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ARTICLE

Improving copper-dye-sensitized solar cells efficiency by manipulating the electrolyte solution

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The use of a copper(I) dye, bearing a 2,9-dimesityl-1,10-phenanthroline and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid, was investigated in DSSCs with various electrolyte solutions based on two different redox mediators, namely the common I^-/I_3^- couple and an interesting copper electron shuttle. The experimental results put in evidence the importance of the redox mediator concentration and the crucial role of additives such as 4-*tert*-butylpyridine and lithium bis(trifluoromethanesulfonyl)imide on the performance of sustainable "full-copper" DSSCs, consolidating the way to DSSCs with earth-abundant components.

Introduction

Since the discovery of Grätzel-type dye-sensitized solar cells (DSSCs) as a convenient way for the conversion of solar to electrical energy [1], there has been a phenomenal amount of work to improve their photoconversion efficiency (η) [2]. In particular, a lot of effort has been devoted to optimize the sensitizer [3-8] and the redox mediators [8-13]. Except for a few organic or zinc(II) porphyrin-sensitized solar cells which reach up to 14% efficiency [14-16], the best photovoltaic performances (*ca.* 11 % efficiencies) have so far been achieved with ruthenium complexes such as *cis*-di(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylate)Ru(II) and the related doubly deprotonated complex (N719) [17] with the iodide/triiodide couple (I^-/I_3^-) as electrolyte [18,19]. Cyclometalated ruthenium complexes represent good alternatives for application in DSSCs, due to their higher stability [20-28]. However, a drawback of these sensitizers is the scarcity of ruthenium in the earth's crust and its high cost. For this reason, in the last few years, an exponential amount of work has been dedicated to the use of dyes based on earth abundant metals such as environmental-friendly copper(I) complexes in combination with the I^-/I_3^- redox mediator [6-8, 29-39]. Their photoconversion efficiencies are still lower than the values obtained for state-of-the-art ruthenium(II) dyes, but it is important to point out that the dye structures and dye/electrolyte combinations in the ruthenium-based DSSCs have been optimized for almost 30 years whereas copper-based DSSCs are still in their infancy and, with systematic tuning of dye and electrolyte components [6-8, 35-37] and the use of co-sensitization [38], enhanced performances are progressively being reached.

The actual 4.66% record efficiency, corresponding to a remarkable 63% relative efficiency (η_{rel} [40]) respect to a N719-sensitized control cell set at 100%, was obtained with a copper(I) complex having as anchoring ligand a 4,4'-dicarboxylic acid-6,6'dimesityl-2,2'-bipyridine and, as ancillary ligand, a 4,4'-bis(N,N diethylaminestyryl)-6,6'dimethyl-2,2'-bipyridine, using the I^-/I_3^- redox mediator [39]. It should be pointed out that this record value was reached with unmasked cells [39] and therefore could be overestimate. In fact, masking the cells is crucial in order to have accurate values of photo-conversion efficiency [41].

Besides, the long term incompatibility of copper complexes with I^-/I_3^-, due to the low solubility of CuI [42,43], and the problems related to this redox couple [8], led to the preparation of iodine-free copper(I) solar cells. The use of $[Co(2,2'-bipyridine)_3]^{2+/3+}$ as redox couple was the first important step towards the development of this kind of DSSCs [44]. In parallel, the fact that $Cu^{+/2+}$ mediators can outperform both iodine-based and Co-based electrolytes in combination

