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New iridium complex as additive to the spiro-OMeTAD in perovskite solar cells with enhanced stability

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A new iridium complex, IrCp*Cl(PyPz)[TFSI], has been synthesized and used as additive for the hole transporter material, spiro-OMeTAD, in perovskite solar cells. The cells prepared with this Ir additive present higher efficiency than reference cells, and similar to cells prepared with Co additive. We have determined that the presence of metal complexes as additives decreases the recombination rate, as it has been observed by impedance spectroscopy. Very interestingly, while the efficiency after 3 months decreases by 22% and 70% for reference cell and cell with Co additive, respectively, the efficiency of devices containing the Ir additive is only decreased by a 4%. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4890545>]

Perovskites Solar Cells (PSCs) have attracted an enormous attention due to their impressive light to power conversion efficiency, easy manufacturing with low temperature processes, and simple layer deposition by solution methods.¹ PSCs were firstly prepared in sensitized configuration using liquid electrolyte obtaining promising results,² however, the undoubtedly major breakthrough was achieved when the all-solid configuration was exploited in 2012.^{3,4} Nowadays, efficiency of PSCs has broadly surpassed 17%,⁵ and many groups worldwide are in a competition to reach higher efficiencies and stabilities. A wide series of strategies have been reported for this purpose, which mainly consist in: (i) using different mixture of halides precursors;^{3,6-9} (ii) exchanging the organic cation methylammonium (MA)^{7,10,11} by other organic or inorganic cations;^{7,10,12} or (iii) using different selective contacts, especially hole transporter material (HTM).^{13,14}

Precisely, the use of new materials or modifications as HTM is a very large field to be explored. It has been demonstrated the effective use of solution-processable inorganic HTM as CuI¹⁵ and CuSCN,^{16,17} reporting efficiencies as high as 12.4%.¹⁷ Nevertheless the most extended HTM employed in PSCs are organic wherein the organic synthesis of conductive polymers or new molecules used as additives has a fundamental role. The most commonly used HTM in PSCs is spiro-OMeTAD (2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene).¹⁴ It is well known from the previous experience in Dye Sensitized Solar Cells (DSCs) that the solar cell performance is increased significantly when additives as 4-tert-butylpyridine and lithium bis(trifluoromethylsulphonyl)imide are added to the spiro-OMeTAD layer.¹⁸ In addition, it has also been reported that certain complexes, such as tris[2-(1H-pyrazol-1-yl)-4-tertbutylpyridine] cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (Co(PyPz)₃[TFSI]₃), further enhance the device performance. This Co additive greatly increases the overall efficiency of the PSCs through a simultaneous enhancement of both open circuit voltage, V_{oc} , and Fill Factor, FF , due to the reduced carrier recombination and lower Fermi level of HTM.¹⁹

