Organic Electrolytes

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Efficient Organic-Dye-Sensitized Solar Cells Based on an Iodine-Free Electrolyte**

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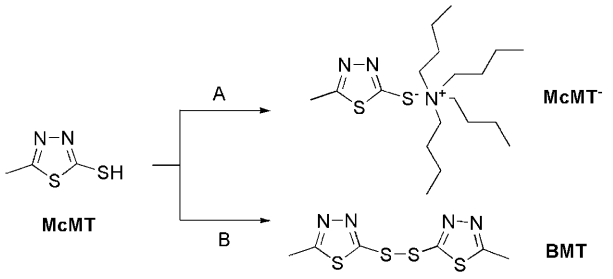
Dye-sensitized solar cells (DSCs) have been investigated intensely since Grätzel and O'Regan reported significant improvements in 1991,[1] thus manifesting DSCs as a new promising type of solar energy-to-electricity conversion device. To further improve the energy conversion efficiency and stability, many efforts have been made to optimize different components of DSCs. Although the traditional electrolyte based on the iodide/triiodide (I^-/I_3^-) redox couple works efficiently in DSCs, the disadvantages, such as corrosion of metal-based current collectors (for example silver, copper), sublimation of iodine, and absorption of visible light, limit the large scale production and commercial application of DSCs. Therefore, as a central component of such devices, the electrolyte has been widely studied. Finding an alternative redox couple plays a crucial role in the future development of DSCs. To date, metal complexes,[2] hole conductors,[3] p-type semiconductors,[4] Br^-/Br_3^-,[5] $SCN^-/(SCN)_2$,[6] $SeCN^-/(SeCN)_3^-$,[7] and also organic radicals (TEMPO)[8] have been introduced to DSCs as redox mediators for dye regeneration. However, DSCs based on these redox couples typically show lower efficiencies than those employing the I^-/I_3^- electrolyte, and most of them also present safety issues. The reasons why these new redox couples seemingly cannot match the performance of the I^-/I_3^- couple can probably be attributed to higher recombination losses, higher charge-transfer resistance at the counter-electrode, and/or mass-transport limitations. Recently, Grätzel and co-workers reported an organic redox couple derived from 5-mercapto-1-methyltetrazole, which gave an efficiency of 6.4% with Z907Na-based DSCs under standard illumination conditions ($100\ mW\,cm^{-2}$).[9] The result provided a new strategy to develop an iodine-free redox couple and also showed application in flexible DSCs. 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT) derivatives have been intensely studied owing to their interesting electrochemical behavior[10] and also potential application for photovoltaic devices.[11] Herein, we adopt an organic redox couple consisting of the thiolate form ($McMT^-$) and disulfide dimer (BMT) derived from McMT for metal-free dye-sensitized solar cells. The synthesis routes and structures of McMT, $McMT^-$, and BMT are shown in Scheme 1. $McMT^-$ was obtained by the reaction between McMT and tetrabutylammonium hydroxide (TBAOH) in methanol (MeOH) under reflux for 3 h. BMT was synthesized by oxidation of McMT potassium salt with I_2 at room temperature in MeOH.



Scheme 1. Synthetic routes and structures of the organic redox couple components. A) MeOH, TBAOH, reflux, 3 h; B) 1) MeOH, K_2CO_3, RT, 2 h, 2) I_2, RT, 10 min, 61%. TBA = tetrabutylammonium.

After optimization of the ratio of different components, a final electrolyte A with 0.2 M $McMT^-$, 0.2 M BMT, 0.05 M $LiClO_4$, 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile (MeCN), and ethylene carbonate (EC) mixed solvent (6/4, v/v) was employed for DSC fabrication. For comparison, an iodine-based electrolyte B with the same ratio, 0.2 M tetrabutylammonium iodide (TBAI), 0.2 M I_2, 0.05 M $LiClO_4$, 0.5 M TBP in MeCN/EC (6/4, v/v), was also prepared. When the colorless $McMT^-$ ion and BMT were mixed in the solvent, the color of solution turned light yellow.

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To determine the standard redox potential of $McMT^-$/BMT, cyclic voltammetry (CV) was performed using 0.2 M lithium perchlorate ($LiClO_4$) as supporting electrolyte. The measurements were carried out at 20 °C over the potential range 0.5 to −1.2 V at a scan rate of 50 mV s^{-1}. The solution that was studied contained 20 mM $McMT^-$ and 10 mM BMT in MeCN. A glassy carbon working electrode, a platinum foil counter-electrode, and an Ag/Ag^+ reference electrode were used. The potential versus the normal hydrogen electrode (NHE) was calibrated to the ferrocene/ferrocenium (Fc/Fc^+) couple by introducing a correction of 630 mV.[12] From the CV curve of $McMT^-$/BMT (Supporting Information, Figure S1), the reducing (−0.92 V) and oxidizing potential (0.07 V) versus Ag/Ag^+ were obtained, with a corresponding standard potential (E_o) of −0.425 V versus Ag/Ag^+ (−0.475 V vs. Fc/Fc^+) or 0.155 V versus NHE.

