *ionic liquids, 1,2,3-triazolium, dye-sensitized solar cells, click chemistry*
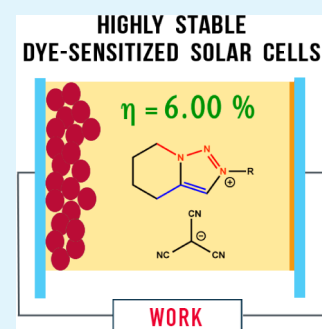
1. INTRODUCTION

Following the advent of dye-sensitized solar cells (DSCs) in 1991,[1] continued research efforts have led to impressive efficiency gains in recent years.[2,3] Among the light-harvesting technologies available to date, dye-sensitized solar cells stand out due to their ease of fabrication and relatively low cost of production.[4] Despite the many attractive features of this emerging technology, the transition from laboratory to marketplace has been hampered by a number of issues.[4−6] Notably, poor device stability stemming from the use of volatile liquid electrolytes is particularly problematic, necessitating judicious and hence expensive cell-sealing techniques.[4−6] Therefore, replacing the volatile liquid electrolytes with more thermally stable alternatives is a matter of industrial importance and is urgently required. As such, research into new materials including polymer electrolytes, solid-state hole conductors, as well as ionic liquid-based electrolytes has been ongoing.[7−9] Although much current interest has shifted toward solid-state devices based on organolead halide perovskites,[10] the issue of device stability remains unresolved and the commercialization process is further impeded by the use of toxic lead-containing materials.[11]

Ionic liquids (ILs) tend not to suffer from the aforementioned problems. They typically possess high ionic conductivities, wide electrochemical windows, and negligible vapor pressure and are also nonflammable[12−16]—making them very attractive materials for use in various electrochemical applications. Ionic liquid-based dye-sensitized solar cells first emerged in 1996.[17] Subsequently, much improvement has been made, and as far as we are aware, the current efficiency record for ionic liquid-based DSCs stands at 8.2% under full sun illumination with a ruthenium-based dye.[9] Research in this area has largely focused on a very narrow group of cations, with the imidazolium salts dominating the literature. Other families of

ionic liquids that have been investigated for DSC applications include pyridinium, pyrrolidinium, sulfonium, ammonium, and phosphonium salts.[18−20] Here, we report the use of novel 1,2,3-triazolium salts for DSC applications, yielding results that compare very favorably to their imidazolium counterparts.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All reagents used were obtained commercially and used as received without further purification unless otherwise stated. ^{1}H NMR spectra and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer, using Me$_4$Si as an external standard. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument using a literature method.[21,22] Viscosity measurements were recorded using a HAAKE RheoStress 1 Rheometer (ThermoScientific) equipped with a HAAKE DC50 Thermostat (ThermoScientific). Melting points were determined using a Stuart Scientific melting point apparatus SMP3.

Synthesis of Bicyclic Triazole (1). Freshly distilled 6-chloro-1-hexyne (0.13 mol, 15.2 g) was heated under reflux with NaN$_3$ (1.5 equiv, 12.7 g) and NaI (10 mol %, 2.0 g) in a 1:1 water/methanol mixture (130 mL) for 72 h. (***Caution!*** *Due care and attention should be taken when handling NaN$_3$.*) The reaction mixture was allowed to cool to room temperature and was transferred to a dropping funnel. The azide mixture was added dropwise to a stirred solution containing CuSO$_4$·5H$_2$O (10 mol %, 2.1 g) and sodium ascorbate (20 mol %, 5.2 g) in 500 mL of distilled water at room temperature over a period of 6 h. The mixture was stirred for another 24 h. An EDTA/NH$_4$OH$_{(aq)}$ solution (1.0 M, 100 mL) was added to the reaction mixture to quench the reaction. Any solid that formed was filtered, and the aqueous solution was extracted with ethyl acetate (3 × 200 mL). The organic extracts were combined and dried over Na$_2$SO$_4$. Removal of the solvent under reduced pressure at 50 °C gave **1** as a yellow liquid.

Yield: 77%. ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 7.42 (s, 1H), 4.35 (t, J = 6.2 Hz, 2H), 2.82 (t, J = 6.4 Hz, 2H), 2.15–2.00 (m, 2H), 1.95–1.84 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 133.26, 130.62, 46.02, 22.78, 20.18, 20.16; ESIMS m/z: [M + H]$^+$ calcd for C$_6$H$_{10}$N$_3$, 124.0875; found, 124.0872.

