

# Improving performance of copper(I)-based dye sensitized solar cells through I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte manipulation

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## Abstract

The performances of dye-sensitized solar cells (DSSCs) containing a heteroleptic bis(diimine)copper(I) dye and an I<sub>3</sub><sup>-</sup>/I<sup>-</sup> liquid electrolyte have been investigated as a function of the electrolyte composition. Starting from a standard electrolyte with LiI (0.1 M), I<sub>2</sub> (0.05 M), 1-butyl-3-methylimidazolium (BMII) ionic liquid (0.6 M), 1-methylimidazole additive (0.5 M) in 3-methoxypropionitrile (MPN), a series of ten electrolytes was initially screened; the solvent, additives, concentration of I<sub>2</sub>, and sources (LiI and/or BMII) and concentrations of I<sup>-</sup> were varied. The highest short-circuit current densities ( $J_{sc} = 7.85$  and  $7.60$  mA cm<sup>-2</sup>) and photoconversion efficiencies ( $\eta = 2.64$  and  $2.70\%$  relative to  $6.56$  and  $6.11\%$  for two N719 references) were observed for DSSCs with an electrolyte comprising I<sub>2</sub> (0.03 M), BMII (0.6 M), 4-*tert*-butylpyridine (TBP, 0.4 M) and guanidinium thiocyanate (GNCS, 0.1 M) in MPN solvent; no LiI was added. This composition was further optimized by varying the amounts of TBP and GNCS. A low concentration of I<sub>2</sub> (0.015 M) is optimal. The presence or absence of GNCS has little effect on overall DSSC

performance, but increasing the concentration of TBP is detrimental to DSSC performance, and an absence of TBP is beneficial. Open-circuit voltage decay (OCVD) measurements confirm that the addition of GNCS and/or TBP reduces recombination rates at the TiO<sub>2</sub>-dye interface. The best DSC parameters obtained for the copper(I)-based dye were  $J_{SC} = 7.80 \text{ mA cm}^{-2}$ , open-circuit voltage ( $V_{OC}$ ) = 501 mV and  $\eta = 2.76\%$  (relative to 6.72% for N719).

Keywords: DSSC; copper dye; I<sub>3</sub><sup>-</sup>/I<sup>-</sup> liquid electrolyte; photoconversion efficiency; solar cell

## **1 Introduction**

Since the inception of the Grätzel n-type dye-sensitized solar cell (DSSC) [1,2] for the conversion of solar to electrical energy, there has been a phenomenal growth in the number of publications dealing with the development of dyes and optimization of DSSC components. State-of-the-art DCS photoconversion efficiencies now reach ~11-14% using ruthenium(II)-based, organic or zinc(II) porphyrin-based dyes [3-16]. Our research contributions to this field have focused on the development of dyes containing Earth-abundant metals, in particular copper [17]. In the last couple of years, photoconversion efficiencies of DSSCs sensitized with bis(diimine)copper(I) dyes have exceeded 3% [18] (relative to ~7.5% for the standard ruthenium(II) dye N719) with a record 4.66% reported by Odobel and coworkers [19]. One factor that contributes to the lower efficiencies of copper(I)

dyes compared to state-of-the-art dyes is the limited energy range over which bis(diimine)copper(I) complexes absorb light compared to ruthenium dyes. This can be addressed by ligand design, broadening the spectral response and extending the typical MLCT band out towards the red end of the spectrum [19-24]. DSSCs containing copper(I) dyes typically show lower values of the short-circuit current density ( $J_{sc}$ ) than ruthenium(II)-based dyes. Again, this can be improved with ligand design through enhancement absorption properties of the dye. A third factor that must be addressed to improve the performance of copper-based DSSCs is ways to increase the open-circuit voltage ( $V_{oc}$ ) and this is best approached through tuning of the electrolyte.

One of the most commonly used redox couples in liquid electrolytes in DSSCs is  $I_3^-/I^-$ , and the composition of the electrolyte has been optimized for DSSCs containing ruthenium(II)-based dyes [25,26]. The essential components of the electrolyte are  $LiI$  and  $I_2$  in a solvent such as acetonitrile, 3-methoxypropionitrile, valeronitrile or benzonitrile and an ionic liquid such as 1-butyl-3-methylimidazolium iodide (BMII). Typically, additives are present [27,28] to improve performance by tuning the  $TiO_2$  conduction band energy and reducing recombination (i.e. back reaction between electrons and oxidized dye). Typical additives include 4-*tert*-butylpyridine (TBP) and guanidinium thiocyanate (GNCS). TBP is known to increase  $V_{oc}$ . Boschloo and Hagfeldt [29] have reported that TBP changes the surface charge of  $TiO_2$  by decreasing the number of protons and  $Li^+$  ions on the surface, thus shifting the band edge of  $TiO_2$  to more negative potentials. TBP also leads to an increase in electron lifetime in the semiconductor [29]. The benefits