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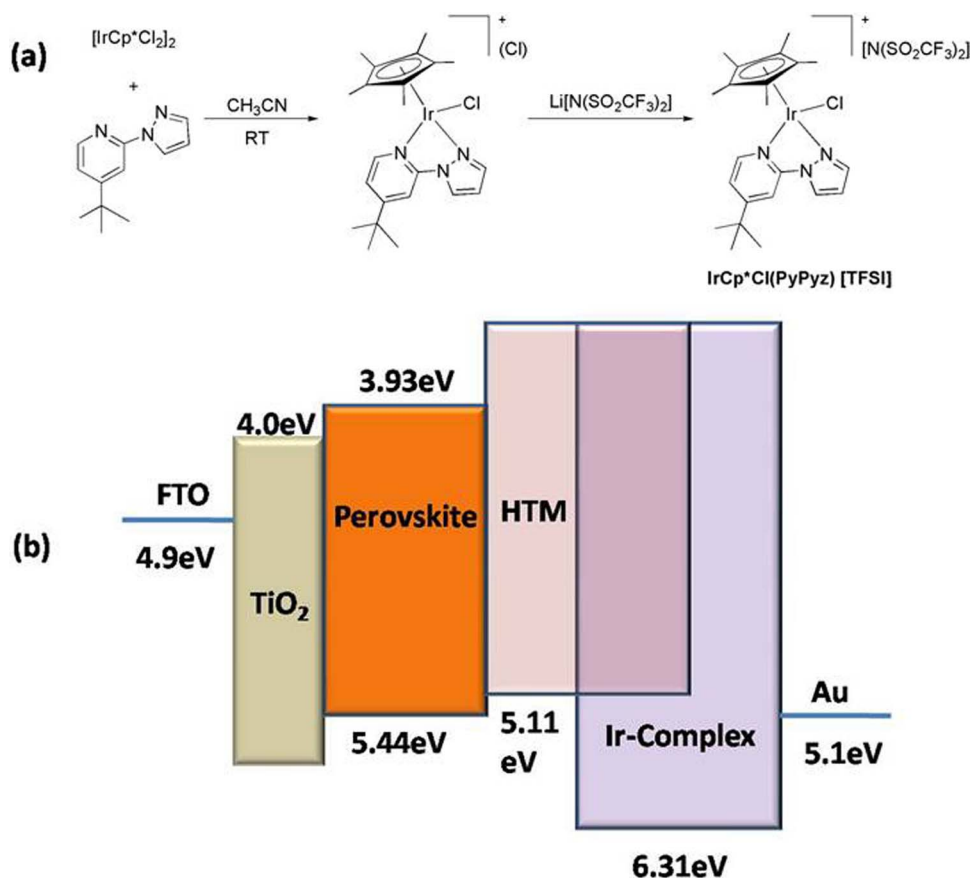


FIG. 1. (a) Synthesis of IrCp*Cl(PyPyz)[TFSI]. (b) Energy levels diagram for each components of the device extracted from previous references^{4,19} and measured for the Ir additive.¹⁷

In this paper we report the development of a new Ir complex, IrCp*Cl(PyPyz)[TFSI], Fig. 1(a), which has been used as additive to spiro-OMeTAD in PSCs, with the aim of improving the properties of the HTM layer and consequently the overall cell performance. Complex IrCp*Cl(PyPyz)[TFSI] was prepared by reaction of [IrCp*Cl₂]₂ and 2-(1H-pyrazol-1-yl)-4-tertbutylpyridine, in CH₃CN at room temperature. The synthetic procedures and the characterization details of this new complex are described in the supplementary material.²⁰ PSCs were prepared by using a glass substrate with F-doped tin oxide (FTO) layer as a transparent conductive contact. A compact layer of TiO₂ was deposited on the substrate and on its top a thin film of CH₃NH₃PbI_{3-x}Cl_x perovskite was grown.³ As HTM three different spiro-OMeTAD-based films were deposited using different additives: (i) no metal complex additive; (ii) the new IrCp*Cl(PyPyz)[TFSI] additive; and (iii) the Co(PyPyz)₃[TFSI]₃ additive. Hereafter, the three different samples are denoted as reference, Ir additive and Co additive, respectively. Finally, an Au electrode is evaporated on the top of HTM. More details can be found in the experimental section. An exhaustive device characterization, by means of current potential (J-V) curves, light absorption, and Impedance Spectroscopy (IS) measurements, has been carried out with the aim of understanding the effect of the new Ir complex on the cell performance.

In order to evaluate the effect of an Ir complex as a new additive for spiro-OMeTAD in perovskites devices, we first studied the effect of IrCl₃ (commercial available, Aldrich), [IrCp*Cl₂]₂,⁶ and the water oxidation catalysts IrCp*(H₂O)₃[SO₄].²¹ None of these iridium species showed any enhancement of the cell's performance. However, the use of the new IrCp*Cl(PyPyz)[TFSI], as additives for the HTM Spiro-OMeTAD, allowed us to observe a real improvement of the perovskite device.