General Synthesis Procedure for Bicyclic Triazolium Iodides (BT-C$_x$$^+I^-$). Compound **1** was reacted with the appropriate alkyl iodide (1.1 equiv) at 90 °C in the absence of any additional solvent. The reaction was monitored by ^1H NMR spectroscopy. Upon complete conversion of **1**, ca. 20 h, the reaction was stopped and cooled to room temperature. Unreacted alkyl iodide was removed by repeated washing with diethyl ether (ca. 100 mL in total). The triazolium iodides obtained were dissolved in dichloromethane (20 mL) and stirred with activated carbon for 18 h. The mixture was filtered over Celite and dried with Na$_2$SO$_4$. Removal of the solvent under reduced pressure at 40 °C gave the desired bicyclic triazolium iodide.

BT-C$_1$$^+I^-$: mp 134 °C; ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 9.25 (s, 1H), 4.58 (t, J = 6.2 Hz, 2H), 4.50 (s, 3H), 3.17 (t, J = 6.4 Hz, 2H), 2.36–2.25 (m, 2H), 2.18–2.05 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.34, 129.72, 49.16, 41.00, 21.50, 20.66, 18.16; ESIMS m/z: 138.00 [cation]$^+$, 126.92 [anion]$^-$, 391.92 [(cation)(anion)$_2$]$^-$.

BT-C$_2$$^+I^-$: mp 114 °C; ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 9.13 (s, 1H), 4.77 (q, J = 7.4 Hz, 2H), 4.58 (t, J = 6.2 Hz, 2H), 3.12 (t, J = 6.4 Hz, 2H), 2.34–2.23 (m, 2H), 2.14–2.02 (m, 2H), 1.68 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.21, 128.27, 49.69, 49.32, 21.52, 20.66, 18.13, 14.85; ESIMS m/z: 152.00 [cation]$^+$, 126.92 [anion]$^-$, 406.00 [(cation)(anion)$_2$]$^-$.

BT-C$_3$$^+I^-$: mp 83 °C; ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 9.18 (s, 1H), 4.69 (t, J = 7.4 Hz, 2H), 4.59 (t, J = 6.2 Hz, 2H), 3.18 (t, J = 6.5 Hz, 2H), 2.41–2.26 (m, 2H), 2.21–2.04 (m, 4H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.25, 128.66, 55.62, 49.28, 23.12, 21.52, 20.71, 18.15, 10.91; ESIMS m/z: 166.13 [cation]$^+$, 459.15 [(cation)$_2$(anion)]$^+$.

BT-C$_4$$^+I^-$: mp 73 °C; ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 9.37 (s, 1H), 4.76 (t, J = 8 Hz, 2H), 4.58 (t, J = 6.2 Hz, 2H), 3.20 (t, J = 8 Hz, 2H), 2.37–2.26 (m, 2H), 2.18–2.00 (m, 4H), 1.54–1.40 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.25, 128.65, 53.98, 49.28, 31.38, 21.53, 20.72, 19.50, 18.15, 13.39; ESIMS m/z: 180.15 [cation]$^+$, 487.18 [(cation)$_2$(anion)]$^+$.

General Procedure for the Synthesis of the Bicyclic Triazolium Tricyanomethanides (BT-C$_x$$^+TCM^-$). The appropriate bicyclic triazolium iodide (10 mmol) was dissolved in water (5 mL), and 1 equiv of NaC(CN)$_3$ was added to the mixture and stirred for 18 h at room temperature. The aqueous solution was extracted with dichloromethane (3 × 10 mL). The organic extracts were combined and stirred with activated carbon for 18 h at room temperature. The mixture was filtered over Celite and dried over Na$_2$SO$_4$. The organic solvents were removed under reduced pressure, and the residue was redissolved in dry dichloromethane (10 mL). The solution was left at −20 °C for 15 h. Any halide salts that precipitated were removed by filtration. Removal of the solvent under reduced pressure at 40 °C for 7 h afforded the desired BT-C$_x$$^+TCM^-$ ionic liquids.

BT-C$_1$$^+TCM^-$: ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 8.20 (s, 1H), 4.58 (t, J = 6.2 Hz, 2H), 4.36 (s, 3H), 3.09 (t, J = 6.4 Hz, 2H), 2.33–2.21 (m, 2H), 2.16–2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.87, 127.93, 121.39, 49.26, 40.40, 21.34, 20.20, 17.98, 5.75; ESIMS m/z: 138.00 [cation]$^+$, 89.92 [anion]$^-$.