The low-cost organic dye, TH305,[13] was employed as photosensitizer for DSC fabrication. The working electrode was prepared by immersing the 10 μm thick TiO_2 film (5 × 5 mm^2), which included an 8 μm transparent layer and a 2 μm scattering layer, into the dye bath containing TH305 in CH_2Cl_2 solution saturated with chenodeoxycholicaicd (CDCA) for 2 h. A thermally platinized FTO glass counter-electrode and the working electrode were then sealed with a 25 μm thick hot-melt film (Surlyn, Solaronix) by heating the system at 120 °C. Devices A and B were completed by filling the electrolytes A and B by pre-drilled holes in the counter-electrodes and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. A black mask (8 × 8 mm^2) was used in the subsequent photovoltaic studies. Under simulated sunlight illumination with the intensity of 100 mW cm^{-2}, an efficiency of 4.0% was recorded for device A with short-circuit photocurrent (J_{sc}) of 12.2 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 762 mV, and a fill factor amounting to 0.42. Device B gave a 5.1% efficiency with J_{sc} 9.7 mA cm^{-2}, V_{oc} 774 mV, and fill factor of 0.68. Based on a state-of-the-art composition of iodine electrolyte, TH305-based DSC showed 7.3% efficiency under the same test conditions (Supporting Information, Table S1). The incident-to-photon conversion efficiency (IPCE) was also determined, showing a maximum of 89% at 460 nm for device A. Between 350 and 500 nm, the IPCE is much higher for device A than for device B (see Figure 1), which is probably responsible for the higher photocurrent of device A. This effect can most likely be ascribed to the weak light absorption of electrolyte A in this spectral region. This assumption gains further support from a separate experiment, in which the absorption spectra of a thin layer of electrolyte A and B confined between two conducting glass substrates separated by a 25 μm Surlyn spacer were recorded to simulate the practical situation of the electrolytes in the DSCs. As shown in Figure 2, it can be seen that electrolyte A has UV/Vis absorption only below 400 nm, but electrolyte B has strong absorption up to 500 nm owing to the presence of I_3^- in the electrolyte. The weak absorption in the visible region of electrolyte A is highly likely to improve the amount of light harvested by the photosensitizer in DSCs, thus explaining the increase in photocurrent observed.

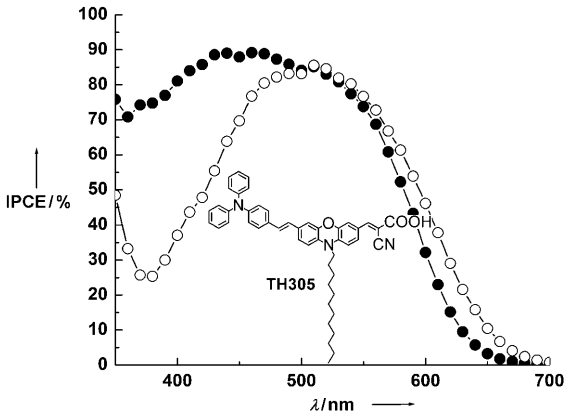

Figure 1. IPCE-spectra of devices A (●) and B (○) and the structure of the TH305 dye.

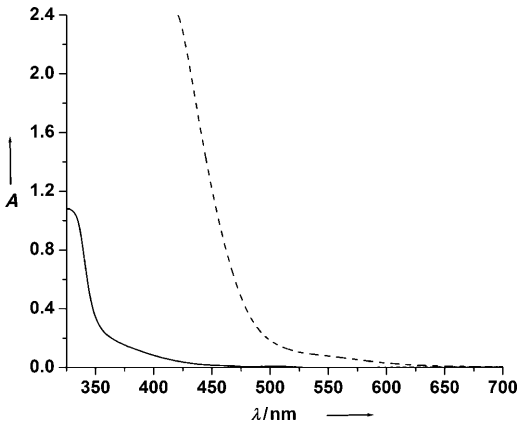

Figure 2. UV/Vis spectra of a thin layer of electrolyte A (——) and B (– – –) confined between two conducting glass substrates.