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with various dyes [45-50] along with the ability of Cu mediators to solve the thermodynamic and kinetic dichotomies of the device operation [51-53] were the springboard for the development of "full-copper" DSSCs [54-55]. A promising photoconversion efficiency (2.06% corresponding to 38.1% relative to N719 set at 100%, masked cells [41]) was reached with a copper(I) dye, bearing one 4,4'-dimethoxy-6,6'-dimethyl-2,2'-bipyridine and a phosphonic acid anchor, and a copper redox mediator bearing two 4,4'-dimethoxy-6,6'-dimethyl-2,2'-bipyridines [55]. In parallel we found that the use of a heteroleptic copper dye (**D1**, Chart 1), bearing one 2,9-dimesityl-1,10-phenanthroline and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid anchoring ligand, in combination with an homoleptic copper(I/II) complex bearing two 2-n-butyl-1,10-phenanthrolines (**E1/E2**, Chart 1) as electron shuttle, allows to reach a fair photoconversion efficiency (1.4% corresponding to 16% η_{rel}, masked cells [41]) although lower than that obtained with the conventional I^-/I_3^- couple as electrolyte [54, 56]. These first examples of full-copper solar cells [54,55] open a new route for cheap and environmentally friendly DSSCs. Now effort should be devoted to improve their photoconversion efficiency.

In the present work, we focus the attention on DSSCs based on **D1** as dye and **E1/E2** as redox mediator, investigating the effect of both the electrolyte solution concentration and the addition of 4-*tert*-butylpyridine and lithium bis(trifluoromethanesulfonyl)imide.
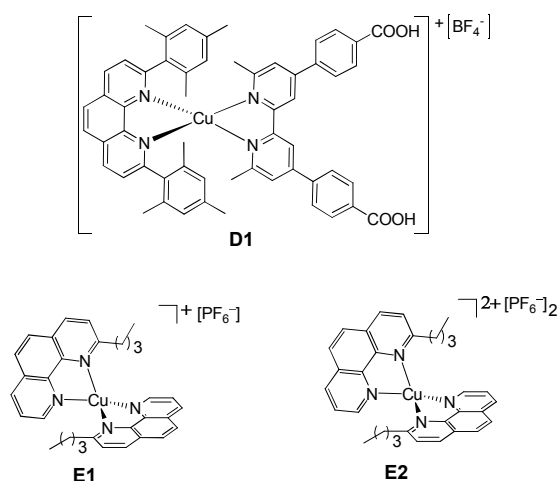

Chart 1. Chemical structures of the investigated dye (**D1**) and copper-based redox mediators (**E1/E2**).

Experimental

Synthesis of copper complexes

The dye and the redox mediators were prepared as we previously reported [54].

Fabrication and evaluation of solar cells

TiO$_2$ electrodes were prepared by spreading (doctor blading) a colloidal TiO$_2$ paste (20 nm sized; "Dyesol" DSL 18NR-T) onto a conducting glass slide (FTO, Hartford glass company, TEC 8, with a thickness of 2.3 mm and a sheet resistance in the range 6-9 Ω/cm^2) that had been cleaned with water and EtOH, treated with a plasma cleaner at 100 W for 10 min, dipped in aqueous TiCl$_4$ solution (4.5 x 10^{-2} M), at 70°C, for 30 min, and washed with ethanol. After a first drying at 125°C for 15 min, a reflecting scattering layer containing >100 nm sized TiO$_2$ ("Solaronix" Ti-Nanoxide R/SP) was bladed over the first TiO$_2$ coat and sintered till 500°C for 30 min. Then the glass coated TiO$_2$ was dipped again into a freshly prepared aqueous TiCl$_4$ solution (4.5 x 10^{-2} M), at 70°C for 30 min, washed with ethanol and heated once more at 500°C for 15 min. At the end of these operations the final thickness of the TiO$_2$ electrode was in the range 8–12 μm, as determined by SEM analysis. After the second sintering, the FTO glass coated TiO$_2$ was cooled at about 80°C and immediately dipped into a methanol solution (1.5x10^{-3} M, previously prepared and maintained in a dry N$_2$ atmosphere) of the dye at room temperature for 24 h. The dyed titania-glasses were washed with EtOH and dried at room temperature under a N$_2$ flux. Finally, the excess of TiO$_2$ was removed with a sharp teflon penknife. A 50 μm thick Surlyn spacer (TPS 065093-50 from Dyesol) was used to seal the photoanode and a platinized FTO counter electrode. Then the cell was filled up with the desired electrolyte solution (see details reported in Table 1). The photovoltaic performance of the cells was measured with a solar simulator (Abet 2000) equipped with a 300 W Xenon light source; the light intensity was adjusted with a standard calibrated Si solar cell ("VLSI Standard" SRC-1000-RTD-KG5); the current-voltage characteristics were acquired by applying an external voltage to the cell and measuring the generated photocurrent with a "Keithley 2602A" (3A DC, 10A Pulse) digital source meter. For a given complex and configuration, at least four different devices were made and characterized in different days; the difference between the average and the highest or lowest efficiency values was usually lower than 5%. The PV parameters were calculated taking into account the values of the active areas (generally in the range 13 – 15 mm^2) measured by a microphotography. In the case of masked devices, a black mask with a 4x4 mm^2 square opening, realized with cutting plotter, was carefully placed over the devices making sure to completely leave uncovered the photoanodes. IPCE measurements were performed in DC mode in the 300 – 900 nm region, with a Bentham PVE300 instrument equipped with a xenon QTH lamp, a TMc300 monochromator and a Stanford SR830 DSP amplificatory.

