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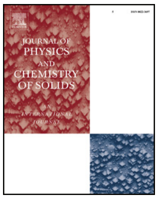

# 4,4′-dinonyl-2,2′-bipyridine as an alternative electrolyte additive for improving the thermal stability of ruthenium dyes in dye-sensitized solar cells

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ABSTRACT

Traditional dye-sensitized solar cells (DSCs) use 4-*tert*-butylpyridine (4-TBP) as a nitrogen additive in the electrolyte to improve the photovoltaic performance. However, 4-TBP reacts with the ruthenium dye N719 (bis (tetrabutylammonium) salt of the *cis*-bis(isothiocyanato)bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) ($RuL_2(NCS)_2$) complex at elevated temperatures, so the efficiency of the cells is reduced greatly. In this study, we tested 4,4′-dinonyl-2,2′-bipyridine (DNB) as a new nitrogen additive instead of 4-TBP in two types of electrolyte, i.e., liquid and ionic liquid, in order to improve the thermal stability of ruthenium dyes. The results showed that the reaction rate between DNB and N719 was relatively slow, and 10 times slower than that with 4-TBP at elevated temperatures. This clearly reduced the thermal degradation of N719. Two series of experiment were conducted at 80 °C from 0 to 1500 h with 7–8 samples per electrolyte. N719 and its degradation products were analyzed by High performance liquid chromatography (HPLC) coupled with Ultraviolet/Visible (UV/Vis) detector and Mass spectrometry (MS). After 1000 h, approximately 30% of N719 was degraded in the liquid electrolyte, whereas only 10% of the N719 was lost in the ionic electrolyte. DSCs prepared with 4-TBP and DNB to compare their photovoltaic performance. The results indicated that DSCs containing either 4-TBP or DNB had equivalent efficiencies of around 3.8%. Thus, DNB has the potential to replace 4-TBP as a nitrogen additive in DSCs.

## 1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable attention from researchers throughout the world due to their potential use as commercialized solar cells [1–3]. Compared with traditional silicon solar cells, DSCs have advantages in terms of their low manufacturing costs [1]. Moreover, flexible DSCs have a wide range of potential commercial applications such as in indoor or mobile devices, as well as for building integrated photovoltaic modules, e.g., glass facades [4–11]. Before their possible commercialization, DSC devices must maintain their durability and stability under light soaking and thermal test conditions. In previous studies, DSCs fabricated with ruthenium dyes such as N3, N719, Z907, and C106 successfully maintained their performance under light soaking conditions at 55–60 °C [12,13]. However, DSCs still have some disadvantages, where the presence and depletion of $I_2$ and $I_3^-$ in the electrolyte [14], unstable platinum catalyst cathodes [15], electrolyte leakage [16], dye desorption [17], and degradation of the dye itself [18] are the main concerns that prevent DSCs from achieving high efficiency and stability, especially at elevated temperatures (> 80 °C). The dye sensitizer is a key component of DSCs, and the stability and durability of DSC devices are related directly to the stability of the dye. The stability of the dyes is reduced at elevated temperature (80 °C), which leads to a loss of efficiency in DSCs, and this is considered to be attributable to dye desorption and reactions with the electrolyte components. In our previous studies, we showed that ruthenium dyes with the general formula $RuLL'(NCS)_2$ degrade thermally in the dark because of reactions between the thiocyanate ligand and nitrile solvents, and the presence of nitrogen additives in the electrolyte [19,20], according to the following three equilibrium reactions (1–3), where 3-methoxypropionitrile (3 MPN) is the solvent and 4-*tert*-butylpyridine (4-TBP) is used as an electrolyte N additive.

$$RuLL'(NCS)_2 + 3MPN \rightarrow [RuLL'(NCS)(3MPN)]^+ + NCS^- \tag{1}$$

$$[RuLL'(NCS)(3MPN)]^+ + 4\text{-TBP} \rightarrow [RuLL'(NCS)(4\text{-TBP})]^+ + 3MPN \tag{2}$$

$$RuLL'(NCS)_2 + 4\text{-TBP} \rightarrow [RuLL'(NCS)(4\text{-TBP})]^+ + NCS^- \tag{3}$$

