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2,2´-Bipyridine – a new electrolyte additive in Dye-sensitized solar cells.

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Abstract

In this work 2,2´-bipyridine (bipy) is introduced as a new nitrogen containing electrolyte additive in Dye-sensitized solar cells (DSCs) as an alternative to the commonly used 4-*tert*-butylpyridine (TBP). Bipy was shown to substitute the thiocyanate ligands in the N719 ruthenium dye ~4 times slower than TBP at elevated temperatures 80-85 ºC and therefore reduce the thermal degradation of N719 relative to TBP. The thermal stability experiments were performed in sealed glass ampules filled with a colloidal solution of N719 dyed TiO_2 nano-particles in an ionic liquid electrolyte with either TBP or bipy as N-additive. The glass ampules were opened after various time intervals between 0-2000 hours of heating at either 80 or 85 ºC and the N719 and its degradation products were extracted from the TiO_2 nano particles and analyzed by LC-UV/Vis-MS. After 1000 hours at 85 ºC in dark, 85 % of N719 was intact in an electrolyte containing 0.2 M bipy whereas the same number was 67% for TBP. DSCs prepared with bipy in the electrolyte was shown to perform equally well as

DSCs with TBP containing electrolytes with light to electricity performance of 4.5% for both N-additives. 2,2′-bipyridine may therefore be used as an alternative to TBP as N-additive in DSCs.

Key words: dye-sensitized solar cell, N719, thermal stability, 2,2'-bipyridine, N-additive

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable interest from researchers worldwide owning to their low cost and ease of fabrication [1-3]. One of the success criteria required for commercial use of DSCs is high durability and stability under light soaking and thermal stress. While DSCs employing the ruthenium dyes N3, N719, Z907 and C106 with the general formula $RuLL'(NCS)_2$ as sensitizers showed excellent stabilities under light soaking conditions at 55-60°C, early reports by Hinsch [4], Kroon [5] and Sommeling [6] raised some concern about the DSC stability at elevated temperatures (80-85 °C) in dark. Degradation of thermally stressed DSCs has been attributed to I_2 and I_3^- depletion in case of DSCs using conventional electrolytes [7], the interface formation of polymeric electrolyte with MPN solvent upon TiO_2 sensitized electrodes of DSCs using new types of electrolytes[8], degradation of the platinum catalyst on the cathode [9], dye degradation and desorption from the TiO_2 surface [6] and electrolyte leakage [10]. Nguyen *et al.* showed that $RuLL'(NCS)_2$ dyes degrade thermally in dark by thiocyanate ligand exchange with nitrile solvents and nitrogen-additives like 4-*tert*-butylpyridine (TBP) and 1-methylbenzimidazole as shown in eq. (1) with half-life times from 150-300 hours at 85 °C in model experiments and in complete DSCs [11-13].

$$RuLL'(NCS)_2 + TBP \quad = [RuLL'(NCS)(TBP)]^+ + NCS^- \qquad (1)$$

The substituted ruthenium dyes are 30-40% as efficient sensitizers as the unsubstituted complexes [14] and thermal dye degradation by N-additives therefore decrease the efficiency of the DSCs. The substitution reaction (eq.(1)) may be avoided by application of sterically hindered pyridines such as 2,6-dimethylpyridine [13]. However, the sterically hindrance apparently also prevents the binding of the pyridine to the TiO_2 photo anode and thereby decrease the open circuit potential (V_{oc}) of the DSC compared to DSCs with TBP as the additive. Furthermore enhanced dye degradation by I_3^- was observed in DSCs with sterically hindered pyridines [13]. Reduced ruthenium dye degradation was observed at elevated temperatures by application of the so-called "robust electrolytes" where guanidine thiocyanate is added to the electrolyte to counteract the thiocyante substitution reactions and nitrile based solvents replaced with ionic liquids. The role of guanidinium was also reported to protect Pt against the photo-corrosion [15], and binding on N719 dye in competition with iodine, thus reducing the concentration of dye – I_2 interaction, and therefore decreasing electron – iodine recombination rate constant[16]. However still, 20-40% of the ruthenium dye (C106) was degraded after 1000 hours in dark at 80˚C [17] .