Results and discussion

We prepared, with the HETPHEN synthetic method [57], the copper(I) dye **D1** (Chart 1) bearing one 2,9-dimesityl-1,10-phenanthroline, where the mesityl groups provide enough steric hindrance to avoid the formation of homoleptic complexes and prevent geometric changes on going from Cu(I) to Cu(II) [58], and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid, chosen as anchoring ligand because of its particular goodness to anchor the dye on the titania surface [31, 54]. The performance of **D1** in DSSCs was investigated with various electrolyte solutions based on two

different redox mediators, namely the common I^-/I_3^- couple and the recently reported copper electron shuttle **E1/E2** (Chart 1) [54]. Dye-sensitized solar cells were fabricated using FTO glass coated TiO$_2$ sensitized with **D1** as photoanode, a platinized FTO as counter electrode and an electrolyte solution containing I^-/I_3^- or **E1/E2** as redox couple (see Experimental). Results of the investigated fully masked thin film DSSCs are presented in Table 1 together with those obtained with the Ru(II) benchmark **N719**. In addition to the absolute photoconversion efficiency (η), Table 1 reports the efficiency relative to a cell based on the **N719** dye and I^-/I_3^- electrolyte set at 100% (η$_{rel}$). Figure 1 shows the current density *vs* voltage curves of the devices under AM 1.5 simulated solar illumination with a power light intensity of 100 mW cm^{-2}.

It turned out that the masked dye-sensitized solar cell, based on **D1** as dye and containing I^-/I_3^- as redox shuttle, has a 3.05 % photo-conversion efficiency (Table 1, entry 2). This performance is remarkable for such a simple dye.

Table 1. Main PV parameters of DSSCs based on copper dye **D1**
(in the presence of a 4x4mm^2 square opening black mask)

	Dye	Electrolyte	J_{SC} mA cm^{-2}	V_{OC} mV	*FF*	η%	η$_{rel}$ %^{a}
1	N719	I^-/I_3^- ^{b}	15.17	659	68.7	6.87	100%
2	D1	I^-/I_3^- ^{c,d}	6.17	670	73.9	3.05	44.4%
3	D1	I^-/I_3^- ^{c,e}	6.41	648	73.0	3.03	44.1%
4	D1	0.085M E1 0.0085M E2 0.05M LiTFSI^{f,g}	4.06	606	63.9	1.57	22.9%
5	D1	0.085M E1 0.0085M E2 0.05M LiTFSI^f 0.14M *t*BuPy	3.69	708	62.7	1.64	23.9%
6	D1	0.038M E1 0.0038M E2 0.022M LiTFSI^f	4.35	630	63.1	1.73	25.2%
7	D1	0.038M E1 0.0038M E2 0.022M LiTFSI^f 0.062M *t*BuPy	2.88	725	59.9	1.25	18.2%
8	D1	0.085M E1 0.0085M E2 0.1M LiTFSI^f 0.28M *t*BuPy	5.77	622	70.1	2.51	36.5%
9	D1	0.038M E1 0.0038M E2 0.1M LiTFSI^f 0.28M *t*BuPy	4.98	543	66.2	1.84	26.8%
10	D1	0.085M E1 0.0085M E2 0.1M LiTFSI^f 0.28 *t*BuPy 0.26M MBIPF$_6$^{h}	2.22	705	56.0	0.88	12.8%

