Synthesis and electron-transfer properties of benzimidazole-functionalized ruthenium complexes for highly efficient dye-sensitized solar cells†

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Novel heteroleptic ruthenium complexes—RD1, RD5, RD10 and RD11—with ligands based on benzimidazole were synthesized and characterized for application to dye-sensitized solar cells (DSSC); the remarkable performance of RD5-based DSSC is understood for its superior light-harvesting ability and slower charge-recombination kinetics.

Dye-sensitized solar cells (DSSC) have attracted attention because of their efficient performance, ease of fabrication and economy of production.1 Much effort has been devoted to the synthesis and characterization of various sensitizers for DSSC, such as ruthenium complexes,2 zinc porphyrins3 and metal-free organic dyes.4 The devices made of ruthenium polypyridyl complexes, such as N3 and N719 dyes, attained an efficiency ~11% of power conversion under one-sun illumination.5 To improve the efficiency of light harvesting, heteroleptic ligands based on thiophene were designed to make ruthenium complexes with large absorption coefficients, thus enhancing the efficiency of the device to 11.5%.6 The synthesis of those thiophene-based ligands was, however, more elaborate than for the commercial N719 dye. Because their electronic mobilities are great, benzimidazole derivatives have been developed as layer materials for electron transport and hole blocking in organic light-emitting diode devices.7 Bearing a similar idea in mind, we designed heteroleptic ruthenium complexes containing benzimidazole substituents in a series for which the corresponding ligands can be synthesized in a simple two-step procedure.

Here we report four novel heteroleptic ruthenium complexes, RD1 [Ru(dcbpy)(1-methyl-2-(pyridine-2-yl)benzimidazolato)(NCS)2], RD5 [Ru(dcbpy)(1-benzyl-2-(pyridine-2-yl)benzimidazolato)(NCS)2], RD10 [Ru(dcbpy)(1-decyl-2-(pyridine-2-yl)benzimidazolato)(NCS)2] and RD11 [Ru(dcbpy)(1,1’-dimethyl-2,2′-bibenzoimidazolato)(NCS)2], for which one 4,4’-dicarboxylic-2,2′-bipyridine (dcbpy) ligand in N3 dye was replaced by a heterocyclic ligand (Chart 1). The DSSC device made of RD5 sensitized on the TiO2 film exhibits photovoltaic performance comparable with the specifications of a device made of N719 dye. The results obtained from photocurrent and photovoltage decays indicate that the electron lifetimes of the devices display a systematic trend RD5 > RD10 > RD1 > RD11, which is consistent with the cell performance in the same order. Femtosecond measurements of infrared transient absorption (TA) of the samples as thin films indicate that, for RD-series sensitizers there exists a decay component on a ns time scale representing the back-electron transfer (BET) occurring at the interface between TiO2 and dye, whereas for dye N719 such a process was not observable. Combining results from both electron-transfer kinetics reasonably explains the order of Voc to be N719 > RD5 > RD10 > RD1 > RD11. In contrast, the IPCE action spectra of the devices account for the order of Jsc to be RD5 > N719 > RD10 > RD1 > RD11. The superior performance of RD5-based DSSC is thus understood for its superior light-harvesting ability and charge-recombination kinetics.

Fig. 1 shows the absorption spectra of RD1, RD5, RD10, RD11 and N719 in DMF; the corresponding spectral (Fig. S1†) and electrochemical (Fig. S2†) properties of these dyes are listed in Table S1.† The UV-visible absorption spectra of these complexes exhibit a band to the red of the corresponding band for dye N719. Even though the molar absorption coefficients (ε/M−1 cm−1) of RD1 (7560 at 539 nm), RD5 (8005 at 537 nm), RD10 (7796 at 537 nm) and RD11 (6483 at 538 nm) are significantly smaller than that of N719 (13610 at 524 nm), the absorbances of the corresponding thin-film spectra on TiO2 films are slightly greater than that of N719 (inset of Fig. 1). This property reflects that the amounts of the RD series dyes adsorbed on TiO2 surface are significantly greater than that of N719 (Table 1).

† Electronic supplementary information (ESI) available: Supplementary figures (Fig. S1–S3), tables (Tables S1–S2) and experimental details. See DOI: 10.1039/c0cc03517c

Chart 1  Molecular structures of RD1, RD5, RD10 and RD11.

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Fig. 1 Absorption spectra of RD1, RD5, RD10, RD11 and N719 in DMF. Inset shows absorption spectra of TiO2 films (active layer of thickness 2 μm) sensitized with the indicated dyes.

Fig. 2a compares the current–voltage characteristics of these four dyes on TiO2 films of thickness 12 + 3 μm with that of N719 under the same conditions of device fabrication; the corresponding photovoltaic parameters are listed in Table 1. The values of \( V_{OC}/V \) are 0.694 for RD1, 0.737 for RD5, 0.710 for RD10 and 0.685 for RD11, showing the effect of various substituents on the imidazole ring and the effect of the bibenzimidazolyl ligand. The values of \( J_{SC}/mA \ cm^{-2} \) are 12.744 for RD1, 15.084 for RD5, 13.612 for RD10 and 11.159 for RD11. This variation of \( J_{SC} \) is inexplicable solely as the effect of dye loading. The trend of \( J_{SC} \) is, however, consistent with the variation of IPCE shown in Fig. 2b. As mentioned for the absorption spectra, the IPCE action spectra of dyes in the RD series exhibit also a red-shifted spectral feature beyond 800 nm, in particular for RD5 showing greater efficiency and breadth than those properties of N719. The total efficiency of power conversion of RD5 attains 7.7%, which is comparable with that of N719 (η = 7.8%). The RD5 device performed slightly better than the N719 device with the thinner TiO2 films (Fig. S2† and Table S2†) because of the superior dye-loading effect of RD5.

