Alternative bases to 4-*tert*-butylpyridine for dye-sensitized solar cells employing copper redox mediator

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ABSTRACT

Novel facile synthetic protocol is developed to prepare electrochemically and optically clean Cu(tmby)$_2$TFSI and Cu(tmby)$_2$TFSI$_2$ in a mixture (tmby = 4,4,6,6-tetramethyl-2,2-bipyridine; TFSI = trifluoromethylsufonylimide). This pure Cu(II/I) redox mediator exhibits improved charge-transfer rate at the counterelectrode (PEDOT) and faster diffusion transport in the solution. Four pyridine derivatives: 4-*tert*-butylpyridine, 2,6-bis-*tert*-butylpyridine, 4-methoxypyridine and 4-(5-nonyl)pyridine are evaluated as electrolyte additives. Base-specific electrochemical properties of the redox mediator are found for Cu(tmby)$_2^{2+/+}$, but not for Co(bpy)$_3^{3+/2+}$ which is used as control system. Due to steric hindrance, 2,6-bis-*tert*-butylpyridine has the smallest influence on the mediator's electrochemistry, but is also ineffective for the V_{OC} enhancement through TiO$_2$ conduction band upshift. Charge-transfer rates at PEDOT surface and diffusion resistances correlate with the basicity (pK$_a$) of the used pyridine derivatives. The dye (Y123)-sensitized solar cells are evaluated by solar conversion performance in addition to electron lifetime, charge extraction and long-term stability tests. The optimization of pyridine bases for the Cu-mediated solar cells represents interplay of basicity and coordination ability. In turn, this allows for tuning of the charge transfer rate at counterelectrode and the mass transport in the electrolyte solution. The 4-(5-nonyl)pyridine is outperforming all the remaining bases in performance metrics of the corresponding solar cells.

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1. Introduction

Dye-sensitized solar cell (DSC) discovered by Grätzel et al. [1], is of considerable technological interest due to high-power conversion efficiency, easy fabrication, low cost and no environmental issues. DSC technology offers unprecedented versatility in the optimization of the cell components and outstanding performance,

particularly under indoor condition (at low intensity light) [2,3]. The tri-iodide/iodide couple (I$_3^-$/I$^-$) is the most often used redox mediator in the liquid-junction DSCs [4], but its corrosiveness, strong visible light absorption and too low redox potential ask for replacement by other redox systems [2,3,5,6].

The redox couple is one of the key components of DSC, serving for dye regeneration and charge transport between the TiO$_2$ photoanode and the cathode. Its proper selection improves the photovoltage and thus boosts the performance of the DSC. The open-circuit photovoltage (V_{OC}) is given by the energy difference between the quasi-Fermi level of the TiO$_2$ and the energy level corresponding to the mediator's redox potential [2,7,8]. Consequently, there are two general strategies for boosting the V_{OC}: (i) increasing the mediator's redox potential [6,7] and (ii) upshifting of the quasi-Fermi level of TiO$_2$ either by crystal-facet engineering [9] or by

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addition of *tert*-butylpyridine (TBP) to the electrolyte solution [10,11]. The first strategy has been highlighted by the use of Co(III/II) complexes [7,12] and by the tetra-coordinated Cu(II/I) complexes [5,6,13–16]. However, the Co complexes also bring some issues such as their low stability, slow mass transport in the electrolyte solution and the large internal reorganization energy requirement between the d^7 (high spin) and d^6 (low spin) states which limits the driving force available for dye regeneration [5,17–19].

The tetra-coordinated Cu(II/I) complexes inherently minimize the limitations caused by the reorganization energy. Examples are: $[Cu(dmp)_2]^{2+/+}$; dmp = bis(2,9-dimethyl-1,10-phenantroline), $[Cu(dmby)_2]^{2+/+}$; dmby = 6,6′-dimethyl-2,2′-bipyridine, and $[Cu(tmby)_2]^{2+/+}$; tmby = 4,4,6,6-tetramethyl-2,2-bipyridine. The dmby- and tmby-complexes, with TFSI (trifluoromethyl sufonylimide) counter-ions, introduced by Saygili et al. [6], offer comparable performance to the Cu-dmp complexes. Recently, the $Cu(tmby)^{2+/+}$ mediator attracted interest by unprecedented efficiency of 28.9% of DSC under ambient lighting, which was even outperforming that of GaAs photovoltaics at the same conditions [16]. Another strong argument in favor of $Cu(tmby)^{2+/+}$-mediated DSCs is the demonstration of easy-made solid-state devices with remarkable efficiency of 11% under 1 sun [20].

The 4-*tert*-butylpyridine is ordinarily used for the desired Fermi level upshift, for preventing the electron recombination and thus for the V_{OC} enhancement [5,10,11]. Consequently, TBP is present in almost every electrolyte solution for liquid-junction DSCs as a standard additive [21]. Furthermore, nitrogen-containing heterocyclic compounds are essential for ionic-liquid based electrolytes, while TBP is sometimes used even in these ionic-liquid formulations [22].