of GNCS remain debatable [30]. Zhang *et al.* [31] have reported that addition of GNCS to the electrolyte leads to enhanced electron injection. Kopidakis *et al.* [32] have shown that the presence of GNCS in the electrolyte slows the rate of electron recombination, but at the same time shifts the band edge to more positive potential. Since a reduction in recombination increases  $V_{OC}$ , whereas a band edge shift to more positive potential lowers  $V_{OC}$ , these effects oppose each other. Proposals that guanidinium ions passivate recombination sites [31,32] have been contested by O'Regan and coworkers [33] who suggest that guanidinium ions compete with  $I_2$  for binding sites on N719. The consequential decrease in the concentration of dye- $I_2$  complexes on the surface leads to a reduction in the rate of electron/ $I_2$  recombination.

The effects of electrolyte composition on copper-based DSSCs are underexplored. It has been demonstrated that values of  $J_{SC}$  and  $V_{OC}$  for DSSCs containing homoleptic copper(I) dyes [34] vary as a function of the composition of electrolytes comprising LiI,  $I_2$ , 1,3-dimethylimidazolium iodide (DMII) or BMII, TBP and GNCS in MeCN and valeronitrile (VN) [35]. This confirms that the photoconversion efficiency of bis(diimine) copper(I) dyes can be improved by manipulation of the  $I_3^-/I^-$  electrolyte. However, systematic studies of the optimization of the  $I_3^-/I^-$  electrolyte for copper(I)-based DSSCs remain lacking.

Recently, we reported the DSSC performances of a series of heteroleptic  $[Cu(L_{anchor})(L_{ancillary})]^+$  dyes in which  $L_{anchor}$  is ((6,6'-dimethyl-[2,2'-bipyridine]-4,4'-diyl)bis(4,1-phenylene))bis(phosphonic acid) (**1**) and  $L_{ancillary}$  is a 2,9-dimethyl-1,10-phenanthroline fused at the 5,6-positions with a 2'-functionalized imidazole or

substituted in the 4,7-positions with hole-transporting domains [36]. One of these ancillary ligands (**2**) which contains an *n*-butoxy-tailed hole-transporting domain was selected for an investigation of the composition of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte on the performance of the copper(I) dye [Cu(**1**)(**2**)]<sup>+</sup> (Scheme 1).

## 2 Experimental

### 2.1 Materials

Ligands **1** and **2** and the homoleptic complex [Cu(**2**)<sub>2</sub>][PF<sub>6</sub>], were prepared as previously described [36,37]. BMII, DMII, DMPI (1,2-dimethyl-3-propylimidazolium iodide), MBI (1-methylbenzimidazole), GNCS, NBB (*n*-butylbenzimidazole), TBP and VN were purchased from Sigma-Aldrich or Alfa Aesar and used as received.

### 2.2 DSSC fabrication

The FTO/TiO<sub>2</sub> working electrodes and the FTO/Pt counter electrodes were purchased from Solaronix (Solaronix Test Cell kit). Each working electrode was heated to 500 °C and allowed to cool to 80 °C prior to dipping into a 1 mM solution of the anchoring ligand **1** for 1 day. The electrodes were washed with DMSO and EtOH, and then dried in a stream of N<sub>2</sub>. The electrodes were soaked in a 0.1 mM MeCN solution of [Cu(**2**)<sub>2</sub>][PF<sub>6</sub>] for 3 days after which it was washed with MeCN and dried in N<sub>2</sub>. The electrodes were assembled using a thermoplast hot-melt sealing foil (Solaronix, Meltonix 1170-60) and filled with the respective electrolyte via vacuum-backfilling and finally assembled using the thermoplast hot-melt sealing foil and a

cover glass. N719 reference electrodes were made by immersing Solaronix Test Cell Titania Electrodes in a 0.3 mM EtOH solution of N719 (Solaronix) for 3 days. The electrodes were removed from the dye-bath, washed with EtOH, and dried in a stream of N<sub>2</sub>. For the counter electrodes, Solaronix Test Cell Platinum Electrodes were used, and volatile organic impurities were removed by heating on a heating plate at 450 °C for 30 min.

*J-V* measurements were performed using a SolarSim 150 (Solaronix) sun simulator, which was calibrated with a Si-reference cell to 1000 Wm<sup>-2</sup> prior to the measurements. All cells were completely masked [38,39]. Voltage decay was measured on a Modulab XM electrochemical system.

### **3 Results and discussion**

#### **3.1 Initial electrolyte screening**

Initial screening of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolytes having different compositions was carried out using the dye [Cu(**1**)(**2**)]<sup>+</sup> (Scheme 1) which was assembled on the electrode surface using our 'surface-as-ligands' approach [17,40]. Each FTO/TiO<sub>2</sub> electrode was soaked in a solution of the anchoring ligand **1** and, after drying, in a solution of the homoleptic dye [Cu(**2**)<sub>2</sub>][PF<sub>6</sub>] (see experimental section for details). The choice of additives and solvents for the electrolytes in the DSSCs was based on those reported in the literature [35,41,42], and their compositions are shown in Table 1.

