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Two Novel Carbazole Dyes for Dye-Sensitized Solar Cells with Open-Circuit Voltages up to 1 V Based on Br^-/Br_3^- Electrolytes

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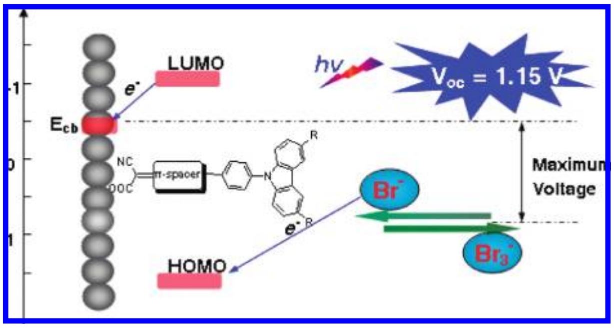
ABSTRACT



Dye-sensitized solar cells (DSCs) based on two novel carbazole dyes (TC301 and TC306) and a Br^-/Br_3^- redox mediator in dried CH_3CN solutions as electrolytes yielded a V_{oc} of 1.156 V and a η value of 3.68% and a V_{oc} of 0.939 V and a η value of 5.22% under simulated AM 1.5, respectively. The dyes TC301 and TC306 have more positive HOMO levels (1.59 and 1.38 V vs NHE) than the redox potential of Br^-/Br_3^--based electrolytes, which have sufficient driving force to regenerate dyes. Under similar conditions with an I^-/I_3^- instead of a Br^-/Br_3^- redox mediator, DSCs sensitized by the dyes TC301 and TC306 produced a V_{oc} of 0.696 V and a η value of 2.36% and a V_{oc} of 0.621 V and a η value of 4.10%, respectively.

Dye-sensitized solar cells (DSCs) have attracted much attention during the past years due to their low production cost and relatively high solar energy conversion efficiency.[1,2] DSCs based on Ru-complex photosensitizers such as N719 and redox mediator I^-/I_3^- couple can provide record high solar energy-to-electricity conversion efficiencies (η) of up to 12% at simulated AM 1.5 irradiation.[3] Despite its good performance, one main drawback of the I^-/I_3^- system is the mismatch between its redox potential $E(I^-/I_3^-)$ (0.5 V vs

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normal hydrogen electrode, NHE)[4] and that of the dye (ca. 1.0 V vs NHE), resulting in an excessive driving force of 0.5 eV and a energy loss incurred during dye regeneration which is one of the main factors limiting the performance of current DSCs. Thus, the search for alternative redox couples with a more positive redox potential than I^-/I_3^- is a current research topic of high priority. Because the potential of Br^-/Br_3^- redox couple $E(Br^-/Br_3^-)$ (about 1.1 V vs NHE)[5] is more positive than that of I^-/I_3^- redox couple, a large V_{oc} enhancement is expected if the Br^-/Br_3^- couple is used in place of the I^-/I_3^- couple for DSCs containing dyes which have also more positive HOMO levels than $E(Br^-/Br_3^-)$. Therefore, it is crucial to design dyes whose HOMO and LUMO levels match the redox potential of Br^-/Br_3^- and the conduction band of TiO_2, respectively. Here we report two novel metal-free organic carbazole dyes **TC301** and **TC306** (Figure 1), which have more positive oxidation potentials than $E(Br^-/Br_3^-)$. By using the novel dyes and Br^-/Br_3^- redox couple, a V_{oc} of 1.15 V and a η of 3.68% for DSC sensitized by the dye **TC301** and a V_{oc} of 0.939 V and a η of 5.22% for DSC sensitized by the other dye **TC306** were achieved, respectively. The value of 1.15 V is the highest V_{oc} ever reported for a single DSC so far.

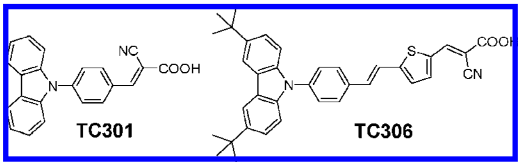

Figure 1. Molecular structures of two novel metal-free organic carbazole dyes **TC301** and **TC306**.