Fig. 3a and b show the electron-transport kinetics of the corresponding devices obtained from an analysis of the photovoltage (Fig. 3a) and photocurrent (Fig. 3b) decay data.8 The electron-diffusion coefficients (D) are similar for each dye, but the time coefficients for electron recombination (\( \tau_R \)) display a systematic trend RD5 > RD10 > RD1 > RD11. This trend indicates that charge recombination between the dye (or \( I_3^- \)) and the TiO2 surface might occur near the imidazolyl ligands. The existence of a hydrophobic chain in the imidazolyl ligand (RD10) longer than for dye RD1, impedes the charge recombination, but the existence of the benzyl substituent in the imidazolyl ligand (RD5) might involve a hindrance to retard the charge recombination.

Fig. 4 displays the normalized TA traces for RD1, RD5, RD10 and RD11 under simulated AM-1.5G illumination (100 mW cm\(^{-2}\)) and active area 0.16 cm\(^2\).

Table 1 Photovoltaic parameters and amounts of dye loaded on DSSC with TiO2 films sensitized with RD1, RD5, RD10, RD11 and N719 under simulated AM-1.5G illumination (100 mW cm\(^{-2}\)) and active area 0.16 cm\(^2\).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye loading/nmol cm(^{-2})</th>
<th>( J_{SC}/mA \ cm^{-2} )</th>
<th>( V_{OC}/V )</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD1</td>
<td>295</td>
<td>12.744</td>
<td>0.694</td>
<td>0.68</td>
<td>6.0</td>
</tr>
<tr>
<td>RD5</td>
<td>216</td>
<td>15.084</td>
<td>0.737</td>
<td>0.69</td>
<td>7.7</td>
</tr>
<tr>
<td>RD10</td>
<td>253</td>
<td>13.612</td>
<td>0.710</td>
<td>0.70</td>
<td>6.8</td>
</tr>
<tr>
<td>RD11</td>
<td>291</td>
<td>11.159</td>
<td>0.685</td>
<td>0.67</td>
<td>5.1</td>
</tr>
<tr>
<td>N719</td>
<td>149</td>
<td>14.157</td>
<td>0.783</td>
<td>0.70</td>
<td>7.8</td>
</tr>
</tbody>
</table>
other RD dyes indicates that the excitation energies were much above the energy barrier. The cyclic voltammetry measurements indicate that the LUMO level of N719 is significantly below those of the RD dyes (Fig. S3†), consistent with our assumption.

The transient of N719 does not decay in the observed ns region, whereas the transients of RD1, RD5 and RD11 exhibit a slow-decay feature with an offset for which the decay characteristics cannot be resolved on this time scale. The slow-decay components of the transients were fitted with time coefficients 1.0 ns for RD1, 3.6 ns for RD5 and 0.42 ns for RD11. These results indicate that there exists a ns-BET process in the RD dyes that was non-observable in N719. The observed BET kinetics are consistent with HOMO levels showing a sequence of RD11 > RD1 > RD5 > N719 (Fig. S3†). Because the dye regeneration of a Ru system occurs typically on a µs scale, the observed BET of the RD dyes on the ns scale are expected to play a role in cell performance. The BET kinetics were observed for thin-film samples that involved no electrolyte, but the trend of the BET decays is consistent with the order N719 > RD5 > RD1 > RD11 for the corresponding devices. Because RD5 has a greater light-harvesting feature to enhance its JSC, it compensates its VOC loss to yield a cell performance comparable with that of N719.

In conclusion, we designed new heteroleptic ruthenium complexes containing benzimidazole substituents for application to dye-sensitized solar cells. These Ru complexes were synthesized according to a standard one-pot procedure with the corresponding heteroleptic ligands produced in only two simple steps. The corresponding devices show performances with the order RD5 > RD10 > RD1 > RD11; the efficiency of power conversion of RD5 is comparable with that of N719. The results obtained from photocurrent and photovoltage decays indicate that the electron lifetimes of the devices display a systematic trend RD5 > RD10 > RD1 > RD11, which is consistent with the cell performance showing the same order. The observed charge-recombination kinetics reasonably explain the order of VOC to be N719 > RD5 > RD10 > RD1 > RD11. The IPCE action spectra of the devices account for the order of JSC to be RD5 > N719 > RD10 > RD1 > RD11. Note that the molecular structure of RD10 is similar to a highly efficient Ru sensitizer (CBTR) recently reported, but the latter benzimidazyl ligand was coordinated with the N–C atoms involving more synthetic steps. We emphasize here that the ease of synthesis is an important factor to be considered in making a highly efficient sensitizer for future commercialization. Work is in progress along this line to design and to synthesize more efficient heteroleptic ruthenium complex sensitizers with superior light-harvesting ability and slower charge recombination.

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Notes and references