Electrolytes E1, E4, E5 and E6 have previously been optimized for ruthenium(II) dyes [41,42], while electrolyte E8 is based on that reported by Colombo *et al.* for use with copper(I) dyes with carboxylic acid or carboxylate anchoring groups [35]. The

composition of electrolyte E10 corresponds to the standard composition used in our previous reports of copper(I)-based DSSCs. Several characteristic components of the electrolyte solution are changed across the series of electrolytes E1–E10 (Table 1): (i) the concentration of the I<sub>2</sub> and of the sources of I<sup>-</sup> (LiI and/or ionic liquid) as well as their ratio to each other, (ii) the additives TBP, NBB or GNCS, and (iii) the solvent. Historically, a mixture of MeCN and VN has been used to keep the vapour pressure of the electrolytes as low as possible and, therefore, minimize solvent evaporation. More recently, MPN has become a common choice of solvent in liquid DSSCs. Electrolyte E7 consists of the same components as E6, but uses an 85:15 v/v mixture of MeCN and VN instead of MPN.

Duplicate DSSCs were assembled for each electrolyte and their photoconversion efficiencies,  $\eta$ , were measured over a period of a week to confirm the stability of the devices. All cells were fully masked. A comparison of the  $\eta$  values for the better performing DSSC of each pair is displayed in Fig. 1. Electrolytes E6, E7 and E8 show superior performance with [Cu(1)(2)]<sup>+</sup> sensitized DSSCs with respect to E10 (our standard electrolyte in previous studies), while use of electrolytes E1–E5 and E9 leads to lower photoconversion efficiencies. Interestingly, E6 and E7 are the only electrolytes that do not include any lithium ions, which is in contrast to the results by Colombo *et al.* [35] who concluded that the presence of LiI in DCSs with copper-dyes is beneficial. The only source of I<sup>-</sup> in the E6 and E7 electrolytes is the ionic liquid BMII. The significant improvement from E6 to E7 was obtained by a change in the solvent from a mixture of MeCN and VN (85:15 v/v) to MPN. All DSSCs, irrespective of their performance, are stable over a week (Fig. 1).

Fig. 2 shows the  $J$ - $V$  curves for DSSCs using E6, E7 and E8 in comparison to those with E10 on the day of sealing the DSSCs and one week later. Values of  $V_{OC}$ ,  $J_{SC}$ , fill factor ( $ff$ ) and  $\eta$  are given in Table 2. The data are compared to the performance of a DSSC containing the ruthenium dye N719; the electrolyte for these DSSCs was E10. The final column in Table 2 gives the relative efficiencies of the copper-containing DSSCs with respect to devices with N719 for which the efficiency is set to 100%. Fig. 2 and Table 2 reveal that the improved performance of E7 with respect to the other three electrolytes arises from significantly enhanced  $J_{SC}$ . On the day of DSSC fabrication, the  $J_{SC}$  for the DSSC with electrolyte E7 is  $7.85 \text{ mA cm}^{-2}$  compared to  $4.30 \text{ mA cm}^{-2}$  for E10 (our 'standard electrolyte') on the same day. Fig. 2 shows no gain in  $V_{OC}$  on going from E10 to E7. DSSCs containing electrolytes E6 and E8 exhibit both higher  $J_{SC}$  and  $V_{OC}$  values compared to cells with E10. Values of  $ff$  are comparable ( $\sim 70\%$ ) for all of the DSSCs (Table 2)

### 3.2 Optimization of the electrolyte E7

Based on the performance of DSSCs containing electrolyte E7 (Table 2, Fig. 1 and 2), the four components of E7 were systematically varied to determine the optimal composition for combination with the dye  $[\text{Cu}(\mathbf{1})(\mathbf{2})]^+$  in DSSCs. Table 3 shows the electrolyte compositions that were investigated. To understand the influence of each component, only one parameter was changed at a time. Electrolytes E7a-E7d were prepared to study the effect of a change in  $\text{I}_2$  concentration on DSSC performance. All other component concentrations remained constant. The concentration of  $\text{I}_2$  is calculated by weight per volume, and the actual  $\text{I}_2$

concentration in the electrolyte after equilibration with the other electrolyte components was not determined. In electrolytes E7e-E7g, the concentration of BMII was halved with respect to electrolytes E7a-F7c (Table 3). In electrolytes E7h-E7j, the concentration of BMII is further reduced; pairs of electrolytes E7a/E7h, E7b/E7i, and E7c/E7j contain the same  $[I_2]$  and differ only in the  $[BMII]$ .