BT-C$_2$$^+TCM^-$: ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 8.17 (s, 1H), 4.61 (q, J = 7.4 Hz, 2H), 4.54 (t, J = 6.2 Hz, 2H), 3.05 (t, J = 6.4 Hz, 2H), 2.37–2.18 (m, 2H), 2.10–1.99 (m, 2H), 1.66 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.64, 126.50, 121.37, 49.64, 49.22, 21.35, 20.20, 18.00, 14.33, 5.74; ESIMS m/z: 152.00 [cation]$^+$, 89.92 [anion]$^-$.

BT-C$_3$$^+TCM^-$: ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 8.22 (s, 1H), 4.63–4.49 (m, 4H), 3.10 (t, J = 6.4 Hz, 2H), 2.34–2.23 (m, 2H), 2.16–2.02 (m, 4H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm) 140.68, 126.93, 121.48, 55.79, 49.27, 22.87, 21.38, 20.26, 18.03, 10.75, 5.89; ESIMS m/z: 166.12 [cation]$^+$, 90.00 [anion]$^-$.

BT-C$_4$$^+TCM^-$: ^1H NMR (400 MHz, CDCl$_3$, δ ppm): 8.25 (s, 1H), 4.66–4.54 (m, 4H), 3.11 (t, J = 6.5, 2H), 2.35–2.24 (m, 2H), 2.15–1.98 (m, 4H), 1.51–1.39 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 140.67, 127.01, 121.50, 54.10, 49.28, 31.16, 21.40, 20.30, 19.45, 18.05, 13.28, 5.91; ESIMS m/z: 180.13 [cation]$^+$, 90.00 [anion]$^-$.

2.2. Device Fabrication.

The photoanode consists of a 7 μm thick film of 32 nm sized TiO$_2$ particles screen-printed on fluorine-doped tin oxide (FTO) conducting glass and further coated with a 4 μm thick second layer of 400 nm light-scattering TiO$_2$ particles (400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd. (CCIC), HPW-400). After a sintering process, followed by a 40 mM TiCl$_4$ treatment in water at 70 °C for 30 min, the photoanodes were sintered at 500 °C for 30 min prior to dipping into a 0.2 mM solution of C106 dye (Dyesol) in a mixture of DMSO, acetonitrile, and *tert*-butyl alcohol (volume ratio, 0.1:1:1) for 15 h. For the assembly of DSCs, the dye-containing TiO$_2$ electrode and platinum-coated counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket of 25 μm in thickness made of the ionomer Surlyn 1702 (Dupont).
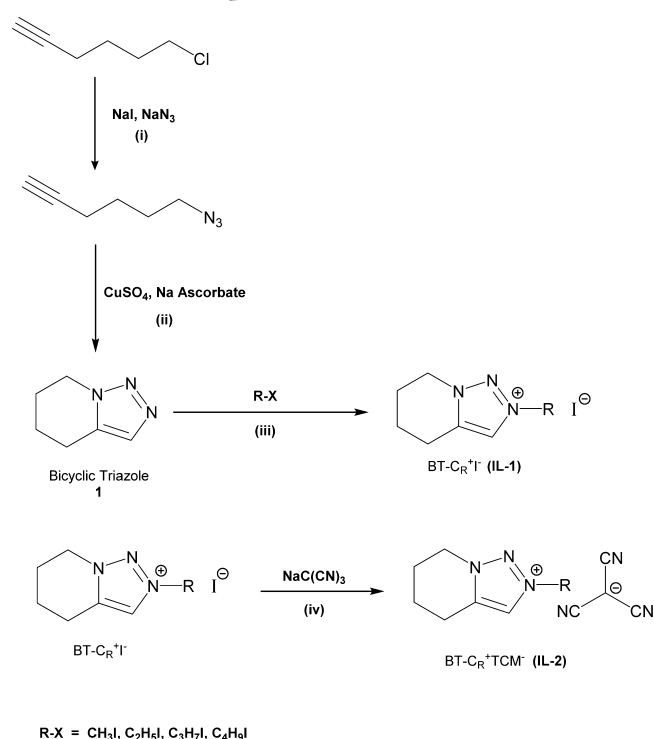
2.3. Device Characterization and Photovoltaic Measurements.

Photovoltaic Measurements. Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 450 W xenon lamp (Oriel, USA). $I–V$ curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The devices were masked to attain an illuminated active area of 0.159 cm^2.

Transient Photovoltage and Photocurrent Setup. Photovoltage transients were recorded by using a pump pulse generated by red light emitting diodes controlled by a fast solid-state switch with a white light bias. A red light pulse with a pulse width of 100 ms was incident on the photoanode side of the cell, and its intensity was controlled to keep a suitably low level to generate the exponential voltage decay where the charge recombination rate constants are obtained directly from the exponential decay rate. A white bias light, also incident on the same side of the device, was supplied by white diodes. Small perturbation transient photocurrent measurements were performed in a similar manner to the open-circuit voltage decay measurement.