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Previous studies have shown that substituted ruthenium dyes only have efficiencies of 30–40% as sensitizers [21,22]. The reduction in the dye concentration after the reaction with electrolytes decreases the efficiency of the DSCs. A possible approach for preventing this problem is the use of other sterically hindered pyridines such as 2,6-dimethylpyridine [21]. Steric hindrance is also disadvantageous because it apparently prevents the binding of pyridine to the $TiO_2$ photo-anode. Thus, the open circuit voltage of the DSC is decreased slightly compared with DSCs where 4-TBP is employed as an additive. Furthermore, enhanced dye degradation by $I_3^-$ has been observed in DSCs with sterically hindered pyridine [22,23]. Another method for reducing ruthenium dye degradation is to apply so-called “robust electrolytes,” where guanidine thiocyanate (GuNCS) can be added to the electrolyte to counteract the thiocyanate substitution reaction and nitrile-based solvents may be replaced with ionic liquids. Nevertheless, 20–40% of the ruthenium dye (C106) is still degraded after 1000 h in the dark at 80 °C [24].

Recently, we reported that using 2,2′-bipyridine as a new electrolyte additive helped to improve the thermal stability of the dye [25]. In addition, the efficiency of DSCs with 2,2′-bipyridine was similar to that of DSCs containing 4-TBP.

In this study, we explored the possibility of using 4,4′-dinonyl-2,2′-bipyridine (DNB) as a new N additive. We expected that the longer alkyl attached to the bipyridine ring in DNB would slow down or prevent the reaction between DNB and $RuLL'(NCS)_2$ dyes at high temperatures, while still maintaining a positive $V_{oc}$ like the traditional N additives 4-TBP and 1-methylbenzimidazole. We investigated the thermal stability of N719 with DNB as an N additive in liquid and ionic liquid electrolytes, i.e., so-called “non-robust” and “robust” electrolytes, respectively. Moreover, we implemented DNB in functional DSC devices to determine their photovoltaic performance compared with DSCs prepared using 4-TBP in the electrolytes.

## 2. Experimental

The thermal dye stability tests performed in this study were based on the procedures used for C106 and/or N719 in various electrolytes in previous studies [24,25].

### 2.1. Materials

Ruthenium dye N719, a bis(tetrabutylammonium) salt of the *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) ($RuL_2(NCS)_2$) complex, was obtained commercially under the trade name ruthenium 535-bis TBA from Solaronix SA (Aubonne, Switzerland). We purchased the following from Sigma Aldrich: 4-TBP ≥ 98%; DNB, 97%; 3-MPN, ≥ 98%; lithium iodide (LiI), 99.99%; GuNCS, > 99%; 1-methyl-3-propylimidazolium iodide (MPII), ≥98%; 1-ethyl-3-methylimidazolium tetracyanoborate (EMITCB), 97%; and tetrabutylammonium iodide (TBAI), > 99%. Iodine ($I_2$), 99.8% and acetonitrile, 99.9% (GC) were obtained from Merck. Titanium dioxide paste (Dyesol 18 NR-T) was obtained from Dyesol.

### 2.2. Glass ampoule experiments

Powder was collected from the heated $TiO_2$ paste (Dyesol 18 NR-T) and then dyed with N719, as described previously [24,25]. The N719 dyed $TiO_2$ powder was then used in thermal glass ampoule experiments. Electrolyte A (liquid electrolyte) comprised: TBAI, 0.6 M; LiI, 0.1 M; $I_2$, 0.05 M; GuNCS, 0.1 M; and DNB, 0.1 M, in 3-MPN. Electrolyte B (ionic liquid electrolyte) comprised: MPII, 0.7 M; $I_2$, 0.05 M; DNB, 0.1 M; GuNCS, 0.1 M; and EMITCB, 1 M. It should be noted that it is quite difficult to dissolve DNB in the solvent so we used DNB at a concentration of 0.1 M and heated it at 50–60 °C to ensure that the DNB was totally dissolved.