Fig. 3 shows  $J-V$  curves for DSSCs containing the dye  $[Cu(1)(2)]^+$  and electrolytes E7a-E7d. These electrolytes vary only in the concentration of  $I_2$  (Table 3). A decrease in  $[I_2]$  from 0.30 M (electrolyte E7a) to 0.06 M (E7b) to 0.015 M (E7c) results in a substantial rise in  $J_{sc}$  (Fig. 3 and Tables 4 and S1); maximum values were 6.16 and 6.01  $mA\ cm^{-2}$  for two independent DSSCs containing E7c. Use of  $[I_2] = 0.015\ M$  also led to the highest  $V_{oc}$  (547 and 549 mV, Table S1). Fill-factors for the DSSCs with electrolytes E7a-E7c lie in the range 64-73%. However, when the  $I_2$  concentration is further reduced to 0.005 M (electrolyte E7d), the  $ff$  values fall to 52 and 56% for duplicate cells, and no further gain in  $J_{sc}$  is observed (Fig. 3).

Trends in DSSC photoconversion efficiencies as a function of both  $[I_2]$  and  $[BMII]$  are shown in Fig. 4, and the DSSC parameters are summarized in Tables 4 and S1. At low  $I_2$  concentrations, changing the BMII concentration does not significantly affect the DSSC efficiency. The detrimental effect on the photoconversion efficiencies of increasing the concentration of  $I_2$  to 0.3 M can be compensated to some extent by increasing the BMII concentration (right side of Fig. 4). The DSSCs combining  $[Cu(1)(2)]^+$  and electrolytes E7c or E7g achieve the highest values of  $J_{sc}$  (ranging from 6.01–6.16  $mA\ cm^{-2}$  for the duplicate cells) and consistently good values of  $V_{oc}$  (547–552 mV for the duplicate cells), leading to the

highest values of  $\eta$  (2.10–2.27%); see Tables 4 and S1 for all data. Interestingly, the highest  $V_{oc}$  values (579 and 593 mV, Table S1†) are observed when electrolyte E7e (the highest  $I_2$  concentration tested) is combined with the dye  $[Cu(1)(2)]^+$ , but these DSSCs exhibit very poor  $J_{sc}$  (Tables 4 and S1) leading to photoconversion efficiencies of ca. 0.6%. This initial phase of the electrolyte optimization indicates that a low  $I_2$  concentration is beneficial and that, with this caveat, variation of the BMII concentration within the range 0.01–0.6 M has only a small impact.

Once the optimized concentrations  $I_2$  and BMII had been determined, the influence of changes in the concentrations of the additives TBP and GNCS was investigated. The best performing electrolyte from the previous experiments, electrolyte E7c, was used as a starting point. Electrolytes E7k and E7l have, respectively, a 10-fold increased concentration of GNCS with respect to E7c, and no GNCS. Electrolytes E7m and E7n comprise 10-times more TBP than E7c, and no TBP, respectively. Table 5 presents parameters for duplicate DSSCs containing electrolytes E7c and E7k-E7n, and Fig. 5 compares their performances. The data in Table 5 are compared to a reference DSSC sensitized with the standard ruthenium dye N719; the electrolyte for this cell was the standard E10 (Table 1). The last column in Table 5 gives the photoconversion efficiency for each DSSC relative to N719 set to 100%.

Although the presence or absence of GNCS leads to some variation in  $J_{sc}$  and  $V_{oc}$  (Fig. 6), it does not have a significant influence on the overall efficiency. DSSCs with electrolytes E7c, E7k and E7l show relative values of  $\eta$  in the range 29.5-33.8% (absolute values 1.98-2.27%). As discussed earlier, GNCS is known to reduce surface

electron recombination, but also shifts the band edge to more positive potential. These two contrary effects lead to a complicated response of the DSSCs upon a change in GNCS concentration. The lower  $J_{SC}$  values observed in the absence of GNCS in E7l (Table 5) are consistent with reduced charge injection from the dye into the semiconductor as a consequence of the higher conduction band edge of  $TiO_2$  as reported by Zhang [31]. By adding GNCS to the electrolyte solution at a concentration of 0.01M (E7l to E7c in Fig. 6),  $J_{SC}$  improves, but with a simultaneous decrease in  $V_{OC}$ . A 10-fold increase in the concentration of GNCS (E7c to E7k in Fig. 6) results in an increase in  $V_{OC}$  consistent with reduced surface recombination. This was confirmed by voltage decay measurements (see below). However, the origin of the loss in current density is unclear.