3. RESULTS AND DISCUSSION

3.1. Design and Synthesis of Bicyclic 1,2,3-Triazolium Ionic Liquids.

The high viscosity of ionic liquids slows down the dye regeneration process in DSCs, leading to less efficient devices.[23] Hence, a series of bicyclic triazolium salts (Scheme 1) were specially designed and prepared via the copper-catalyzed azide alkyne click reaction. It was envisaged that the bicyclic cation structure would disrupt the packing of the ions, thereby reducing electrostatic interactions and ultimately leading to ILs with a low viscosity. Moreover, the tricyanomethanide anion, with three electron-withdrawing nitrile groups, is able to diffuse the negative charge and provide low viscous ionic liquids.[18] Tseng and co-workers prepared similar salts in 2011 that were evaluated as solvents in the synthesis of rutaecarpine.[24] The synthetic procedure proposed by Tseng et al. involves the preparation and handling of potentially explosive and shock-sensitive short-chain alkyl azide intermediates, which is not ideal. Consequently, we present here a new route to prepare this family of salts. Freshly distilled 6-chloro-1-hexyne was first heated under reflux with NaN$_3$ (1.5 equiv) and NaI (10 mol %) in a 1:1 water–methanol mixture for 72 h. The reaction mixture was then transferred to a dropping funnel and slowly added to a stirred, highly dilute solution of CuSO$_4$·5H$_2$O (10 mol %) and sodium ascorbate (20 mol %) in distilled water. These conditions were carefully selected to favor the intramolecular azide alkyne click reaction, which yields the bicyclic triazole **1**. Following purification, **1** was then reacted with various alkyl iodides to afford bicyclic triazolium salts

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Scheme 1. Route Used To Prepare the Bicyclic 1,2,3-Triazolium Ionic Liquids[a]

R-X = CH₃I, C₂H₅I, C₃H₇I, C₄H₉I

[a]Reagents and conditions: (i) NaN$_3$ (1.5 equiv), NaI (10 mol %), 100 °C, 72 h; (ii) CuSO$_4$·5H$_2$O (10 mol %), sodium ascorbate (20 mol %), RT, 6 h; (iii) appropriate alkyl iodide (1.1 equiv), 80 °C, 24 h; (iv) NaC(CN)$_3$ (1 equiv), RT, overnight.

bearing different alkyl chains. Subsequent metathesis with NaC(CN)$_3$ (1 equiv) yielded the tricyanomethanide (TCM$^-$) salts. Full experimental details are provided in the Experimental Section. The physical properties of the newly synthesized salts are reported in Table 1.

All the iodide salts prepared were solids at room temperature, with melting points decreasing with increasing alkyl chain length. Longer alkyl chains have greater inductive effects, stabilizing the positive charge on the nitrogen to a greater extent, leading to decreased electrostatic interactions of the ions.[12,13] Moreover, cations with a longer alkyl chain are more asymmetric, which is also known to result in decreased melting points.[12,13] On the other hand, all the tricyanomethanide salts synthesized were liquids at room temperature, with viscosities ranging from 37 to 86 mPa·s. The viscosity of the ionic liquids increases when increasing the alkyl chain length from C2 to C4 (from 37 to 86 mPa·s), as is expected due to increased van der Waals forces and the reduced rotational freedom of larger

cations.[13] Surprisingly, BT-C$_1$$^+TCM^-$ is more viscous than BT-C$_2$$^+TCM^-$ (Table 1) and does not fit this trend.

3.2. Photovoltaic Performance of 1,2,3-Triazolium Ionic Liquid-Based DSCs. These new ionic liquids were then used to prepare eutectic ionic liquid-based electrolytes with the following general composition: DMII/GNCS/NMB/**IL-1**/**IL-2**/I$_2$ (6:0.33:1.74:6:8:1.2 by mol, DMII = dimethylimidazolium iodide, GNCS = guanidinium thiocyanate, NMB = N-methylbenzimidazole, **IL-1** = BT-C$_1$$^+I^-$, **IL-2** = BT-C$_1$$^+TCM^-$). Four different electrolytes were prepared that differ according to the length of the alkyl chain on the cations in **IL-1** and **IL-2**, from C$_1$ to C$_4$. DSCs employing these electrolytes (coded E1−E4) together with a commercially available ruthenium-based photosensitizer (C106) were fabricated as described in the Experimental Section . Photovoltaic characteristics of the resulting devices are presented in Table 2.