In this work our aim is to find a new N-additive which does not react (or only very slowly) with the RuLL´$(NCS)_2$ dyes at elevated temperatures and still maintain the positive V_{oc} enhancement observed with the traditional N-additives TBP and 1-methylbenzimidazole. A possible N-additive candidate is 2,2'-bipyridine (bipy). Our working hypothesis is that the sterically hindrance of the nitrogen atoms in bipy molecule induced by the other pyridine ring will prevent or slow down the rate of eq. (1) at elevated temperatures, however without preventing the attachment to the TiO_2 surface and shift of the conduction band to more negative potentials. Herein, we have investigated the thermal stability of the ruthenium dye N719 in model "test tube" experiments with application of a various electrolytes with bipy or

TBP added as N-additive. Furthermore, we have measured the light to electricity performance of DSCs prepared with bipy and TBP containing electrolytes.

2. Experimental section

The thermal dye stability tests performed in this work is similar to our recent thermal stability testing of C106 in various electrolytes [17].

2.1 Materials

The ruthenium dye N719, a bis(tetrabutylammonium) salt of the *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) complex was commercially available under the trade name Ruthenium 535-bis TBA from Solaronix SA (Aubonne, Switzerland). 4-*tert*-butylpyridine (TBP), 2,2′-bipyridine and sulfolane was purchased from Sigma-Aldrich. 1,3-dimethylimidazoliumiodide, 1-ethyl-3-methylimidazolium iodide, 1-ethyl-3-methylimidazolium tetracyanoborate was obtained from IoLitec-Ionic Liquids, Heilbronn, Germany. The titanium dioxide paste (Dyesol 18 NR-T) was obtained from Dyesol.

2.2 Preparation of TiO_2 powder and N719 dyed TiO_2 powder

The powder was collected from the heated TiO_2 paste (Dyesol's 18NR-T) and then dyed with N719 following the protocol described in our recent publication [17]. The dark red colored TiO_2|N719 powder was used for the thermal glass ampule experiments.

2.3 Preparation of electrolytes

The electrolyte E was prepared identically to the electrolyte B in [17] except that no N-additive was added.

Electrolyte E: 1,3-Dimethylimidazoliumiodide (4.560g, 0.70M), 1-Ethyl-3-methyl-imidazoliumiodide (4.881g, 0.70M), 1-Ethyl-3-methyltetracyanoborate (6.120 g, 0.95M), Iodine (0.730g, 0.10 M), Guanidiniumthiocyanate (GuNCS, 0.160g, 0.047M), Sulfolane (15 ml). Total volume 29 ml. Electrolyte A: To electrolyte E (13 ml) was added *4-tert*-butylpyridine (0.357 g, 0.20 M). Electrolyte B: To electrolyte E (13 ml) was added 2,2′-bipyridine (0.41g, 0.20 M).

2.4 Glass ampule experiments

N719 dyed TiO_2 powder (14-18 mg) was transferred to a glass ampule and 0.8 ml of electrolyte A or B was added. Dissolved air in the electrolyte was removed on a vacuum line by one freeze-pump-thaw cycle followed by flame sealing of the glass ampule. The sealed ampules were heated for 0-2000 hours in GC ovens operated at 80℃ and 85℃ respectively.

2.5 N719 extraction protocol

The glass ampules were opened and the electrolyte was carefully removed [17]. The purified isolated red TiO_2 powder was extracted by addition of 600 μl of a solution comprised of DMF (3.5 ml) + H_20 (3.5 ml) and 1.2 ml of tetrabutylammonium hydroxide (40% in water) to the Eppendorf test tube followed by thoroughly vortex and spin down (20000g) for 3 min. An aliquot of the red supernatant mixture (400 ml) was transferred to a HPLC vial and acidified by 20μl formic acid.