Increasing the concentration of TBP leads to the expected [27,29,43,44] increase in  $V_{OC}$  (to 576 and 579 mV, Table 5 and Fig. 7) due to a reduced recombination rate. However, it also causes a reduction in  $J_{SC}$  (Fig. 7) and, overall, the DSSC performance decreases (Table 5). The low  $J_{SC}$  values may arise from reduced ion mobility since greater amounts of TBP significantly increases the viscosity of the electrolyte solution. Based on results of Ashbrook and Elliott [45], the inferior  $J_{SC}$  values may also be attributed to formation of a copper(II)-TBP adduct (Cu(II) being present in the excited state of the dye) to remove some of the dye molecules from participation in photoinjection for a period of time; under illumination, the TBP renders some of the copper dye inactive [45]. Use of electrolyte E7n with no TBP has the opposite effect: higher  $J_{SC}$  and lower  $V_{OC}$  with respect to the cells with E7c (0.4 M TBP). The reduction in  $V_{OC}$  (E7c to E7m) is

mainly attributed to an increased recombination rate (see voltage decay measurements below) and is consistent with the absence of surface passivation by TBP as reported by Boschloo and Hagfeldt [29].

Fig. 8 shows voltage decay curves for the duplicate [Cu(1)(2)]<sup>+</sup>-sensitized DSSCs listed in Table 5. Pairs of DSSCs show consistent results and retain a value of  $V_{OC} \geq 110$  mV after 40 seconds. However, there are significant differences in the values of  $V_{OC}$  after 40 s, as well as the initial decay within the first 5-10 s, for DSSCs containing different electrolytes. In agreement with the literature (discussed above), the incorporation of GNCS and TBP significantly reduces the surface recombination rate. DSSCs with electrolytes E7k and E7m, having a 10-times more GNCS and TBP, respectively, compared to DSSCs with E7c, show reduced recombination rates. In contrast, the recombination rate is significantly higher in the absence of either of these additives (E7l and E7n).

#### **4 Conclusions**

The composition of the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> liquid electrolyte in DSSCs sensitized with [Cu(1)(2)]<sup>+</sup> has been tuned to improve photoconversion efficiency. Our starting point was our standard electrolyte (optimized for ruthenium(II) dyes). This electrolyte comprises LiI (0.1 M), I<sub>2</sub> (0.05 M), BMII (0.6 M), 1-methylimidazole (0.5 M) in MPN solvent. An initial screening of ten compositions in which the solvent, additives, concentration of I<sub>2</sub>, and concentration and origin (LiI or BMII) of I<sup>-</sup> was varied led to optimal performance with an electrolyte comprising I<sub>2</sub> (0.03 M), BMII (0.6 M), TBP (0.4 M) and GNCS (0.1 M) in MPN; no LiI was added. High values of  $J_{sc}$  (7.85 and 7.60 mA

cm<sup>-2</sup>) contributed to values of  $\eta = 2.64$  and  $2.70\%$ , for duplicate, masked DSSCs. However, values of  $V_{OC} = 489$  and  $499$  mV could be improved upon by tailoring the additives and concentrations of I<sub>2</sub> and BMII. A low concentration of I<sub>2</sub> (0.015 M) proved best, and at this concentration, altering the amount of BMII (0.1–0.6 M) in the electrolyte has little effect on the overall photoconversion efficiency. Although GNCS lowers the rate of electron recombination (confirmed by OCVD measurements), whether or not it is present in the electrolyte has minimal effect upon  $\eta$ . An increase in the concentration of TBP lower DSSC performance. The final optimized electrolyte comprised I<sub>2</sub> (0.015 M), BMII (0.6 M), and GNCS (0.01 M) in MPN (no LiI); the best performing DSSC containing this electrolyte with the dye [Cu(1)(2)]<sup>+</sup> gave values of  $J_{SC} = 7.80$  mA cm<sup>-2</sup>,  $V_{OC} = 501$  mV and  $\eta = 2.76\%$  (relative to  $6.72\%$  for N719). This investigation complements that of Colombo *et al.* [35] in showing that there is a need to further tailor the composition of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> liquid electrolytes for use with copper(I)-based sensitizers.

### **Acknowledgements**

We thank the Swiss National Science Foundation (Grant number 200020\_144500), the European Research Council (Advanced Grant 267816 LiLo) and the University of Basel for financial support.

### **Appendix**

Supplementary Information available: Table S1: DSSC parameters for duplicate cells.