Effect of the Alkyl Chain Length. Among the four electrolytes, E2 shows the best solar cell performance with an efficiency of 6.00% when illuminated at 100 mW cm^{-2}. Devices based on electrolytes E3 and E4 exhibit a severe "bump" in the I−V curve, leading to an overestimated fill factor (FF) when measured at 100 mW cm^{-2}. This effect is possibly triggered by the higher viscosity of those ionic liquids with longer alkyl chains (Table 1), leading to more severe diffusion problems of the I$_3$$^-$/I$^-$ redox couple, causing a drop in J$_{SC}$ values due to slower dye regeneration kinetics. The diffusion limitations were further confirmed via photocurrent transient measurements, during which the cells were illuminated under short-circuit conditions for 4 s, while the changes in their short-circuit current densities were monitored. If no diffusion problems are present, the J$_{SC}$ values should remain fairly constant, presenting as a plateau, which is nearly the case for the E2-based device when illuminated at 100 mW cm^{-2} (Figure 1a). However, with the E1-, E3-, and E4-based devices, we observe that the J$_{SC}$ values drop with extended illumination time. This suggests that these electrolyte systems suffer from diffusion problems, resulting in inefficient dye regeneration, which ultimately causes the J$_{SC}$ values to decay with illumination time. Therefore, in order to avoid inflated power conversion efficiencies for the E1-, E3-, and E4-based devices that exhibit "bumps" in their I−V curves, the cells were exposed to lower sun intensities instead, at which diffusion limitations are less apparent (Figure 2).

Overall, the new ionic liquid-based electrolyte systems work very well and exhibit similar power conversion efficiencies between 6% and 7% at low light intensities (Table 2), with the exception of the E1-based device. The formation of needle-like crystals was observed within the device employing the E1 electrolyte. The presence of crystallites within the cell most likely inhibits the transport of the I$_3$$^-$/I$^-$ redox species, resulting

Table 1. Physical Properties of the Bicyclic 1,2,3-Triazolium Ionic Liquids

ionic liquids	physical state at 23 °C	melting point [°C]	viscosity at 23 °C [mPa·s]
BT-C$_1$$^+I^-$	solid	134	
BT-C$_1$$^+TCM^-$	liquid		56
BT-C$_2$$^+I^-$	solid	114	
BT-C$_2$$^+TCM^-$	liquid		37
BT-C$_3$$^+I^-$	solid	83	
BT-C$_3$$^+TCM^-$	liquid		73
BT-C$_4$$^+I^-$	waxy solid	73	
BT-C$_4$$^+TCM^-$	liquid		86

Table 2. Photovoltaic Characteristics of DSCs Measured at Various Sun Intensities

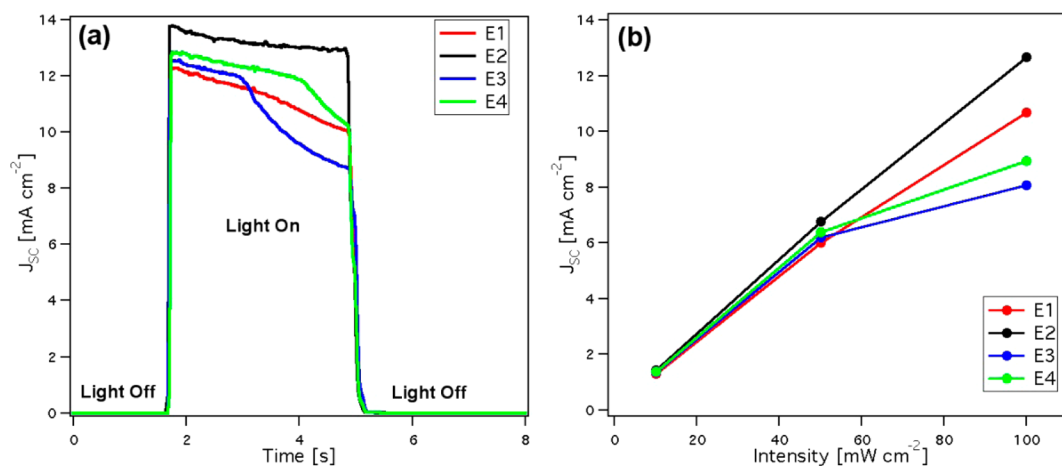| entry	electrolyte code	IL-1	IL-2	intensity [mW·cm^{-2}]	J_{SC} [mA·cm^{-2}]	V_{OC} [mV]	fill factor	efficiency [%]
1	E1	BT-C$_1^+$I$^-$	BT-C$_1^+$TCM$^-$	10	1.30	604	0.64	5.05
				50	6.02	657	0.73	5.80
				100	10.70	673	0.73	5.25
2	E2	BT-C$_2^+$I$^-$	BT-C$_2^+$TCM$^-$	10	1.45	596	0.79	6.85
				50	6.77	643	0.76	6.63
				100	12.68	657	0.72	6.00
3	E3	BT-C$_3^+$I$^-$	BT-C$_3^+$TCM$^-$	10	1.37	631	0.82	7.07
				50	6.19	668	0.76	6.31
4	E4	BT-C$_4^+$I$^-$	BT-C$_4^+$TCM$^-$	10	1.40	589	0.80	6.62
				50	6.40	628	0.74	5.91