2.6 Product analysis

HPLC samples were analyzed on a Waters Cortecs RPC18 column with the dimensions 2.1×100 mm and column material of d=1.6 μm. The elution condition was similar to [17].

2.7 Relative substitution rates of TBP and bipy with N719.

A solution (1ml) of bipy (0.5 M), TBP (0.5) M and N719 (0.5 mM) in Dimethylformamide (DMF) was transferred to each of ten glass ampules, and sealed as described above. The glass ampules were heated for various time intervals between 0- 300 h at 100 ºC in dark. After heating the glass ampules were opened and analyzed by HPLC – UV/Vis – MS.

2.8 DSC fabrication and characterization

The cell fabrication and characterization procedure were reported elsewhere [18]. The DSCs were prepared with four electrolyte solutions: Electrolyte E plus the N-additives TBP (0.1 M and 0.5 M) and bipy (0.1 M and 0.5 M).

3. Results and discussion

3.1 Product analysis

Figure 1a shows a HPLC chromatogram of the dye extract of dyed TiO_2 particles stored in electrolyte B in dark at ambient temperature for three months in a sealed glass ampule. Figure 1b and c show the chromatograms of the experiments performed in the electrolytes A and B (A contains TBP and B does bipy) after 1000 hours of thermal treatment at 80 °C, respectively. Figure 1a shows a chromatogram of a pure and intact N719 sample with the main isomer of N719 eluting after 9.00 min and its minor isomer **4** (5%), $RuL_2(NCS)(SCN)$ at $R_t = 7.55$ min.

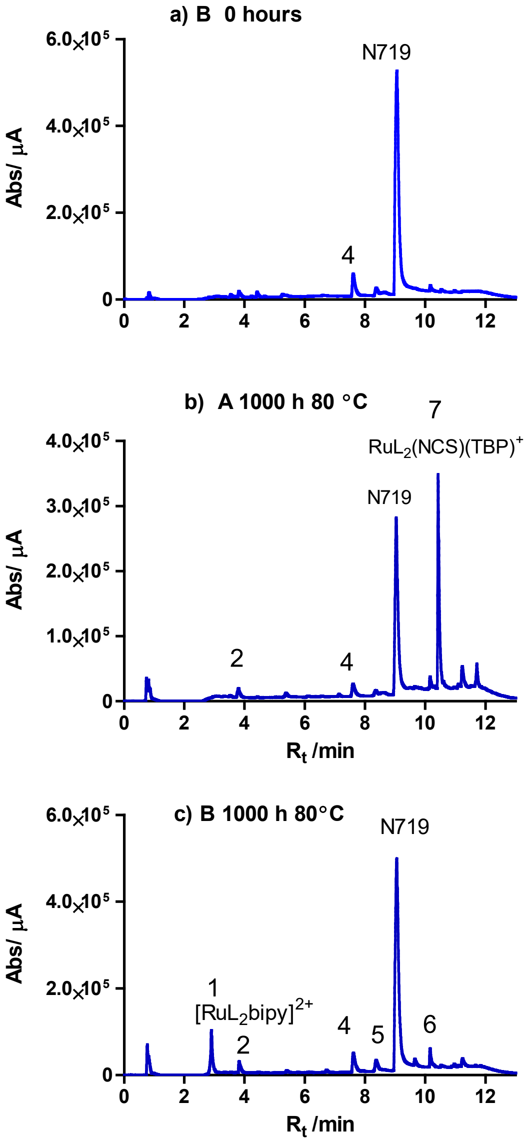

Figure 1 a) HPLC chromatogram of dye extracts of N719 dyed TiO_2 particles in electrolyte B after 3 months at ambient temperature in dark. Figure 1b) and 1c) shows the HPLC analysis of the experiments performed in electrolyte A and B respectively after 1000 hours of thermal treatment at 80 °C.