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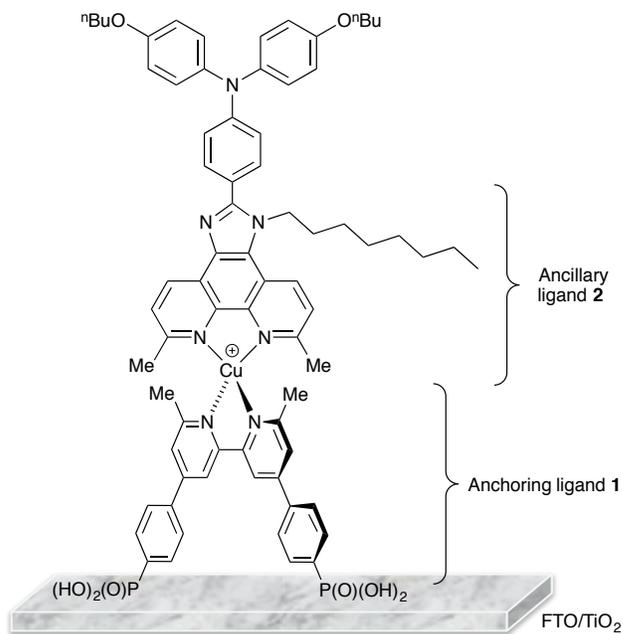
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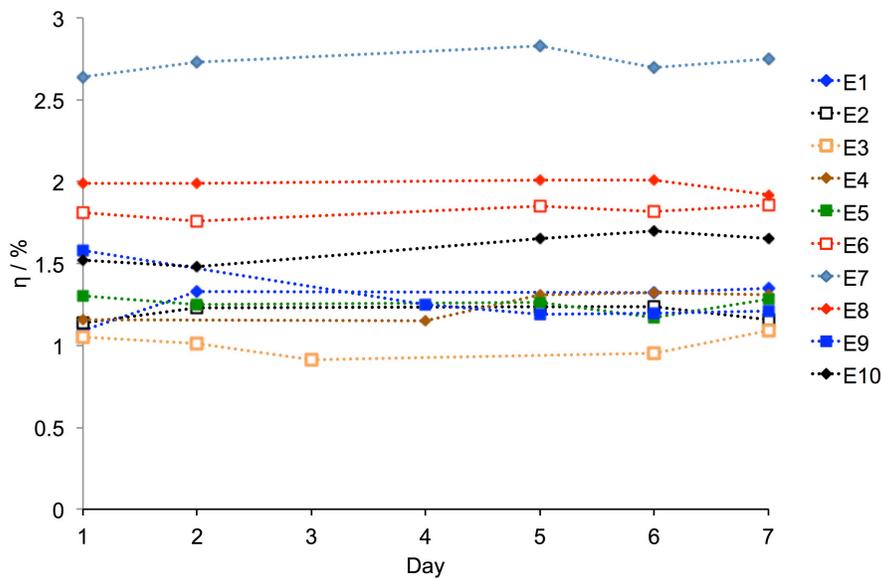
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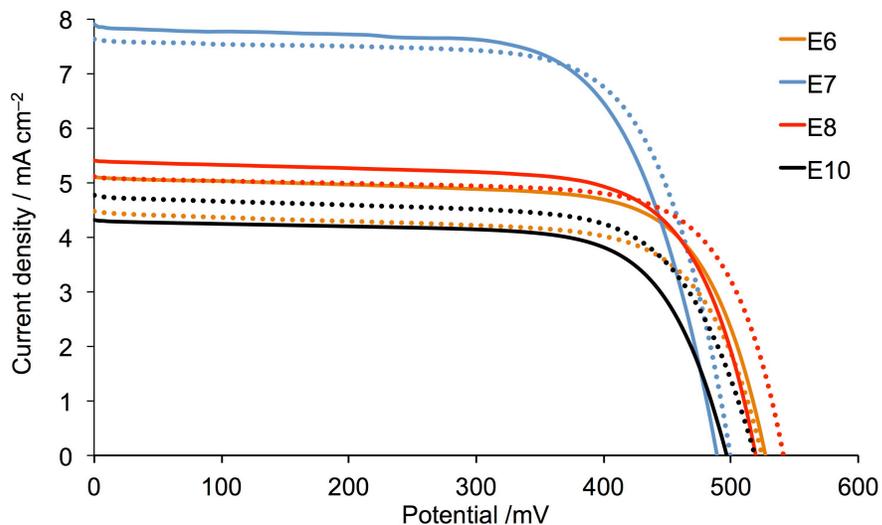
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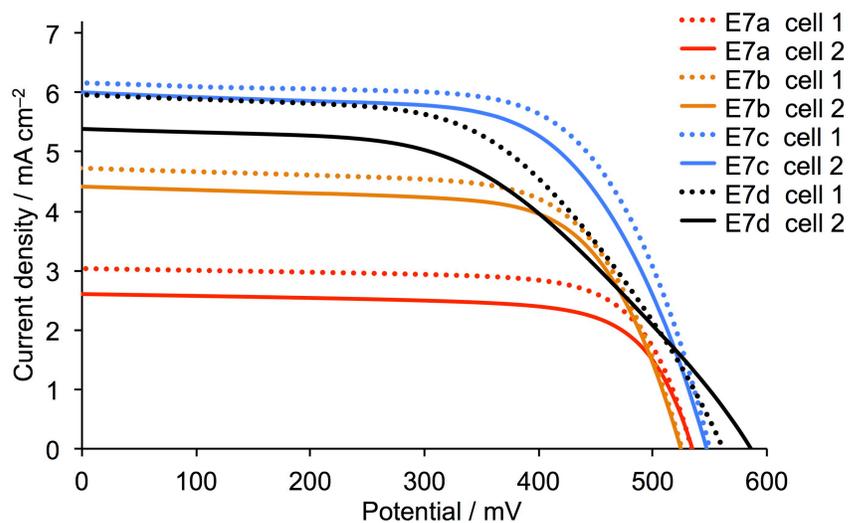
Scheme 1. The copper(I) dye  $[\text{Cu}(\mathbf{1})(\mathbf{2})]^+$  used in this study.