In the I-mediated and Co-mediated systems, the TBP addition does not practically influence the cathode's charge-transfer and ionic diffusion in electrolyte solution. However, TBP has significant negative effect in the Cu-mediated systems [6] which is yet to be solved [23]. Herein, we report on different bases, viz: 2,6-bis-*tert*-butylpyridine (BTBP), 4-methoxypyridine (MOP) and 4-(5-nonyl) pyridine (NOP), which we examined in comparison to the reference TBP base for the $[Cu(tmby)_2]^{2+/+}$-mediated DSCs. The pyridine bases with different functional groups are expected to show different interaction with the TiO$_2$ surface and the Cu(II/I)-complexes, while the bases with lower pK$_a$ can also improve the dye anchoring. The TiO$_2$ photoanode was sensitized by the standard Y123 dye: 3-{6-{4-[bis(2,4-dihexyloxybiphenyl-4-yl)amino-] phenyl}-4,4-dihexylcyclopenta-[2,1-b:3,4-b]dithiophene-2-yl}-2-cyanoacrylic. The molecular structures of the Y123 dye, $[Cu(tmby)_2]^{2+/+}$ complexes and the used bases are shown in Figure S1. Furthermore, we developed in this work a new facile synthetic protocol towards electrochemically and optically clean $[Cu(tmby)_2]^{2+/+}$ redox mediator, which was an open problem in the earlier works on this subject [5,6,23].

2. Experimental section

All chemicals were purchased from Aldrich, TCI or Merck, and used as received.

2.1. Synthesis of copper complexes

Here we disclose, for the first time, a simple chemical synthetic route to get a clean $[Cu(tmby)_2]^{2+/+}$ redox mediator. Besides an unprecedented product's purity, the main advantage of our new recipe is that it avoids the awkward preparative electrolysis [5]. $[Cu(tmby)_2]$TFSI was synthesized by the reaction of CuI with tmby as detailed in our earlier work [6]. The Cu(II) counterpart of the complex, $[Cu(tmby)_2]$TFSI$_2$ was prepared by our newly developed

protocol as follows: 1 equivalent of CuTFSI$_2$ (194 mg, 0.31 mmol; Solvionics) was mixed with 3 equivalents of tmby (200 mg, 0.93 mmol) in 30 mL of ethanol/water (1/1, v/v). The reaction mixture was stirred for 3 h at room temperature. The solution was filtered and the product was washed with water and diethyl ether. The resulting crystalline solid (≈ 280 mg yield) varied its color depending on the content of Cu(I) impurity in the product (see below). The color changed from brown (for higher Cu(I) content) to purple (for lower Cu(I)-content). This material is further abbreviated as CuYS.

2.2. Electrode materials

The TiO$_2$ photoanode was fabricated as follows: FTO glass substrate (NSG-10, Nippon Sheet Glass) was cleaned with a detergent solution (Deconex) in ultrasonic bath for 45 min and then rinsed with water and ethanol. After the treatment with a UV-O3 cleaner (Model No. 256–220, Jelight Company, Inc.) for 15 min, FTO glass was immersed into a 40 mM TiCl$_4$ solution at 70 °C for 30 min and rinsed with water and ethanol to allow the formation of a blocking layer. This step was repeated twice. A porous TiO$_2$ layer was formed on the FTO glass via screen printing technique using a paste consisting of 30 nm sized TiO$_2$ particles (Dyesol). Then the second layer with 400 nm sized particles (scattering layer) was deposited and calcined. The TiO$_2$ films were sintered with a ramped temperature profile, keeping the temperature at 125, 250, 370, 450, and 500 °C for 5, 5, 5, 5, and 30 min, respectively, with 5 min ramp duration between each temperature. The resulting TiO$_2$ film thickness was 8 μm (4 μm + 4 μm). Finally, the film was treated with 20 mM TiCl$_4$ solutions and followed by another sintering process at 500 °C for 60 min to increase the surface area of the TiO$_2$ particles. Before sensitization, the TiO$_2$ electrodes were annealed for 30 min at 500 °C and (after cooling down to ca. 80 °C) immersed into the dye solution overnight. The latter was 0.1 mM Y123 dye (Dyenamo AB) in acetonitrile/*tert*-butanol (1/1 v/v). For the counter electrode fabrication, the FTO glass (TEC 6, Pilkington) was cleaned with Hellmanex III (2% wt in water), ethanol, and acetone with 30 min duration for each bath, and coated with PEDOT via electrochemical deposition from EDOT as detailed elsewhere [24].

2.3. Fabrication of devices

The working electrodes and counter electrodes were assembled in a sandwich-type DSC in a dry-box with 25 μm of Surlyn (DuPont) as a sealant and spacer between electrodes. The electrolyte was injected into the device through a predrilled hole in the counter electrode under vacuum and sealed with Surlyn and thin glass. The electrolytes consisted of 0.2 M Cu(I) and 0.06 M Cu(II) complexes with 0.1 M LiTFSI and 0.6 M bases in acetonitrile. The edges of FTO sheets were coated by ultrasonic soldering (Cerasolzer alloy 246, MBR Electronics GmbH) to improve electrical contacts.

The symmetrical dummy cells were fabricated with two identical PEDOT electrodes which were separated by 30 μm Surlyn (DuPont). The cells were filled with an electrolyte solution, which was identical to that used for DSC devices (see above). The cells were filled through a predrilled hole in one FTO support, and closed by a Surlyn seal. The sheet edges of FTO were coated by ultrasonic soldering. The cell spacing was measured by digital micrometer and found to be from 22 to 29 μm. To account for casual fluctuations in cell spacing, the measured voltammetric currents on dummy cells were normalized for constant spacing of 25 μm.

2.4. Methods

UV−Vis optical spectra were measured by a Hewlett-Packard