In the A electrolyte experiment (Figure 1b) with TBP as additive two main peaks are observed after 1000 hours at 80 °C. The first peak is due to N719 itself whereas the other one at $R_t = 10.43$ min is due to the substitution product $[RuL_2(NCS)(TBP)]^+$ (**7**). In the electrolyte

B experiment with 2,2′-bipyridine as additive, a new unexpected peak was detected at R_t = 2.87 min. The fast elution on the reverse phase C18 column indicates that the product is polar. The peak has a λ_{max} = 478 nm in the visible part of the UV/Vis spectrum and the electro-spray mass spectrum shows a ruthenium isotope pattern around *m/z* = 373 (Figure 2a). Expansion of the ruthenium isotope pattern (Figure 2b) reveals that the difference between the isotope peaks are $\Delta m/z = 0.5$ which means that the ion is double charged with a molecular weight M_w = 746. The compound may be identified as $[RuL_2(bipy)]^{2+}$ (**1**) and its formation can be explained by the substitution reaction in eq. (2):

$$RuL_2(NCS)_2 + bipy = [RuL_2(bipy)]^{2+} + 2\ NCS^- \qquad (2)$$

The bipy molecule reacts with N719 at elevated temperatures, however with an approximately 4-5 times slower substitution rate than TBP as judged from a comparison of the peak intensities of the substitution products **1** and **7** in Figure 1.

Beside the above mentioned main products, minor degradation products **2**, **3**, **5** and **6** were observed in thermal degradation experiments performed in electrolyte A and B (see Table 1). These products account together for less than 7 % of all the ruthenium products of the samples.

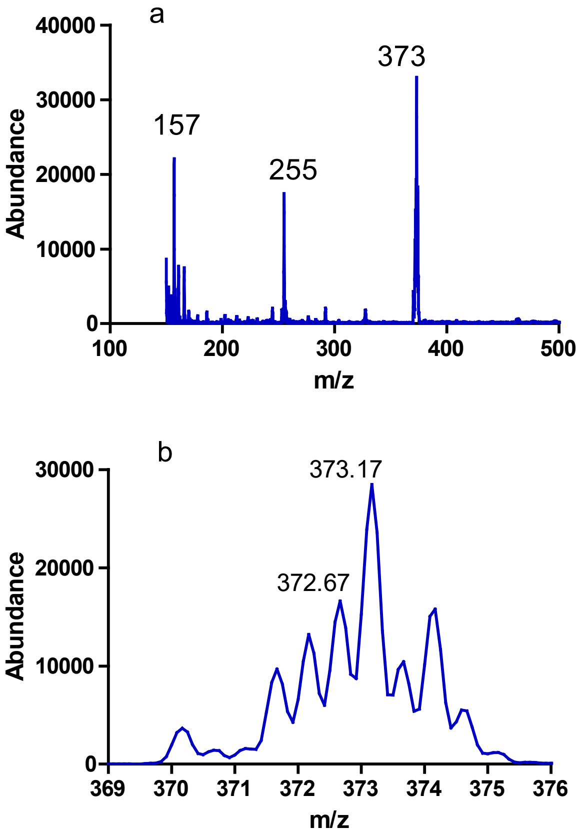

Figure 2 a) Electro spray mass spectrum of the HPLC peak eluting at R_t = 2.87 min. The peak is identified as the $[RuL_2(bipy)]^{2+}$ with a M_w = 746 and a *m/z* = 373. b) The expanded spectrum of *m/z* = 373.

Table 1 Thermal degradation products of N719 in electrolyte A and B.

Product	**Symbol**	**R_t/min**	***m/z***	**λ_{max}/nm**
$[RuL_2(bipy)]^{2+}$	**1**	2.87	373 $[M^+ = 746]$	478
$RuL_2(NCS)(CN)$	**2**	3.78	675 $[M+H]^+$	500
$[RuL_2(NCS)(CH_3CN)]^+$	**3**	4.40	689 $[M]^+$	486
$RuL_2(NCS)(SCN)$	**4**	7.55	706 $[M]^+$	523
$RuL_2(NCS)(I)$	**5**	8.29	775 $[M]^+$	540
$RuL_2(NCS)_2$	N719	9.00	706 $[M]^+$	526
$RuL_2(NCS)(B(CN_4))$	**6**	10.15	764 $[M+H]^+$	490
$[RuL_2(NCS)(TBP)]^+$	**7**	10.43	783$[M]^+$	510