From a photovoltaic perspective, we find that devices A and B show comparable photovoltage values, although the redox potential of $McMT^-$/BMT (0.155 V vs. NHE) is more negative than that of I^-/I_3^- (0.4 V vs. NHE).[14] The open-circuit voltage V_{oc} of DSCs is determined by the energy difference between the quasi Fermi level of TiO_2 ($E_{F,n}$) and the potential of the redox couple in the electrolyte. The quasi Fermi level depends on both the conduction band (CB) edge position of TiO_2 and the electron concentration in TiO_2.[15] For the new electrolyte studied, not only the redox potential of $McMT^-$/BMT is shifted towards negative potentials, but the $E_{F,n}$ for device A is shifted to negative values as well. From charge extraction measurements (Figure 3a),[16] it can be seen that the $E_{F,n}$ for device A is about 100 mV more negative than that of device B. Consequently, only a slightly lower V_{oc} was obtained for device A even though the formal redox potential of $McMT^-$/BMT is considerably more positive than for the I^-/I_3^- couple. The electron lifetimes (τ_e) of devices A and B are plotted as a function of extracted charge (Q_{oc}) under open-circuit conditions, as shown in Figure 3b. Device A has a much longer τ_e than device B. At a given Q_{oc}, the τ_e value of device A is higher by a factor of about five compared to that of device B, which may be ascribed to a slower electron recombination rate between TiO_2 and the electrolyte. The

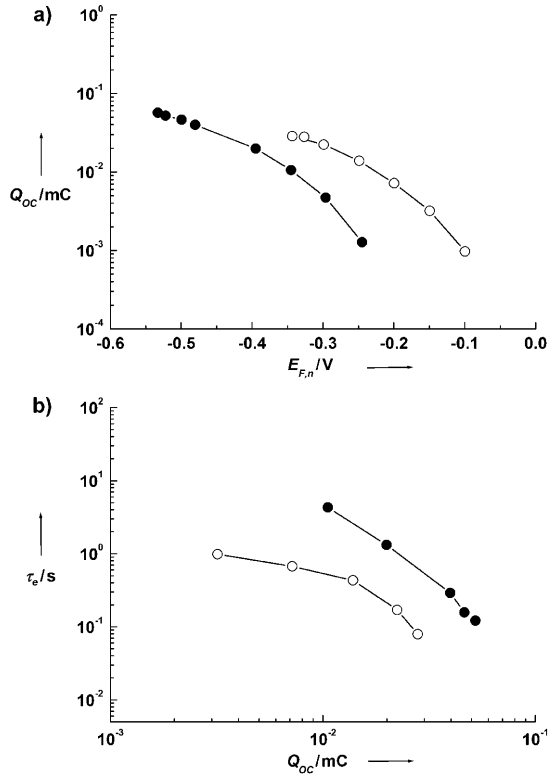

Figure 3. a) Charge extraction and b) electron lifetime of devices A (●) and B (○).

electron transport time (τ_{tr}) was also determined for the devices A and B (Supporting Information, Figure S3). The τ_{tr} values of both devices A and B under short-circuit conditions decrease with J_{sc} following a power-law relation. No significant difference in τ_{tr} between the devices A and B could be observed. This result indicates that the two electrolytes do not significantly differ with respect to the influence on the electron transport process from the TiO_2 surface to the conducting glass substrate.

An electrochemical impedance spectroscopy (EIS) analysis can offer insights into interfacial charge-transfer processes in DSCs. Figure 4 shows the Nyquist plots of the devices A and B under the same illumination conditions. By fitting the EIS spectra to an electrochemical model, some important parameters can be extracted. R_{rec} and R_{CE} represent the charge-transfer resistances at the dye/TiO_2/electrolyte interface and counter-electrode, respectively. The electron lifetime (τ_e), expressing the electron recombination between electrolyte and TiO_2, may also be extracted from the angular frequency (ω_{rec}) at the mid-frequency peak in the Bode phase plot using the relation $\tau_e = 1/\omega_{rec}$. τ_e and R_{rec} of device A are 419 ms and 1020 Ω, respectively; these values are much higher than the corresponding values for the device B, amounting to 87 ms and 270 Ω, respectively. This result suggests that the electron recombination rate between the TiO_2 film and the $McMT^-$/BMT-based electrolyte in device A is greatly suppressed. This trend is in accordance with the τ_e versus Q_{oc} results above. However, device A shows much higher R_{CE} (640 Ω) than device B (8 Ω), which probably causes the lower fill factor recorded for the former photovoltaic device.