^{a}Relative efficiency respect to a N719-sensitized control cell set at 100%. ^{b}0.6M *N*-methyl-*N*-butylimidazolium iodide, 0.03M iodine, 0.1M guanidinium thiocyanate, 0.5M *t*-BuPy in 15/85 (v/v) mixture of valeronitrile/acetonitrile. ^{c}0.26M *N*-methyl-*N*-butylimidazolium iodide, 0.01M LiI, 0.017M iodine, 0.28M *t*-BuPy in 15/85 (v/v) mixture of valeronitrile/acetonitrile. ^{d}by working with 0.65M *N*-methyl-*N*-butylimidazolium iodide, 0.025M LiI, 0.04M iodine, and 0.28M *t*-BuPy, PV parameters

are: J_{sc} = 6.1 mA cm^{-2}, V_{OC} = 592 mV, FF= 71, η = 2.5% [56]. ^{e}0.025M guanidinium iodide is present. ^{f}LiTFSI is lithium bis(trifluoromethanesulfonyl)imide; all the electrolyte solutions containing the **E1/E2** redox couple are in acetonitrile. ^{g}by working with 0.17M Cu(I), 0.017M Cu(II) and 0.1M LiTFSI in acetonitrile, PV parameters are: J_{sc} = 3.8 mA cm^{-2}, V_{OC} = 593 mV, FF = 61, η=1.4% [56]. ^{h}MBIPF$_6$ is [*N*-methyl-*N*-butylimidazolium][PF$_6$].

Remarkably, the DSSC based on **D1** as dye and I^-/I_3^- as redox shuttle (entry 2) has a photoconversion efficiency much higher than that previously reported by using the same 4-*tert*-butylpyridine concentration but a 2.5 times more concentrated electrolyte solution based on the same redox shuttle (η = 2.5 %; η$_{rel}$ = 28%, masked cell) [56], due to an increase of J_{SC}, V_{OC}, and *FF*. This result is of particular interest, showing that it is possible to improve the DSSC efficiency by simply manipulating the electrolyte solution concentration. Addition of guanidinium iodide doesn't have a significant effect on the photoconversion efficiency since the observed increase of J_{SC} is perfectly balanced by the corresponding decrease of V_{OC} (compare entries 2 and 3).

Figure 1. Current Density-Voltage characteristics of masked DSSCs in the presence of **D1** as dye and various electrolytes.