The N719 dyed $TiO_2$ powder (14–18 mg) was transferred to a glass ampoule and 0.8 mL of electrolyte A or B was added. Any dissolved air in the electrolyte was removed with a vacuum line in one freeze-pump-thaw cycle, before flame sealing the glass ampoules. The sealed ampoules were heated at 0–1500 h in GC ovens operated at 80 °C. Each series of experiments used 7–8 ampoule samples.

The dye was then extracted from the red $TiO_2$ powder after carefully removing the electrolyte according to a previously reported protocol [24,25]. The dye solutions were then analyzed by HPLC, UV/Vis, and MS using a Waters Cortecs RPC18 column with dimensions of 2.1 × 100 mm and d = 1.6 μm for the column material [24].

### 2.3. DSC fabrication and characterization

The cell fabrication and characterization procedures were reported previously [26]. Fluorine doped Tin Oxide (FTO) conducting glass (Solaronix, sheet resistance: $8\,\Omega\,cm^{-2}$) was first cleaned, treated with 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min, and washed with distilled water. The $TiO_2$ paste was coated on the FTO glass with an area of $0.25\,cm^2$ by doctor blading. The $TiO_2$ electrode was then sintered at 500 °C for 30 min, before immersing in a dye solution comprising 0.5 mM ruthenium 535 bis-TBA (N719, Solaronix) in methanol, and maintaining at room temperature in the dark for 24 h. The dye-adsorbed $TiO_2$ electrodes were rinsed with methanol and dried in an argon flow.

A counter electrode was formed on the opposite glass plate by spreading Pt-catalyst T/SP (Solaronix) with a doctor blade. The counter electrode was sintered at 450 °C for 30 min. The two glass substrates were assembled into a cell using polymeric sealant (Surlyn® 1707, Dupont™). Finally, the cell was filled with electrolyte B solution containing either DNB at 0.1 M or 4-TBP at 0.1 M as the additives. The electrolyte was injected into the cell while heating at 50–60 °C. The filling holes were sealed with Surlyn®.

Photovoltaic measurements were performed for the DSCs under a solar simulator (AM 1.5, $100\,mW\,cm^{-2}$) using a 450-W xenon lamp and a power source calibrated with an amorphous-Si standard. The DSCs were masked over an active area of $0.25\,cm^2$ on the anode electrode. The current–voltage (J–V) characteristics of the cells were analyzed using a model 2400 digital source meter (Keithley, UK). The method involved applying an external bias under the given illumination conditions and measuring the generated photocurrent.

## 3. Results and discussion

### 3.1. Product analysis

Fig. 1a–b shows chromatograms obtained from the experiments with electrolytes A and B (A is the liquid electrolyte and B is the ionic liquid electrolyte) after thermal treatment at 80 °C for 803 h and 1000 h, respectively. A main peak at $R_t = 8.9$ min is shown in Fig. 1a–b. This peak was attributable to the main isomer of the starting compound, N719. The minor isomer $RuL_2(NCS)$ (SCN) was detected at $R_t = 7.55$ min.

In Fig. 1a–b, the peak at $R_t = 12.05$ min was defined as the substitution product $[RuL_2\,(DNB)]^{2+}$ (**5**) according to its mass spectra. The electrospray mass spectrum contained a ruthenium isotope pattern around $m/z = 499$ (Fig. 1c). Expansion of the ruthenium isotope pattern (Fig. 1c) demonstrated that the difference between the isotope peaks was $\Delta m/z = 0.5$, which means that the ion was double charged with a molecular weight of $M_w = 998$. We obtained similar results with bipyridine. Compared with N719, the substitution product of bipyridine was polar so it eluted faster. In contrast to the bipyridine substitution, product **5** was less polar, and thus it eluted later at the end. For the peak, $\lambda_{max} = 504$ nm in the visible part of the UV/Vis spectrum and it exhibited more red shift compared with $[RuL_2\,(bipy)]^{2+}$ where $\lambda_{max} = 478$ nm [25]. Therefore, product **5** was predicted to be a more efficient dye sensitizer than $[RuL_2\,(bipy)]^{2+}$. The compound was