Figure 1. (a) J_{SC} transients measured at 100 mW cm^{-2} and (b) the linearity of the J_{SC} response with respect to illumination intensity for the DSCs based on electrolytes E1−E4.
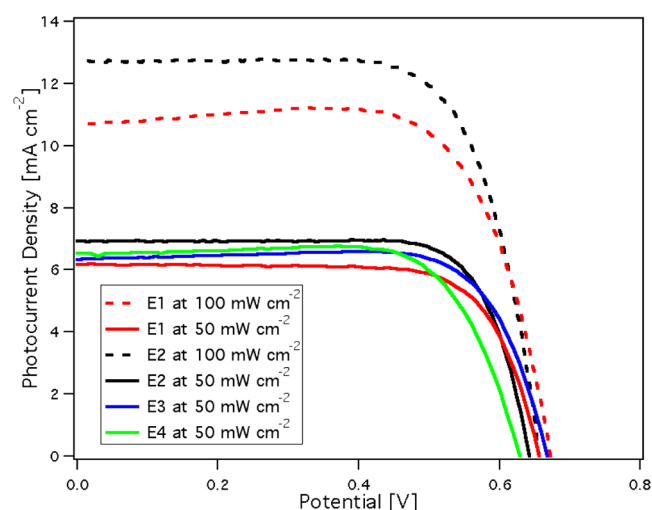

Figure 2. Photovoltaic characteristics of the DSCs measured at 50 mW cm^{-2} for the DSCs based on the electrolytes E1−E4 and also at 100 mW cm^{-2} for the E1- and E2-based devices.

in detrimental dye regeneration and, hence, a lower J_{SC} value. Furthermore, incomplete pore filling of the device is also quite likely. Nevertheless, despite the formation of crystallites, the diffusion limitation of the I$_3^-$/I$^-$ redox couple is remarkably less severe than the E3 and E4 systems, as evident in the less prominent drop in J_{SC} for the current transient (Figure 1a), as well as in the more linear response of J_{SC} with illumination intensity (Figure 1b). This behavior yields a higher J_{SC} value

and ultimately superior cell performance at 100 mW cm^{-2} for the E1-based device in comparison to the E3- and E4-based devices (Table 2). However, since the E1 electrolyte is not entirely liquid and is, therefore, a nonstandard device, subsequent discussion will focus on the devices based on the E2, E3, and E4 electrolytes.

Notably, it is the E3-based device, and not E2, that affords the highest V_{OC} value. Typically, an increase in V_{OC} is indicative of a prolonged electron lifetime in the TiO$_2$ film or a more negative shift of the TiO$_2$ conduction band edge.[25] Photovoltage transient measurements performed on the E2-, E3-, and E4-based devices reveal that the E3-based cell indeed exhibits extended electron lifetimes compared to the E2 and E4 systems, which are very similar (Figure 3a). Photocurrent transient studies were also performed on the same cells, and the results are shown in Figure 3b. At the same TiO$_2$ film capacitances, the E3-based device gives a higher V_{OC} value than the E2- and E4-based devices, consistent with a more negative shift of the TiO$_2$ conduction band edge. The data show that V_{OC} values decrease in the order E3 > E2 > E4, excluding a straightforward correlation between the V_{OC} values and the length of the alkyl chain on the ionic liquid cation. With the short-circuit current density (J_{SC}), again, there is also no simple correlation with the length of the alkyl chain on the cations. Although the E3- and E4-based systems have similar viscosities (Table 1), a higher J_{SC} value is observed in the E4-based device. This is most likely due to the more positive shift of the TiO$_2$ conduction band edge (Figure 3b), resulting in more efficient photoelectron injection from the C106 dye. The E2 electrolyte system, which is based on the BT-C$_2^+$TCM$^-$ ionic liquid, is