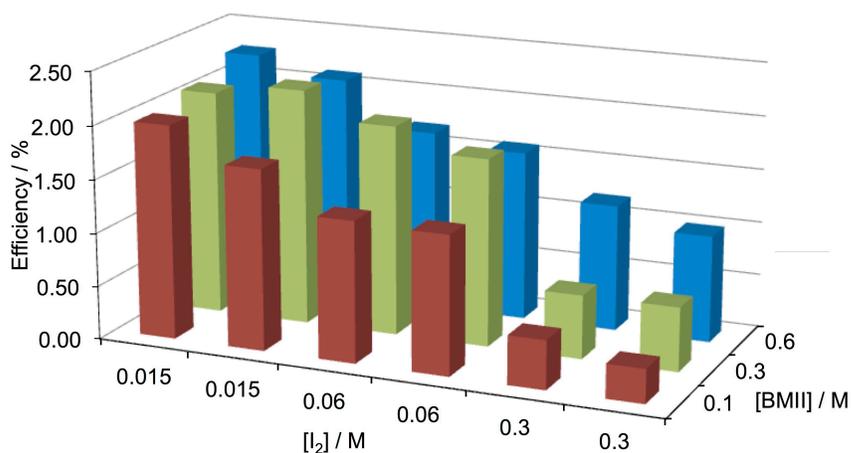
**Fig. 1.** Photoconversion efficiencies and stabilities of DSSCs containing the dye  $[\text{Cu}(\mathbf{1})(\mathbf{2})]^+$ . Electrolytes E1–E10 are defined in Table 1.



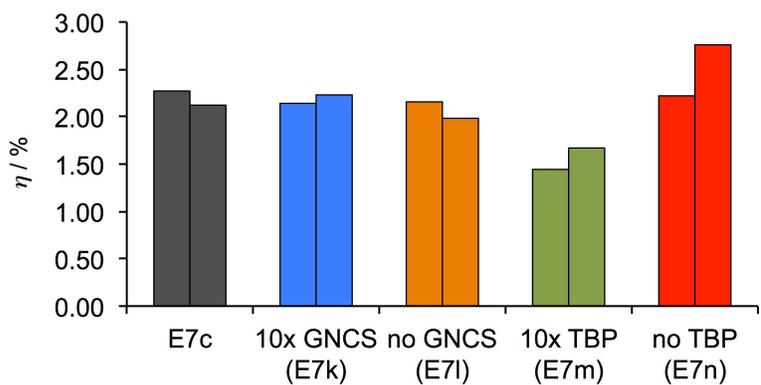
**Fig. 2.**  $J$ - $V$  curves for DSSCs containing the dye  $[\text{Cu}(1)(2)]^+$  and the best performing electrolytes from the initial screening; curves were recorded on the day of sealing the DSSCs (solid curves) and after one week (dotted curves).



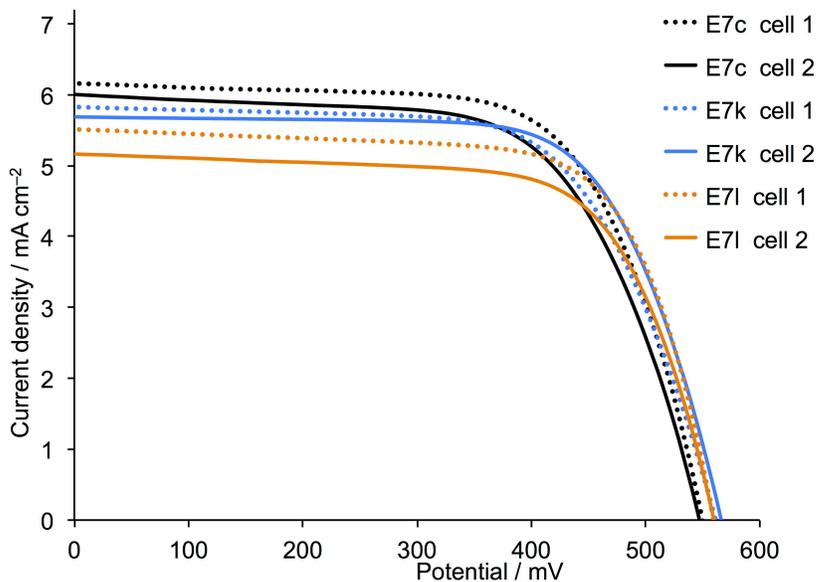
**Fig. 3.**  $J$ - $V$  curves for duplicate DSSCs containing the dye  $[\text{Cu}(1)(2)]^+$  and electrolytes E7a-E7d (Table 3) to show the effect of reducing the concentration of  $\text{I}_2$  from 0.30 to 0.005 M.