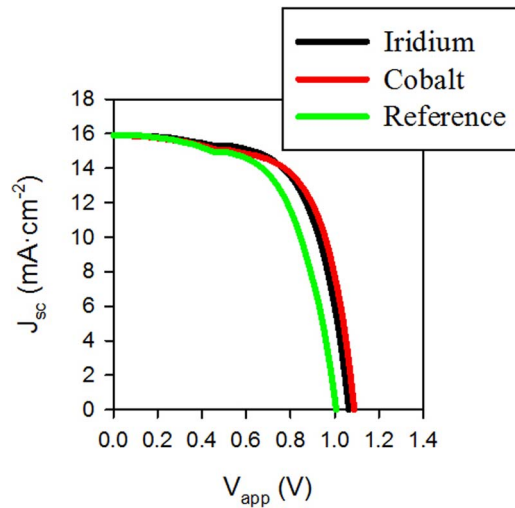


FIG. 2. J-V curves of PSCs under 1 sun illumination (100 mW/cm^2 , 1.5 AM), for samples prepared with different additives to the HTM.

TABLE I. Photovoltaic parameters of devices depicted in Fig. 2. Short circuit current, J_{sc} , open circuit potential, V_{oc} , Fill Factor, FF , and efficiency, η .

Device	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	η [%]
Reference	15.29	1.000	0.60	9.20
10% cobalt	15.56	1.085	0.64	10.8
10% iridium	15.90	1.064	0.64	10.8

$\text{IrCp}^*\text{Cl}(\text{PyPyz})[\text{TFSI}]$ was characterized by cyclic voltammetry following the Bazan's description,²² thus obtaining values of 6.31 eV for the HOMO level.¹⁷ From Fig. 1(b) it is clearly observed that the generated charges in the perovskite can be energetically injected into the HTM (holes) and to the titania compact layer (electrons). In addition, the HOMO level of $\text{IrCp}^*\text{Cl}(\text{PyPyz})[\text{TFSI}]$ lays below the HOMO level of spiro-OMeTAD, analogously to the reported case of spiro-OMeTAD and Co complex $\text{Co}(\text{PyPyz})_3[\text{TFSI}]_3$.¹⁹ It has been suggested that the transfer of electrons from the HOMO of spiro-OMeTAD to the HOMO of the Co complex induces the creation of hole carriers in spiro-OMeTAD, leading to an increase in its conductance.¹⁹

The characteristic J-V curves and the solar cell parameters obtained for solar cells prepared with the three different HTM are shown in Fig. 2 and Table I, respectively. It is clearly observed that the main effect of the metal complexes used as additives on the PSC performance consists of increasing the open circuit potential, V_{oc} , and Fill Factor, FF , while the short circuit current only presents a small increment. Samples with metal complexes as additives in the spiro-OMeTAD show a significant enhancement performance of 17% in comparison to the reference device, see Table I. Therefore, the new Ir complex induces a beneficial effect on the device performance similar to that previously reported for the Co complex additive.

In order to deeper explore the effect of metal complex additives on PSC performance, the devices were characterized by IS under illumination, with the aim of determining the recombination resistance, R_{rec} , that it is inversely proportional to the recombination rate. IS has been used in the characterization of PSCs as important tool in the determination of recombination dynamics.^{9,15,23-25} R_{rec} has been obtained by fitting the IS data with the previously described equivalent circuits.^{9,23,25}

Fig. 3 reveals the presence of two different recombination regimes, which are observed at low and at high applied voltages, V_{app} , respectively. These two regimes have been previously observed and attributed to two different recombination processes.^{9,23,25} On the one hand, the recombination rate has a significant effect on the V_{oc} , especially at high V_{app} (close to the V_{oc}).^{9,15} In this region,