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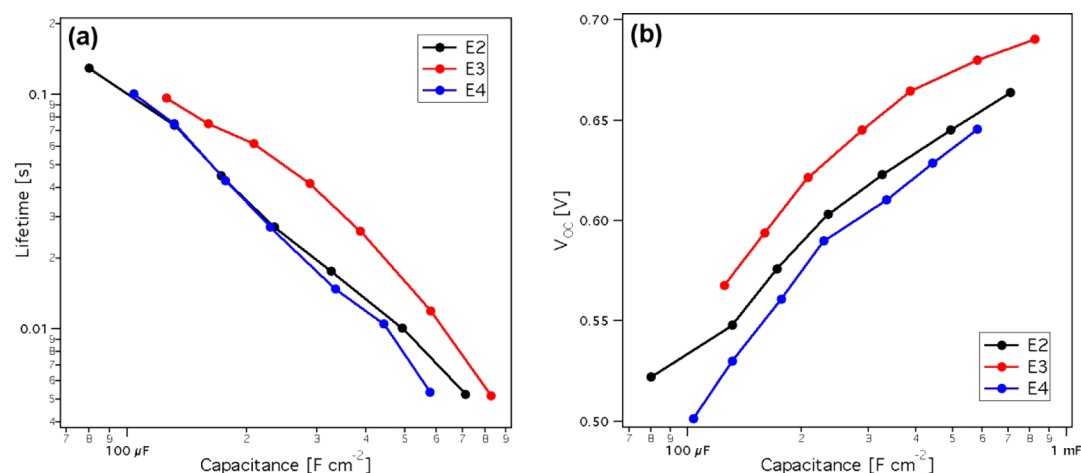dx.doi.org/10.1021/am502838u | ACS Appl. Mater. Interfaces 2014, 6, 13571−13577

Figure 3. (a) Differences in electron lifetimes within the TiO_2 films measured by transient photovoltage decay and (b) in V_{OC} of the DSCs measured by transient photocurrent decay based on the electrolytes E2–E4.

clearly superior to the other devices, with an observed J_{SC} value of 12.68 mA cm^{-2} at full sun intensity. This may be attributed to the significantly lower viscosity of the BT-C$_2$$^+TCM^-$ ionic liquid, compared with its C3 and C4 counterparts, leading to improved diffusion of the redox mediator.

Long-Term Stability of the Devices. In order to investigate the long-term stability of these ionic liquid-based devices, the best performing cell, i.e., the one incorporating the E2 electrolyte, was subjected to an accelerated aging test at 60 °C under constant full sun illumination (100 mW cm^{-2}) for 1000 h. During this time, the J_{SC} value essentially remained unchanged, and there was only a very slight deterioration in both V_{OC} (less than 20 mV) and fill factor (Figure 4). To understand the origin of this voltage drop, the evolution of the TiO_2 electron lifetimes and of the conduction band shifts in the TiO_2 film with extended light soaking time were investigated. As Figure 5a illustrates, the electrons within the TiO_2 film are longer-lived with prolonged light soaking and remain unaltered after 336 h. Longer electron lifetimes indicate that recombination processes are more suppressed, expectedly leading to a higher V_{OC}.[25] However, it was observed that the V_{OC} value decreased by approximately 20 mV during the course of the experiment. A plausible explanation for this observation is the positive shift in the TiO_2 conduction band (Figure 5b) caused by cations present in the electrolyte adhering more readily to the TiO_2 surface with prolonged light and heat biasing.[26] Nevertheless, these changes are small, resulting in the retention of ca. 90% of its initial power conversion efficiency after 1000 h—dropping from 6% to 5.3%. These findings demonstrate that the E2 ionic liquid-based electrolyte is able to afford highly stable dye-sensitized solar cells. This result is comparable to the best previously reported eutectic ionic liquid-based device, which maintained 93% of its device performance after a similar 1000 h stress test.[9]

