



Neutral organic redox pairs based on sterically hindered hydroquinone/benzoquinone derivatives for dye-sensitized solar cells

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ABSTRACT

Substituted derivatives of hydroquinone/benzoquinone were studied as organic redox mediators in the electrolyte for dye-sensitized solar cells (DSSCs). Thus, di-*tert*-butylhydroquinone (DTHQ), thymohydroquinone (ThymHQ) and phenylhydroquinone (PhHQ), were combined with their oxidized counterparts to form the pairs DTHQ/DTBQ, ThymHQ/ThymbQ, and PhHQ/PhBQ. In general, the characteristic parameters of the DSSCs with the substituted derivatives surpassed those of the DSSC with the unsubstituted hydroquinone/benzoquinone electrolyte. The short-circuit current (J_{SC}) of the devices using DTHQ/DTBQ and ThymHQ/ThymbQ (13.61 mA cm^{-2} and 12.56 mA cm^{-2} , respectively) are comparable to the J_{SC} obtained for cobalt(II/III) tris(bipyridine) as a reference electrolyte (14.54 mA cm^{-2}). However, parameters such as open-circuit voltage (V_{OC}) and fill factor (FF) (547 mV and 0.48, respectively) are far from competitive. The best photovoltaic performance was obtained for the pair ThymHQ/ThymbQ using a triphenylamine (TPA)-based organic dye (LEG4) as sensitizer and a hybrid counter electrode with poly(3,4-ethylenedioxythiophene) (PEDOT) and graphene. These experimental conditions give under 1 sun (98%) the highest efficiency ($\eta = 3.19\%$); low-light intensities of 12.3% and 51.8% suns lead to efficiencies of 3.34% and 3.29%, respectively. Electrochemical impedance spectroscopy (EIS) revealed that the main cause for loss in photocurrent is the low recombination resistance compared to Co(II/III) as reference electrolyte. Based on the EIS analysis, a down-shift of the conduction band of TiO_2 was found for all assembled devices containing the organic redox mediators, which explains the low V_{OC} values for these derivatives.

1. Introduction

Dye-sensitized solar cells (DSSCs) are third generation solar cells that can be produced in a variety of colors and shapes and can work under diffuse light conditions (O'Reagan and Grätzel, 1991; Zhang et al., 2016). They are comprised of a photoanode – typically a transparent conductive glass substrate of fluorine-doped tin oxide ($\text{SnO}_2:\text{F}$, FTO) – a thin layer of a nanostructured semiconductor (e.g., TiO_2), which is then sensitized with dye molecules, and a counter electrode (CE) with a thin layer of a catalyst such as platinum (Pt) or poly(3,4-ethylenedioxythiophene) (PEDOT) (Kalyanasundaram et al., 2010). Importantly, as dye molecules excite upon photon absorption followed by electron injection, the oxidized state of the dye is reduced to its ground state by an electron transfer from a redox couple in a liquid electrolyte filled between the electrodes. Together, these components

contribute to the overall performance of the cell; the redox couple in the liquid electrolyte plays an important role to attain high energy conversion efficiencies (Feldt et al., 2010; Wu et al., 2016).

The redox couple I^-/I_3^- is widely used because it presents large recombination resistance and provides high electron lifetimes (Ito et al., 2005; Teuscher et al., 2014). Nonetheless, this redox couple has several disadvantages such as corrosiveness, absorption of light in the visible range, sublimation, and a large potential drop due to the mismatch of the redox potential of I^-/I_3^- compared to the highest occupied molecular orbital (HOMO) level of the sensitizer dye (Sun et al., 2015; Yum et al., 2012). In the pursuit of alternative redox shuttles, cobalt complexes such as $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (where bpy = 2,2'-bipyridine) have shown a rather good match of the redox potential with the HOMO of the dye. Cobalt complexes require a lower driving force for dye regeneration, leading to higher open circuit voltages (V_{OC}), favorable

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power conversion efficiencies (η), and other characteristic parameters (e.g., short circuit current density, J_{SC} , and fill factor, FF) (Safdari et al., 2016; Bella et al., 2016). However, the large size of such coordination complexes decreases the diffusion coefficient of the active species in the electrolyte, the rate of dye regeneration, and the efficiency of the cell. Another unwanted issue with these colored complexes relates, in some cases, with the absorption of light in the visible range competing with the dye (Aghazada et al., 2016). This issue can be solved by optimization of organic redox couples, as shown with the use of disulfide/thiolate redox couples, which exhibit low absorption in the visible range (Wang et al., 2010). Alternatively, some interesting outcomes regarding iodine/iodide redox mediators in DSSCs made use of a hydrogel electrolyte consisting of carboxymethylcellulose and I^-/I_3^- in an aqueous systems (Bella et al., 2017), or membrane-based separators (Nair et al., 2015; Shanti et al., 2016).

On the other hand, the organic redox pair hydroquinone/benzoquinone (HQ/BQ) has spurred a great body of research due to its importance in biological processes (Alligrant et al., 2010). Interestingly, the electron transfer of the redox couple is a thermodynamically reversible process (Shaidarova et al., 2003). In non-aqueous media and in the absence of proton donor/acceptors, the hydroquinone dianion undergoes two successive one-electron steps (Fig. 1a). In the presence of proton donor/acceptors, the electron transfer process is coupled with the proton transfer processes (Fig. 1b) (Guin et al., 2011).