The spectra of the dyes **TC301** and **TC306** in dried CH_3CN solutions showed absorption bands with η_{max} at 374 and 429 nm, respectively (Figure 2a). The molar extinction coefficients, $\varepsilon(\eta_{max})$, were determined to be 12300 and 20900 M^{-1} cm^{-1} at the absorption maxima. The absorption spectra of the dyes attached on TiO_2 films (Figure 2b) with η_{max} appearing at 384 and 411 nm. In the presence of 0.8 M LiBr, the η_{max} attached on TiO_2 films were red-shifted 10 nm for the dye **TC301** and 14 nm for the dye **TC306**, respectively, and also the absorption intensities have increased.

It is well-known that adsorption/intercalation of potential-determining cations such as Li^+ into the porous TiO_2 electrode can broaden the absorption of dye on TiO_2.[6] Red-shift of absorptions of the dyes on TiO_2 films lead to E_{0-0} changes; thus, LUMO levels of the dyes changed from −1.23 to −1.09 V for the dye **TC301** and from −1.06 to −0.96 V for the dye **TC306**, which were sufficiently more negative than the potential of conduction band edge of TiO_2 electrode (E_{cb}, −0.5 V vs NHE) (Table 1). The relatively large energy gap between the LUMO and the E_{cb} provides the possibility for the addition of 4-*tert*-butylpyridine (TBP) to the electrolyte, which can shift the E_{cb} more negatively and, consequently, improve the voltage and the total efficiency.[7] The first oxidation potentials (E_{ox}) corresponding to the HOMO levels of the dyes were measured by cyclic voltammetry (CV) in dried DMF solutions. The E_{ox} were determined to be 1.59 V (vs NHE) for the dye **TC301** and 1.38 V (vs NHE) for the dye **TC306**, which were more positive than $E(Br^-/Br_3^-)$, indicating that the oxidized dyes formed after electrons injection into the conduction band of TiO_2 could accept electrons from Br^-/Br_3^- redox mediators thermodynamically.

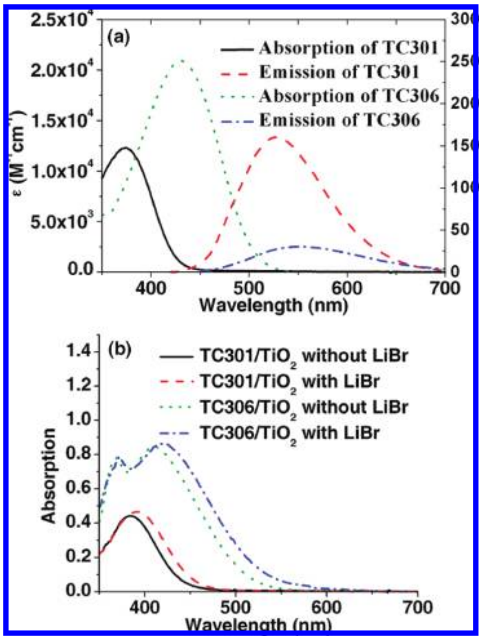

Figure 2. (a) Absorption and emission spectra of the dyes **TC301** and **TC306** in dried CH_3CN solutions (2×10^{-5} M). (b) Absorption spectra of the dyes **TC301** and **TC306** on TiO_2 films immerged in dried CH_3CN solutions with 0.8 M LiBr and without electrolyte.

Dye-sensitized solar cells based on a Br^-/Br_3^- redox mediator (devices A) containing 0.9 M 1,2-dimethyl-3-butylimidazolium bromide (DMBIBr), 0.08 M Br_2, and 0.5 M TBP electrolyte in dried CH_3CN solutions yielded a V_{oc} of 1.156 V and a η value of 3.68% for the dye **TC301** and a V_{oc} of 0.939 V and a η value of 5.22% for the dye **TC306** (Figure 3a,c and Table 2). DSCs containing 0.9 M DMBIBr, 0.8 M LiBr, 0.08 M Br_2, and 0.5 M TBP electrolyte in dried CH_3CN solutions also based on Br^-/Br_3^- redox mediator (devices B) yielded a V_{oc} of 1.041 V and a η value of 3.66% for the dye **TC301** and a V_{oc} of 0.915 V and a η value of 5.07% for the dye **TC306**. Under the same conditions, DSCs based on I^-/I_3^- redox mediators (devices C) containing 0.6