4. CONCLUSION

In conclusion, we have demonstrated a new synthetic strategy to obtain bicyclic 1,2,3-triazolium salts. The judicious selection of both cation and anion yielded low viscosity room-temperature ionic liquids, which were successfully applied in high-performance dye-sensitized solar cells. The best performing device, when measured at 100 mW cm^{-2}, gave an efficiency of 6.00%, which corresponds to a short-circuit photocurrent
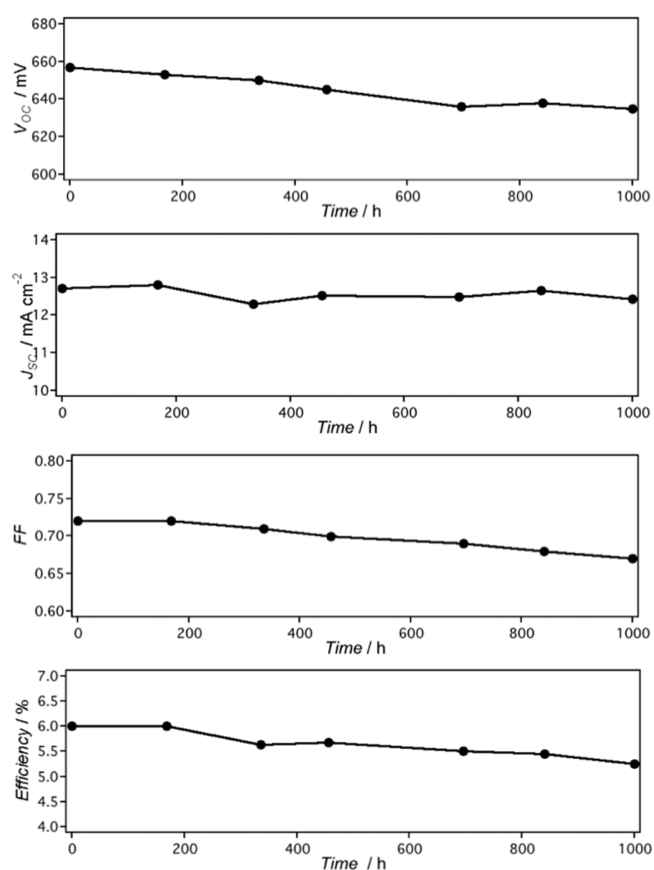

Figure 4. Variations in photovoltaic parameters of the E2-based device with time during constant 100 mW cm^{-2} light soaking at 60 °C.

density (J_{SC}) of 12.68 mA cm^{-2}, an open-circuit photovoltage (V_{OC}) of 657 mV, and a fill factor (FF) of 0.72. The devices were shown to be very stable, retaining up to ca. 90% of their initial performance after a 1000 h accelerated aging test. These bicyclic 1,2,3-triazolium-based ionic liquids represent alternatives to the imidazolium salts that have been unrivalled for the past decade or so. Therefore, it is expected that these encouraging results, which are of importance to the industrial application of DSCs, will generate greater interest in this
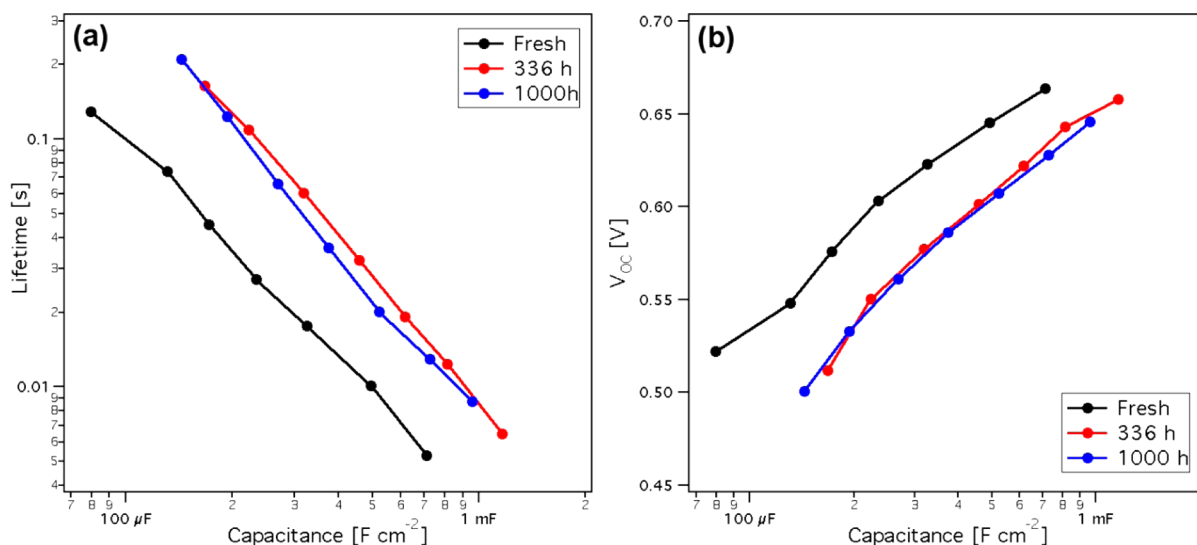
Figure 5. Evolution of (a) electron lifetime within the TiO_2 film and of (b) V_{OC} and hence TiO_2 conduction band shift in the E2-based device with time during constant 100 mW cm^{-2} light soaking at 60 °C.

relatively underexplored family of ionic liquids, leading to more practical applications in the future.

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Notes
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