Previous experiments have shown that quinones and their electron transfer processes are coupled with proton transfer processes of the corresponding hydroquinones, in the absence or presence of proton donors or acceptors (Bhat, 2012). When there are proton acceptors in the media, the mechanism starts with the deprotonation of the hydroquinone (QH_2) compound, then an oxidation step forms the radical $QH\cdot$, which is further deprotonated leading to the radical anion $Q\cdot^-$ that, upon oxidation, yields a quinone (Q) (Fig. S5 in Supporting Info). The overall reaction proceeds as depicted in Fig. 1b, with a two-electron/two-proton process between the neutral hydroquinone and benzoquinone, suggesting that HQ/BQ-like redox pairs in their neutral forms can undergo electron transfer steps and could regenerate the dye in DSSC.

When hydroquinone is treated with tetramethylammonium hydroxide (TMAOH), it gives the bis-tetramethylammonium hydroquinone dianion (TMAHQ) ionic species, shown in Fig. 1a. In previous reports, the anionic hydroquinone species (TMAHQ/BQ) was used as a redox mediator in DSSCs with dye N719 as sensitizer and Pt as CE; these systems showed promising photovoltaic characteristics: $V_{OC} = 750$ mV, $J_{SC} = 17.2$ mA cm $^{-2}$, FF = 0.663, and 8.4% conversion efficiency. With the same redox mediator, but with PEDOT as CE and the organic dye CM-309, the following parameters were achieved: $V_{OC} = 755$ mV, $J_{SC} = 12.10$ mA cm $^{-2}$, FF 0.678, and $\eta = 6.2\%$ (Cheng et al., 2012, 2013).

One drawback of using TMAHQ in organic redox mediators is the limitation of the lifetime of the solar cell (Yu et al., 2013). Deprotonated hydroquinones are prone to decomposition in open air conditions, which compromises the overall performance of the DSSC.

Independently and innovatively, we examine the photovoltaic

performance of a series of DSSCs using neutral HQ derivatives bearing various bulky substituents on the aromatic ring. Our molecular design provides neutral, stable organic redox shuttles. The HQ derivatives, and the corresponding BQ pair, are stable in air. Our approach also simplifies the chemical composition of the electrolyte by decreasing the number of charged species in the liquid phase. To this end, the derivatives 2,5-di-tert-butylhydroquinone, phenylhydroquinone and 2-isopropyl-5-methylhydroquinone (thymohydroquinone) are paired with their benzoquinone counterparts to render the redox pairs DTHQ/DTBQ, PhHQ/PhBQ and ThymHQ/ThymBQ, respectively (Fig. 2). In solution, these redox pairs were optically characterized by UV-Vis spectroscopy and by cyclic voltammetry, followed by determination of their photovoltaic parameters (for instance, J_{SC} , V_{OC} , FF, and η) from current density-voltage plots once the DSSC were assembled. Likewise, a series of internal processes of the assembled DSSCs were determined by electrochemical impedance spectroscopy (EIS).

2. Experimental

Details of the synthesis and characterization of the derivatives are described in the Supporting Information.

2.1. Materials

All chemicals were purchased from Sigma-Aldrich unless otherwise noted. The organic dyes 3-{6-[4-[bis(2',4'-dibutylxybiphenyl-4-yl)amino-]phenyl]-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiophene-2-yl}-2-cyanoacrylic acid, LEG4, and 3-{6-[4-[bis(2',4'-dihexyloxybiphenyl-4-yl)amino-]phenyl]-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiophene-2-yl}-2-cyanoacrylic acid, Y123, were purchased from Dyenamo AB (Stockholm, Sweden).

2.2. Solar cell preparation

Glass substrates with fluorine-doped tin oxide (FTO, Pilkington, TEC15) were cleaned in an ultrasonic bath for 1 h in the following order of solvents: water, ethanol, and acetone. The FTO substrates were pretreated by immersion for 30 min in a 40 mM aqueous $TiCl_4$ solution at 70 °C, and then washed with water, to form a thin blocking layer. Mesoporous TiO_2 films of 0.25 cm 2 were prepared as follows: a transparent active layer was made with colloidal TiO_2 paste (Dyesol DSL 30 NRD-T) by screen-printing technique and dried at 120 °C for 6 min between each layer of TiO_2 applied. Subsequently, a light-scattering layer (Dyesol WER2-0) was deposited on top by screen-printing. The substrates were then gradually heated in an air atmosphere oven (Nabertherm controller P320), applying a four-level program: 125 °C (10 min), 250 °C (10 min), 350 °C (10 min), and 450 °C (30 min). After sintering, the electrodes were treated in aqueous titanium tetrachloride ($TiCl_4$) at 70 °C for 30 min, then washed with water and ethanol. The thicknesses of the TiO_2 films were measured with a profilometer (Veeco Dektak 3); the thicknesses are 6 μ m and 2 μ m for transparent and scattering layers, respectively. A final heating step at 500 °C (30 min)

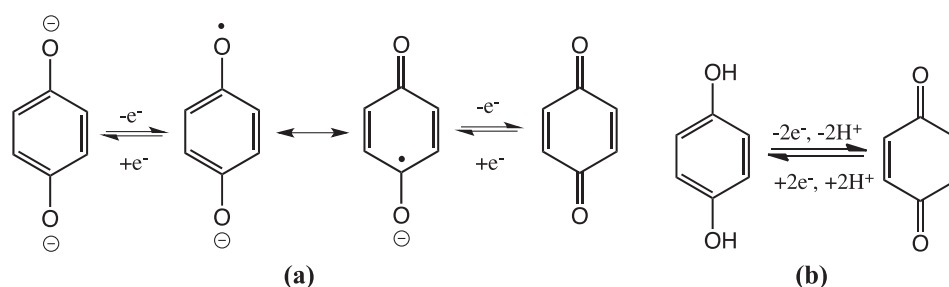


Fig. 1. Organic redox pair hydroquinone/benzoquinone (HQ/BQ) electron transfer steps: (a) absence of a proton donor/acceptor and (b) in presence of a proton donor/acceptor.

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