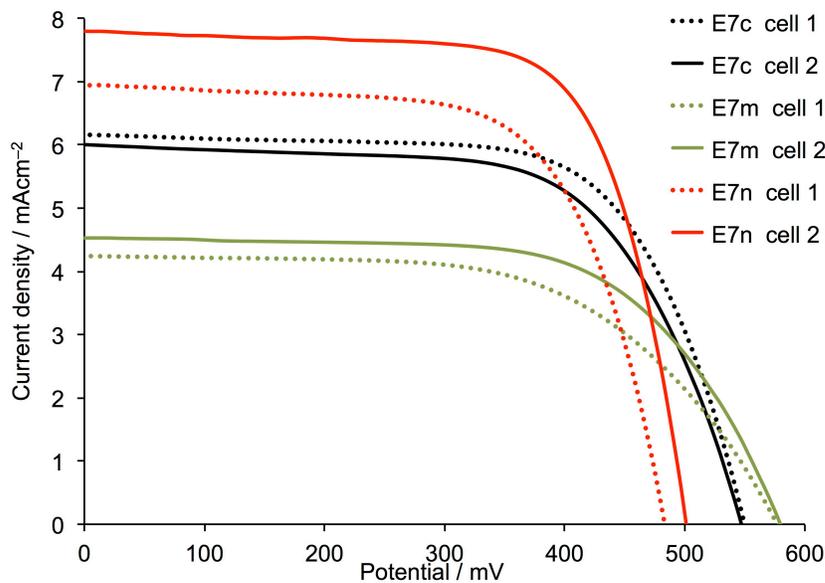
**Fig. 4.** 3D-plot of the efficiencies of duplicate DSSCs sensitized with  $[\text{Cu}(1)(2)]^+$  and varying  $\text{I}_2$  and BMII concentrations.



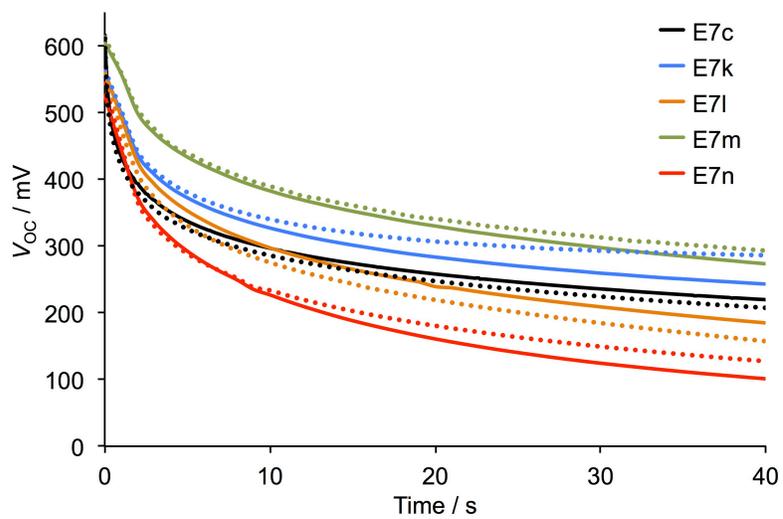
**Fig. 5.** The effects of increasing the concentrations of, or leaving out, the GNCS and TBP additives in the  $\text{I}_3^-/\text{I}^-$ -based electrolyte in duplicate DSSCs containing the dye  $[\text{Cu}(1)(2)]^+$ . Electrolytes E7c, E7k, E7l, E7m and E7n are defined in Table 3.



**Fig. 6.**  $J$ - $V$  curves for duplicate DSSCs containing the dye  $[\text{Cu}(\mathbf{1})(\mathbf{2})]^+$  and electrolytes E7c (0.01 M GNCS), E7k (0.10 M GNCS) and E7l (no GNCS); curves were recorded on the day of sealing the DSSCs. Each electrolyte contains 0.015 M  $\text{I}_2$ , 0.6 M BMII and 0.4 M TBP.



**Fig. 7.**  $J$ - $V$  curves for duplicate DSSCs containing the dye  $[\text{Cu}(\mathbf{1})(\mathbf{2})]^+$  and electrolytes E7c (0.4 M TBP), E7m (4.0 M TBP) and E7n (no TBP); curves were recorded on the day of sealing the DSSCs. Each electrolyte contains 0.015 M  $\text{I}_2$ , 0.6 M BMII and 0.01 M GNCS.



**Fig. 8.** Open circuit voltage decay (OCVD) measurements of duplicate  $[\text{Cu}(1)(2)]^{+}$ -sensitized DSSCs containing electrolytes E7c, E7k-E7n.