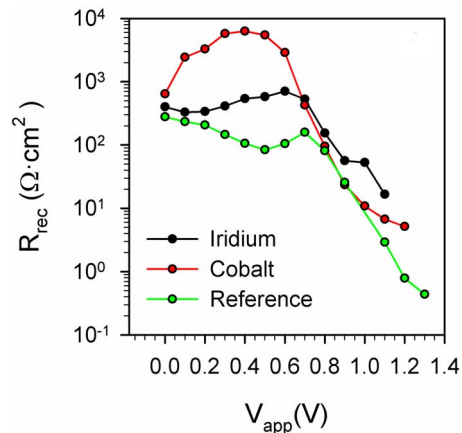


FIG. 3. Recombination resistance vs. applied voltage for the analyzed solar cells obtained from IS measurements under 1 sun illumination.

samples prepared with metal complex additives present higher R_{rec} , which is related to a lower recombination rate, thus inducing the appearance of higher V_{oc} values on the device. In addition, R_{rec} at low V_{app} has also an effect on cell performance affecting the FF , as low R_{rec} produces the effect of a small shunt resistance. The reference sample at low V_{oc} exhibits the lowest R_{rec} , which affects the cell performance by decreasing the FF , see Table I.

As it is depicted in Table I, similar cell parameters values are obtained for those devices prepared from Co and Ir additives. Nevertheless, the mechanisms ruling the device performance enhancement must not necessarily obey to a common origin. Elucidating the nature of the beneficial effect obtained for both metal complex additives and whether the mechanisms involved on the device efficiency enhancement arise from a common effect or not, are key factors for further development of PSC devices. Noh *et al.* studied previously the same Co complex and provided two main reasons for the observed efficiency enhancement promoted by the Co based additive.¹⁹ The former reason is a reduction of the charge recombination with the use of Co complex, which was determined by dark current analysis. The second is related with the presence of an additional UV/vis absorption peak at 520 nm, when Co complex is added to the spiro-OMeTAD, which the authors assumed to arise from the formation of oxidized spiro-OMeTAD radical cation induced by the presence of the Co complex. The oxidation produces a p-doping of the spiro-OMeTAD, thus inducing a downward shift of the hole quasi Fermi level, and consequently an increase of the V_{oc} . We have measured the absorption of the spiro-OMeTAD in solution with no metal complex and with the Co and Ir additives, respectively (Fig. 4). A similar absorption is obtained for all the HTM at wavelengths shorter than 430 nm. However, the Co complex treated solution shows a peak centered at around 520 nm (inset of Fig. 4), similar to that reported by Noh *et al.*¹⁹ As it was explained above, the authors claimed that the partial oxidation of the spiro-OMeTAD induced by the Co complex promotes an increase of the HTM conductance. In spite, this effect is not observed for the reference and Ir treated spiro-OMeTAD. Consequently, the beneficial effect on cell performance induced by the Ir complex can be only attributed to a decrease of the recombination rate, as the IS experiments evidence. In fact, higher recombination resistance (lower recombination rate) is obtained for the device using Ir additive in comparison to the device treated with the Co derivative, see Fig. 3. We have demonstrated in a previous work that recombination in PSCs is strongly governed by interfacial recombination at the selective contact,²³ therefore the additives introduced in the HTM must play a significant role on the charge recombination mechanisms.

Finally, long term stability experiments of the prepared devices were performed. In particular, a comparison of the J-V curves of the fresh devices compared with those obtained for the same samples, after three months stored in air atmosphere and under dark, is depicted in Fig. 5 and the corresponding solar cell parameters are shown in Table II. The efficiency of the reference cell was decreased in a 22% after three months due basically to a decrease of FF . The sample with Co

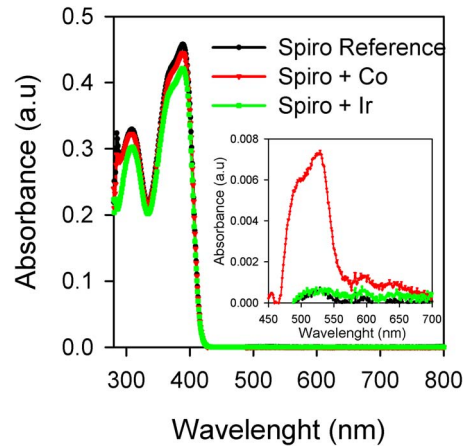


FIG. 4. Absorption spectra for different composition of HTM prepared without metal complexes and with Co and Ir complexes. Inset, zoom of the region with 450–700 nm wavelengths.