- – – Entry 2; —— Entry 4; —— Entry 5; - - - Entry 6;
- – – Entry 7; —— Entry 8; —— Entry 9; —— Entry 10
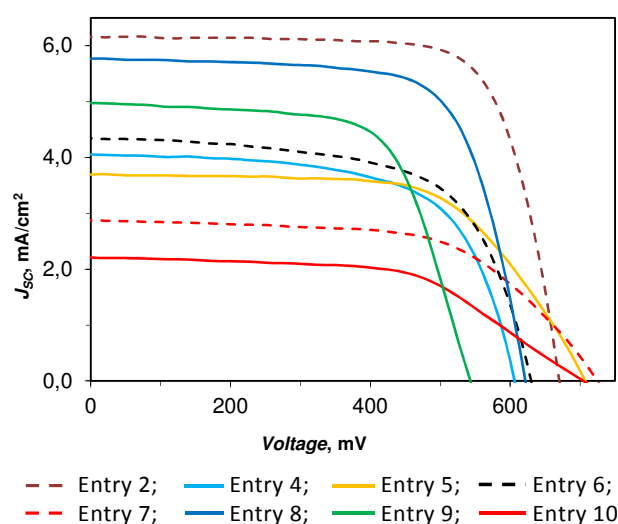
These results prompted us to study the effect of the electrolyte solution concentration in "full-copper" DSSCs. We recently reported that substitution of the I^-/I_3^- redox couple by the **E1/E2** couple leads to a lower but still good efficiency (η = 1.4%; η$_{rel}$ = 16%), by working with 0.17M Cu(I), 0.017M Cu(II) and 0.1M LiTFSI in acetonitrile [56]. In the present work we found that dilution by a factor of two leads to an enhancement of J_{sc}, *FF* and V_{OC} affording a higher photo-conversion efficiency (Table 1, entry 4; η = 1.57 %, η$_{rel}$ = 22.9%). Further dilution, up to a factor of 4.5 with respect to the original concentration, leads to an even better performance (entry 6, η = 1.73 %, η$_{rel}$ = 25.2%), due to a simultaneous increase of J_{sc} and V_{OC}. The increase of the short-circuit photocurrent observed upon dilution of **E1/E2** can be attributed to the less competitive light harvesting of **E1** (λmax= 452 nm [54]) with the dye **D1** (λmax= 478 nm [54]). IPCE measurements (Figure 2) supported this interpretation, in fact devices deriving from entry 4 and entry 6 are very similar and differ only in the 400 – 480 nm region, where in the

presence of a more diluted electrolyte a slightly higher external quantum efficiency was measured accordingly with the corresponding J_{sc}. In both cases, addition of 4-*tert*-butylpyridine (in a molar ratio 2.8, with respect to LiTFSI, (entries 5 and 7) produces a significant increase of V_{OC} (about 100 mV), but the corresponding lower J_{sc} and *FF* lead to a similar (entry 5, η = 1.64 %, η$_{rel}$ =23.9%, to be compared with entry 4) or lower (entry 7, η = 1.25 %, η$_{rel}$ =18.2%, to be compared with entry 6) efficiency.

Figure 2. IPCE characteristics of selected DSSCs in the presence of **D1** as dye and various electrolyte compositions

Entry 4;   – – – Entry 6;   —— Entry 8;   —— Entry 9
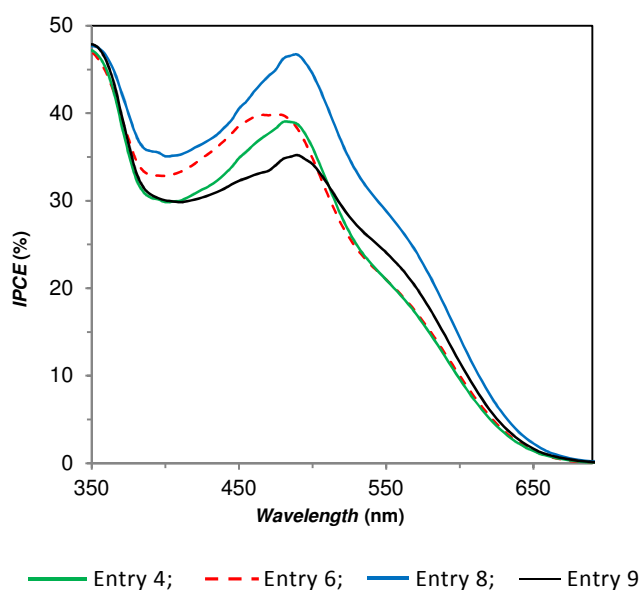
However, surprisingly, by keeping the same **E1/E2** concentration as in entry 4 and adding LiTFSI and *t*-BuPy, maintaining the 1:2.8 molar ratio but with a double concentration, we obtained a significant increase of all the photovoltaic parameters (J_{SC}, V_{OC}, and *FF*) and in these conditions a much higher efficiency is reached (entry 8, η = 2.51 %, η$_{rel}$ = 36.5%). We observed the same effect also in the presence of a **E1/E2** concentration decreased by a factor of 2.3, but with this setting we recorded an increase only for J_{SC} and *FF*, while V_{OC} decreased by almost 100 mV (entry 9 *versus* entry 6), consequently the growth in efficiency was lower compared to entry 8. The corresponding IPCE data, which agree with the current density/voltage measurements, are shown in Figure 2. Finally, the addition of [*N*-methyl-*N*-butylimidazolium][PF$_6$] (MBIPF$_6$/**E1**= 3, molar ratio), in our more powerful electrolyte solution, produced a noteworthy growth of the V_{OC}, but also an important loss in J_{SC} and *FF*, so the efficiency was reduced to about one-third with respect to our best result (entry 10, η = 0.88 %, η$_{rel}$ = 12.8%). This result shows the negative effect of MBIPF$_6$ in the optimization of the electrolyte solution for efficient "full-copper" DSSCs.