3.2 *Relative* N-additive *substitution rates in DMF*

The thiocyanate substitution rate of N719 with TBP in homogeneous solution was compared directly with the corresponding rate between bipy and N719 by a simple competition experiment. The experiment was performed in DMF at 100 ºC in sealed glass ampules. DMF was selected as solvent because it unlike acetonitrile does not react with $RuLL'(NCS)_2$ compounds at elevated temperatures [12]. The result of the competition experiment is shown in Figure 3 and shows that slope (0.22%/ h) of formation of the substitution product **7** is approximately four times faster than formation of **1** (0.053 %/h) in agreement with the findings discussed above.

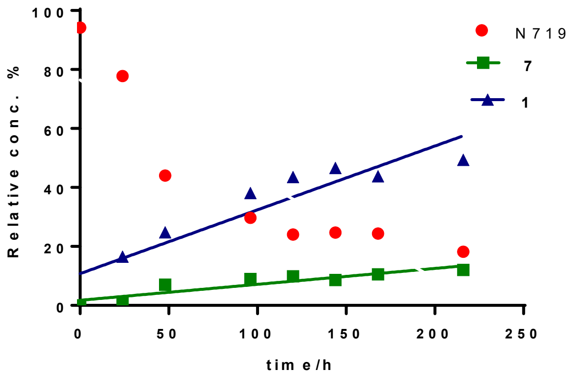

Figure 3. Reaction of N719 with TBP and bipy in DMF at 100 °C. The TBP substitution product **7** (▲) is formed approximately four times faster than the bipy substitution product **1** (■).

3.3 Dye degradation analysis

Figure 4 shows the thermal degradation of N719 at 80 and 85 °C as a function of the heating time. Approximately 50 % of the N719 has been transformed into the TBP substitution product $[RuL_2(NCS)(TBP)]^+$ (**7**) in electrolyte A after 1500 hours of thermal treatment at 80 °C whereas only 20 % of N719 was degraded in the B electrolyte with formation of 13% of the bipy substitution product **1**. Surprisingly the degree of N719 degradation at 85 °C is slightly less than at 80°C. It´s seen that the ratios of the equilibrium concentrations of N719 and the substitution products **7** and **1** are obtained already after 500-1000 hours at 85 °C whereas it takes slightly longer (1500-2000 hours) at 80 °C. From Figure 4 it is possible to extract the equilibrium constants of eq. (1) and eq. (2). The values are shown in Table 2. Interestingly, the equilibrium constants are about two times smaller at 85 °C than at 80 °C.

Table 2 Equilibrium constants K_1 and K_2 of the substitution reactions eq. (1) and eq. (2) respectively.[1]

t / ˚C	[**7**]/[N719]$_{eq}$	K_1[2]	[**1**]/[N719]$_{eq}$	K_2[3]
80	0.74	0.17	0.17	1.9×10^{-3}
85	0.47	0.11	0.09	0.94×10^{-3}

[1] [TBP] = [bipy] = 0.20 M; $[NCS^-]$ = 0.047 M. [2] $K_1 = [\mathbf{7}]\times[NCS^-]/([N719]\times[TBP])$