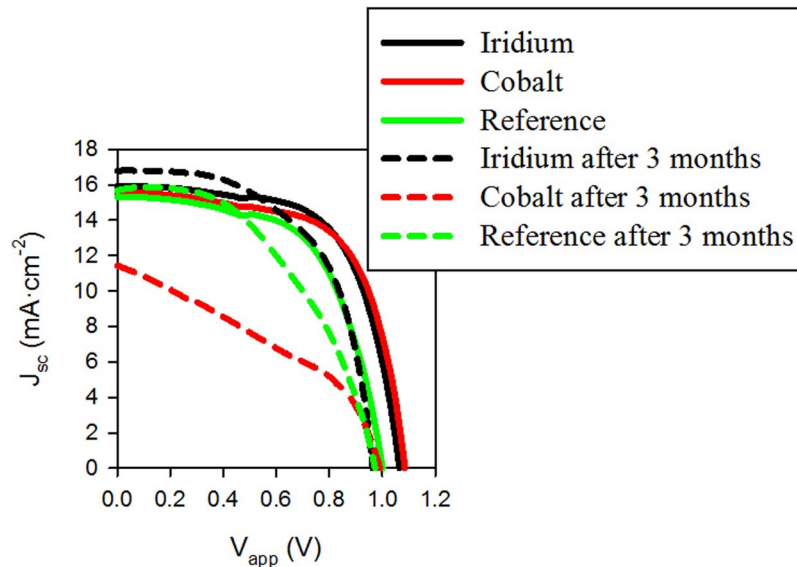


FIG. 5. Current density-voltage curves of solar cells under illumination of 100 mW/cm^2 simulated sun irradiation (1.5 AM). Curves with solid line are as made, dashed lines are the same cells measured three months later.

TABLE II. Photovoltaic parameters of devices depicted in Fig. 5 (measured 3 months later). Short circuit current, J_{sc} , open circuit potential, V_{oc} , Fill Factor, FF , and efficiency, η .

Device	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	η [%]
Reference	15.67	0.973	0.47	7.2
10% cobalt	11.43	0.993	0.37	4.2
10% iridium	16.78	1.059	0.59	10.4

additive experienced the strongest performance decrease with a reduction of 70% respect the fresh sample, which arose from a severe lessening of all the device parameter. The correlation between the partial oxidation of spiro-OMeTAD, observed in inset of Fig. 4, and the poor stability of the device is currently under evaluation. Very interestingly, the performance of the device prepared from

the Ir treated HTM was impressively retained after several months, in fact only experienced a 4% decrease, which is rather smaller than the measurement experimental error.

In summary, a new Ir additive, IrCp*Cl(PyPyz)[TFSI], has been synthesized. The use of this metal complex as an additive of spiro-OMeTAD in PSCs has been evaluated, by comparing with a reference sample without any metal complex additive and with an already reported Co additive. We have observed that cell performance of PSCs increases with the use of both metal complex additives, in a similar way in terms of cell efficiency. The enhanced performance observed for Ir treated devices is due basically to a reduction of the recombination rate, as IS analysis reveals. Especially remarkable device stability has been achieved for devices prepared from Ir treated HTM in comparison to the reference and Co complex devices. The physical origin of the enhanced stability is currently under investigation, and could introduce important implications on the development of high efficient and long-term stable PSCs.

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