Remarkably, the simultaneous increase of the molar ratio LiTFSI/**E1** (in the range 1.2 – 2.6) and *t*-BuPy/**E1** (in the range 3.3 – 7.4) has a positive effect on the performance of the cell, allowing, to our knowledge, to reach the best absolute efficiency (entry 8, η = 2.51 %) reported up to now for a "full-copper" solar cell. It has been reported that 4-*tert*-butylpyridine can have a negative effect in the Cu-mediated redox couple bearing bipyridine or phenanthroline

ligands with methyl groups adjacents to the nitrogen donor atoms [59-62]. In fact, contrary to Cu(I) species, the Cu(II) counterparts tend to accept 4-*tert*-butylpyridine as ligand. It appeared that the so-formed penta-coordinated Cu(II) species have higher reorganization energies for the charge recombination process, causing lower recombination rates; they shift the electrolyte potentials to more negative values and cause higher diffusion resistances of the Cu complexes [62]. In contrast our results show that the presence of 4-*tert*-butylpyridine can have a positive influence on the performance of "full-copper" DSSCs. Therefore, future work should be devoted in order to better understand the role of this Lewis base.

Conclusions

In this work a heteroleptic copper(I) sensitizer bearing one 2,9-dimesityl-1,10-phenanthroline and a 6,6'-dimethyl-2,2'-bipyridine-4,4'-dibenzoic acid, **D1**, was used in DSSCs with the common I^-/I_3^- redox couple or a copper(I)/copper(II) couple. Very good efficiencies were reached. It appeared that the composition, as well as the molar ratios between the various components of the electrolyte solutions, plays a crucial role on the performance of the DSSCs. Upon dilution of the redox shuttle, there is an increase of the short-circuit photocurrent. Such an observation can be attributed to the less competitive light harvesting of the diluted electrolyte with respect to the dye. Manipulation of the electrolyte solution by using an adequate quantity of LiTFSI and *tert*-butylpyridine allows to improve greatly the "full-copper" DSSCs performance. Remarkably, for masked cells based on the same copper(I) dye **D1**, the best absolute efficiency reached with the copper(I)/copper(II) redox shuttle (η = 2.51 %) is 82% the best efficiency reached with the problematic I^-/I_3^- couple (η = 3.05 %), confirming the great potential of "full-copper" DSSCs and consolidating the way to DSSCs with earth-abundant components.

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41 An important information that should be clearly specified in reporting photoelectrochemical performances of DSSCs is whether the devices were masked or unmasked, being photocurrents influenced by this experimental shrewdness. Actually masking is the best practice and should be adopted always in order to have accurate values of photo-conversion efficiency. See H. J. Snaith, *Energy Environ. Sci*., 2012, **5**, 6513.

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