[3] $K_2 = [\mathbf{1}]\times[NCS^-]^2/([N719]\times[bipy])$

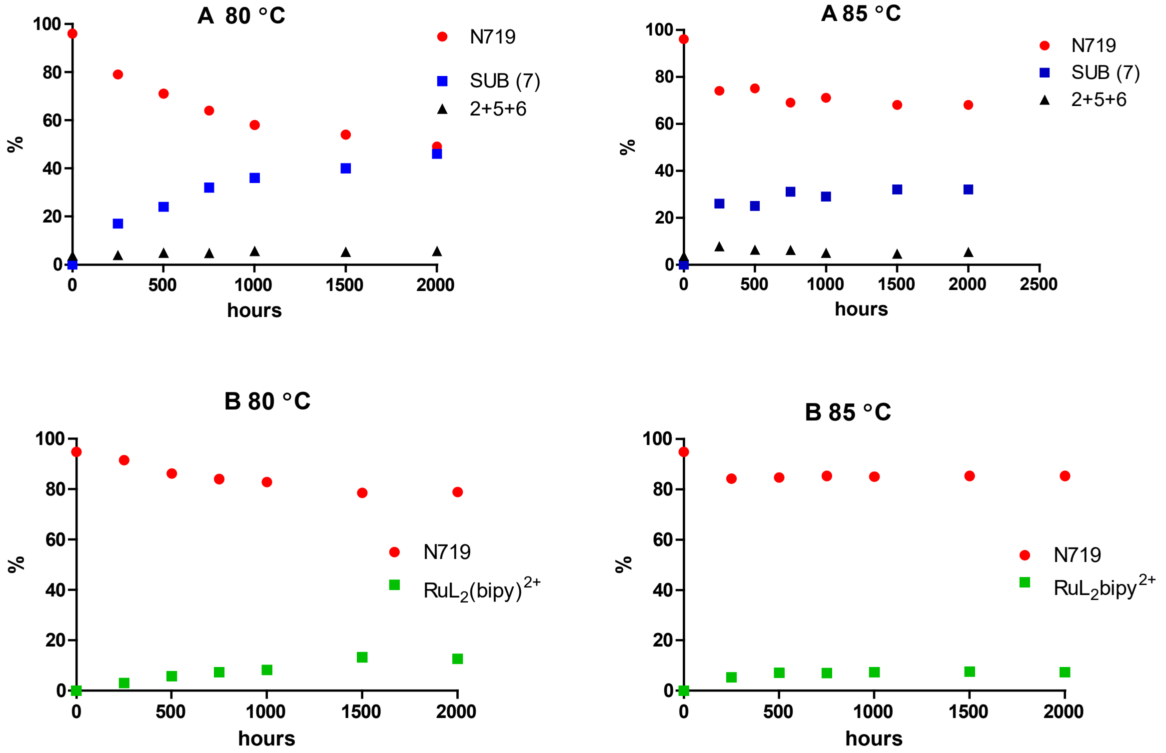

Figure 4 Product analysis of the thermal degradation experiments of N719 bound to TiO_2 nanoparticles in electrolyte A and B

According to IEC61646 standard solar modules should be able to pass the so-called damp-heat test where the module is heated in dark at 85 ° C for 1000 hours at 85 humidity % [19]. Table 3 shows the level of N719 dye degradation after 1000 hours of heating of the TiO_2|N719 particles in electrolyte A or B. The results in Table 3 and Figure 4 clearly show that the N719 dye-degradation is reduced in electrolyte from B relative to electrolyte A. We have previously showed that DSCs completely prepared with the substitution product **7** has a light to electricity efficiency η of 35% of the DSCs prepared with pure N719 [14]. If the crude assumption is made that a linear correlation between η and % N719 is valid then η may be calculated according to eq. (3) where η_0 is the initial efficiency of the DSC [14, 17].

$$\eta = \eta_0 \times [\%\text{N719} + 0.35 \times \%\mathbf{7}]/100 \qquad (3)$$

We do not know the efficiency of $[RuL_2(bipy)]^{2+}$ (**1**) as sensitizer, however, it´s probably even lower than **7** due to a more blue shifted UV/Vis spectrum and no contribution to the light to electricity conversion is assumed for **1**. Table 3 shows the expected efficiencies of DSCs after a 1000 hours thermal stress test. The efficiency loss of hypothetically electrolyte B DSCs is estimated to about 13 % after 1000 hours at 85℃, which is close to the fulfilment of the IEC1646 requirements of maximum 10 % efficiency loss after the damp-heat test.

Table 3 Product analyses given in % of the thermal degradation of N719 bound to TiO_2 particles in electrolyte A and B after 1000 hours of heat at 80 or 85℃.