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Table 1. Absorption, Emission, and Electrochemical Properties of the Dyes **TC301** and **TC306**

dyes	λ_{max} (nm) in CH_3CN^a	emission^b λ_{max} (nm)	$E_{ox}{}^c$ (V vs NHE)	λ_{max} (nm) on $TiO_2{}^d$	$E_{0-0}{}^f$ (V)	$E_{ox} - E_{0-0}$ (V vs NHE)
TC301	374	527	1.59	384^d	2.82	−1.23
				392^e	2.68	−1.09
TC306	429	553	1.38	411^d	2.44	−1.06
				425^e	2.34	−0.96

[a] Absorptions in dried CH_3CN solutions (2×10^{-5} M) at rt. [b] Emission spectra in dried CH_3CN solutions (2×10^{-5} M) at rt. [c] The oxidation potentials of the dyes were measured in dried DMF solutions with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte (working electrode: glassy carbon; reference electrode: Ag/Ag^+; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference and converted to NHE by addition of 630 mV.[8] Counter electrode: Pt). [d] Absorptions of the dyes loaded on TiO_2 films immerged in dried CH_3CN solutions. [e] Absorptions of the dyes loaded on TiO_2 films immerged in 0.8 M LiBr in dried CH_3CN solutions. [f] E_{0-0} were determined by onset wavelengths of the corresponding absorption spetra on TiO_2 films.

M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.06 M LiI, 0.04 M I_2, and 0.4 M TBP in dried CH_3CN solutions produced a V_{oc} of 0.696 V and a η value of 2.36% for the dye **TC301** and a V_{oc} of 0.621 V and a η value of 4.10% for the dye **TC306**. After replacement of I^-/I_3^- with Br^-/Br_3^- in **TC301** dye-sensitized solar cells, device A yielded a significant increasement in V_{oc} (460 mV) but a decrease in J_{sc} (0.42 mA cm^{-2}). Device B yielded a significant increasement in both V_{oc} (345 mV) and J_{sc} (0.5 mA cm^{-2}). Significant increases in V_{oc} by using Br^-/Br_3^--based electrolytes instead of I^-/I_3^- were attributed to the enlarged energy level between the redox potential of the electrolyte and the Fermi level of TiO_2. The V_{oc} of device B is lower than that of device A; this is probably due to the positive shift of the conduct band edge of TiO_2 in the presence of Li^+ ions.[9,10] The higher J_{sc} in device B was attributed to the broad absorption of **TC301** on TiO_2 in the presence of Li^+ ions. Replacement of I^-/I_3^- with Br^-/Br_3^- in **TC306** dye-sensitized solar cells, compared to device C, yielded a large increase in V_{oc} (about 300 mV) for both device A and device B also due to the enlarged energy level between the redox potential of the electrolyte and the Fermi level of TiO_2.

For DSCs sensitized by the dye **TC301**, the incident photon-to-current conversion efficiencies (IPCEs) were between 75% and 80% around 400 nm and IPCE plateaus were between 360 and 460 nm (Figure 3b). For DSCs sensitized by the dye **TC306**, IPCEs were between 71% and 80% around 450 nm, and IPCE plateaus were between 350 and 500 nm (Figure 3d). One can see from parts b and d of Figure 3 that devices A and B produced larger IPCE values below 400 nm compared to device C. This phenomenon is attributive to the lower absorption of bromine than that of iodine in this spectral region. For DSCs sensitized by the dye **TC301**, we found the IPCE value for device C is slightly lower than that for device B and higher than that for device A. For DSCs sensitized by the dye **TC306**, the IPCE value for device C is broader than that for devices A and B. These results are in agreement with absorption spectra of the dyes attached to TiO_2 with 0.8 M LiBr in CH_3CN solutions and photocurrent generation of the devices.