In summary, an iodine-free organic redox couple ($McMT^-$/BMT) was adopted for application in organic-dye-sensitized solar cells. Based on a low-cost organic photosensitizer, TH305, an efficiency of 4.0% was achieved under simulated sunlight illumination (100 mW cm^{-2}). With the same ratio of reduced and oxidized species as used in the $McMT^-$/BMT electrolyte, an iodine-based electrolyte gave a reference efficiency of 5.1%. A higher photocurrent (12.2 mA cm^{-2}) for DSCs based on $McMT^-$/BMT was obtained owing to lower light absorption interference with the dye of the new electrolyte in the visible spectral region. The $McMT^-$/BMT redox couple also appears to significantly decrease the electron recombination rate between TiO_2 and the electrolyte. However, the main reason that the new electrolytes is still outperformed by the traditional iodine-based redox couple can be attributed to the considerably higher charge-transfer resistance at the counter-electrode, lowering the fill factor and the overall efficiency of the device. Obviously, platinum is not an efficient catalyst for the reduction of BMT. This clearly highlights one of the major challenges in DSC research, where all components must be optimized even if only one is modified. Future work will concentrate on the identification of a suitable catalyst for the reduction of BMT at the counter-electrode.

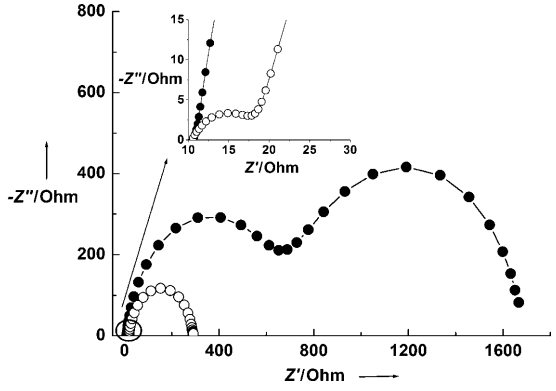

Figure 4. Nyquist plots of devices A (●) and B (○) under the same illumination conditions.

Experimental Section

TiO_2 film fabrication: Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned (in the order of detergent solution, water, and ethanol) using an ultrasonic bath. The conducting glass substrates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. The screen printing procedure was repeated (layer of 2 μm) with TiO_2 paste (Dyesol, 18 NR-T) to obtain a transparent nanocrystalline film of thickness around 8 μm and area of 0.25 cm^2. A scattering layer (ca. 2 μm, solaronix R/SP) was deposited, and a final thickness of 10 μm was attained. The TiO_2 electrodes were gradually heated in an oven (Nabertherm Controller P320) in an air atmosphere. The temperature gradient program has two levels at 325 °C (10 mins), and 500 °C (30 min). After sintering, the electrodes once again passed, as described above, a post-$TiCl_4$ treatment. A second and final sintering, at 500 °C for 30 min, was performed. When the temperature decreased to 30 °C

after the sintering, the electrodes were used to immerse into dye bath for sensitization.

Synthesis of [nBu$_4$N]McMT: 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT; 1.32 g, 10 mmol; Aldrich, 99%) was neutralized with 1M solution of tetrabutylammonium hydroxide in methanol (10 mL, 10 mmol; Aldrich). The reaction was required to proceed under N_2 atmosphere protection. After refluxing for 3 h, the solvent was evaporated and the resulting residue was dried under vacuum at 40°C for 12 h and placed at room temperature for 12 h to give [nBu$_4$N]McMT. The yield is quantitative. No impurity was detected by ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.37$ (t, $J =$ 8.5 Hz, 8H, NCH_2 in NBu_4^+), 2.45 (s, 3H, CH_3), 1.62–1.69 (m, 8H, CH_2 in NBu_4^+), 1.39–1.44 (m, 8H, CH_2 in NBu_4^+), 0.97 ppm (t, $J =$ 7.5 Hz, 12H, CH_3 in NBu_4^+). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.8$, 15.8, 19.9, 24.3, 59.1, 160.6, 183.0 ppm. MS (ESI): negative ion: $m/z =$ 131.1 $[M-NBu_4]^-$, calculated 131.0; positive ion: $m/z = 242.2$ $[NBu_4]^+$, calculated 242.3.

Synthesis of BMT: McMT (1.32 g, 10 mmol) was deprotonated with potassium carbonate K_2CO_3 (0.69 g, 5 mmol) in 20 mL methanol. The mixture was placed in an ultrasonic bath until K_2CO_3 disappeared (about 2 h), and then iodine (1.25 g, 4.92 mmol) was added to the solution and the reaction was sonicated for 10 min until the iodine disappeared completely. The solvent was removed under vacuum and the residue was dissolved in 20 mL CH_2Cl_2. The solution was washed with water (three times 30 mL), and finally the organic phase was collected and dried with anhydrous Na_2SO_4. After removing the solvent, the white solid was dried under vacuum at 40°C for 12 h to give 0.8 g BMT compound (yield, 61%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 2.78$ ppm (s, 6H, $2(CH_3)$). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 16.1$, 166.2, 169.0 ppm. MS (ESI): positive ions: $m/z =$ 263.1 $[M+H]^+$, calculated 263.0; 285.0 $[M+Na]^+$, calculated 284.9.

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