Electrolyte	N-additive	t /° C	% N719+**4**	% SUB (**1** or **7**)	% ∑ **2,5,6**	η/ %
A	TBP	80	58	36	6	70
A	TBP	85	67	28	5	76
B	bipy	80	83	8	9	80

B	bipy	85	85	7	8	85

3.4 Photovoltaic performance of DSC devices

2,2′-bipyridine was evaluated as N-additive compared with TBP in DSCs prepared with electrolyte E with various added concentrations of bipy and TBP. (The electrolytes were similar to A and B). As can be seen from Figure 5 and Table 4, DSCs with bipy as additive showed lower open circuit voltage (50-70 mV) than DSCs with TBP. The case was opposite for the short current I_{sc}. This may be explained by a more tight binding of TBP to the TiO_2 surface relative to bipy. This means that TBP shifts the conduction band of TiO_2 to more negative value than bipy and the V_{oc} of the TBP cells is therefore larger than DSCs with bipy as N-additive. The negatively shifted conduction band, however, reduces the electron injection efficiency and bipy DSCs hence have higher I_{sc} than TBP cells with the result that the overall performance of the bipy and TBP DSCs are nearly the same (η = 4.5%). The new N-additive 2,2′-bipyridine is therefore comparable with 4-*tert*-butylpyridine in terms of improving the DSC performance.

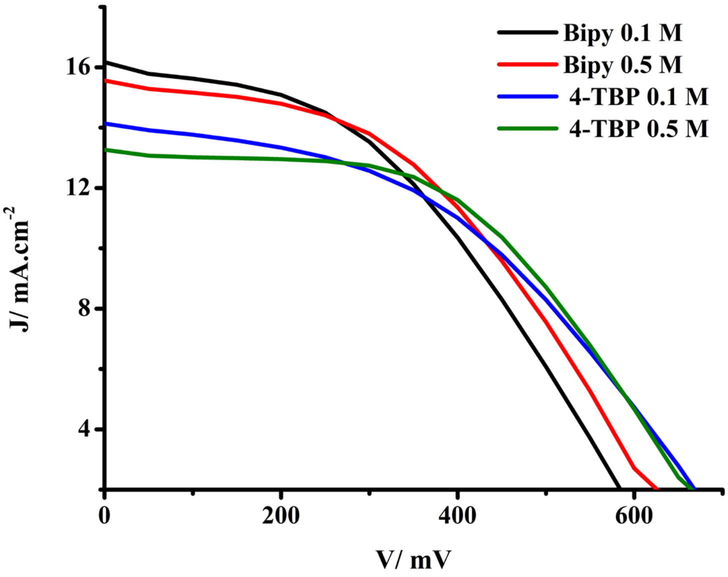

Figure 5 *J-V* curves of DSC fabricated with electrolytes added TBP or bipy at different concentrations.

Table 4 Photovoltaic performance of DSCs with electrolyte E with various concentrations of TBP and bipy as additives. The data is obtained as average of the performance of 8 – 10 individual cells.

Conc. of additives	J_{sc} mA.cm^{-2}	V_{oc} V	*Fill factor*	Efficiency η %
bipy 0.1M	16.2	0.62	0.42	4.2
bipy 0.5M	15.6	0.65	0.45	4.5
TBP 0.1M	14.1	0.71	0.44	4.4
TBP 0.5M	13.3	0.70	0.50	4.7

3. Conclusion

Substitution of *4-tert*-butylpyridine with 2,2´-bipyridine as N-additive in DSCs reduces the thermal degradation of the ruthenium dye N719 at elevated temperature 80-85 ºC. After 1000 hours at 85 ºC in dark 85 % of N719 was intact in an electrolyte (B) containing 0.2 M bipy whereas the same number was 67% for 4-*tert*-butylpyridine. The electrical performance of DSCs prepared with bipy and TBP as N-additives showed similar light to current efficiency of 4.5%. 2,2´-bipyridine may therefore be used as an alternative to TBP as N-additive in DSCs.

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