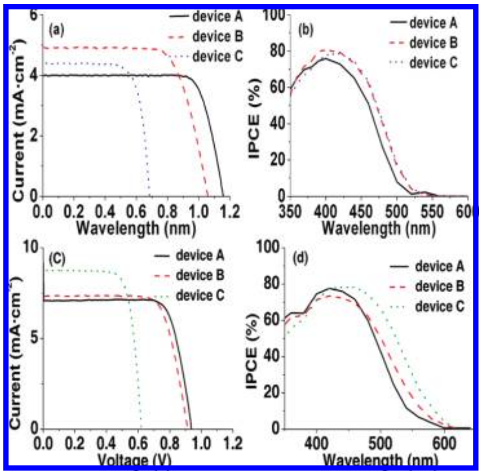

Figure 3. Photocurrent density vs voltage curves and IPCE action spectra for dye-sensitized solar cells sensitized by the dyes **TC301** (a, b) and **TC306** (c, d) with different electrolytes: device A based on 0.9 M DMBIBr, 0.08 M Br_2, and 0.5 M TBP electrolyte in dried CH_3CN sloutions; device B based on 0.9 M DMBIBr, 0.8 M LiBr, 0.08 M Br_2, and 0.5 M TBP electrolyte in dried CH_3CN solutions; device C based on 0.6 M DMPII, 0.06 M LiI, 0.04 M I_2, and 0.4 M TBP electrolyte in dried CH_3CN solutions.

Table 2. Photovoltaic Performance of DSCs Based on the Dyes **TC301** and **TC306** in Different Electrolytes As Shown in Figure 3

dye		J_{sc} (mA cm^{-2})	V_{oc} (V)	ff	η (%)
TC301	device A	4.00	1.156	0.796	3.68
	device B	4.93	1.041	0.713	3.66
	device C	4.42	0.696	0.767	2.36
TC306	device A	7.12	0.939	0.781	5.22
	device B	7.36	0.915	0.752	5.07
	device C	8.76	0.621	0.754	4.10

Figure 4 shows the electrochemical impedance spectra[11−14] for devices A−C under forward bias (−0.7 V) in the dark. The larger semicircles in the Nyquist plots are attributed to the charge-transfer processes occurring at TiO_2/dye/electrolyte interface. Evidently, the charge-transfer resistance at the interface was increased remarkably from

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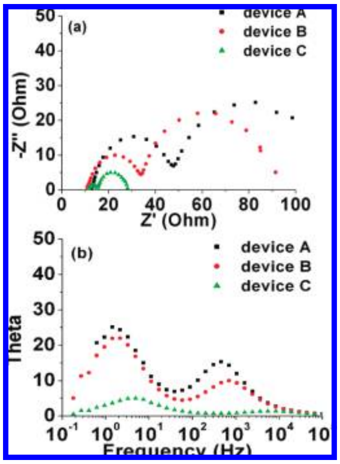

Figure 4. Electrochemical impedance spectra, scanned from 10^{-1} to 10^{5} Hz at room temperature, for the dye **TC301** and devices A−C, respectively: (a) Nyquist plots; (b) Bode phase plots. The cells were measured at −0.7 V in the dark. The alternate current (AC) amplitude was set at 10 mV.

device C to devices A and B. The electron lifetime (τ) in TiO_2 film for DSCs sensitized by the dye **TC301** are 98 and 93 ms for device A and B, which are much larger than that for device C (38 ms). Both results suggest that the charge recombination was inhibited upon replacing I^-/I_3^- with Br^-/Br_3^-. We can conclude that significant increasements in V_{oc} by using Br^-/Br_3^--based electrolytes instead of I^-/I_3^- were attributed to not only the enlarged energy level between the redox potential of the electrolyte and the Fermi level of the conduction band of TiO_2 but also the suppressed charge recombination.

Although very high open-circuit voltage with a good energy conversion efficiency was achieved, we found that stability of DSCs based on Br^-/Br_3^- electrolytes and the novel dyes **TC301** and **TC306** was not very good because of bromination reaction of bromine with unsaturated bonds of the dyes especially in the presence of light irradiation. To achieve long-term stable DSCs based on Br^-/Br_3^- electrolytes, we are synthesizing new dyes without reactive position which could react with bromine.

In summary, we have demonstrated that a DSC consisting of Br^-/Br_3^- redox mediator and the organic dye **TC301** accomplished a very high open-circuit voltage (up to 1.15 V) with a good energy conversion efficiency of 3.68%. And for the dye **TC306**-sensitized solar cell, a high open-circuit voltage (0.939 V) with a considerably good energy conversion efficiency of 5.22% was achieved with a Br^-/Br_3^--containing electrolyte. These results suggest that the Br^-/Br_3^- couple could be a promising alternative to the I^-/I_3^- couple for those dyes with more positive HOMO levels in DSCs. Further efforts on finding new dye with broader absorption to get even better DSC performance are in progress.

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Supporting Information Available: Fabrication of the nanocrystalline TiO_2 solar cells, synthesis and spectra data of the dyes **TC301** and **TC306**. This material is available free of charge via the Internet at http://pubs.acs.org.

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