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We report on a new family of ruthenium poly-pyridyl complexes that bears bis- and tris-tetrazolate mono-dentate ligands along with their spectroscopical, electrochemical, and theoretical characterization. Dye-sensitized solar cells with these complexes show good conversion efficiencies with comparable open circuit voltages to that of N719 without the use of any additives, due to their retarded electron-recombination processes.

In the past two decades high interest in the dye sensitized solar cell (DSSC) research area has been immense due to the DSSC’s low cost of fabrication and ease of production,\(^1\) which makes it a good candidate for commercialization. Recently, DSSC’s efficiencies of 12.3% have been attained using a zinc-porphyrin complex as a sensitizer along with a liquid electrolyte system,\(^2\) and efficiencies of 15% for perovskite-based solid state DSSC’s.\(^3\) Up-to-date, the most commonly used dye is either the well-known N3 dye (N719 when in the di-anionic form) [Ru(NCS)\(_2\)(dcbpy)]\(_2\)] (dcbpy = 4,4’-dicarboxy-2,2’-bipyridine)\(^4\) or the black dye [Ru(NCS)\(_3\)(tctpy)] (tctpy = 4,4’,4’’-tricarboxy-2,2’:6’,2’’-terpyridine)\(^5\) as very efficient sensitizers. However, designing metal based dyes that lack the thiocyanate ligand (SCN\(^-\)) is of great interest. In addition, red-shifting the absorption band of the sensitizer in the visible and near-IR region may have positive effects on DSSCs’ efficiencies.

Recently, a new class of cyclometalated complexes that lack the SCN\(^-\) ligand and have better light harvesting properties than N719 has been introduced by different research groups.\(^6\)-\(^17\) The high interest in this class of ruthenium based dyes is due to their good long term stability and extended absorption in the visible region (down to 800 nm). Most of this class of dyes is based on either bi- or tridentate ligands that bear either pyrazolate, triazole, oxyquinolate, phenyl or pyrimidinyl moieties.

In the present study, we report the design of Ru\(^{II}\) based dyes, T133 through T136, that bear bis- or tris-tetrazolate monodentate ligands along with either two (dcbpy) or one (tctpy) moiety, respectively, Scheme 1 (see Scheme S1 in the Supporting Information for the synthetic strategy). The interesting features of these four dyes are in their chemical stability, ease of synthesis/purification and their photophysical and electrochemical properties. To our knowledge, there are no reports of ruthenium based sensitizers that bear such monodentate ligands in the literature. The four dyes were characterized by \(^1\)H-NMR, APPI mass spectrometry, UV/vis, steady state and lifetime fluorescence measurements and electrochemistry.

 Scheme 1 Structures of the dyes T133 to T136

In the two dyes’ classes (T133-T134 and T135-T136) the tetrazolate ligand bares either an electron withdrawing trifluoromethylphenyl (TFMP) group or an electron rich triphenylamine (TPA) moiety, both of which tune the redox potential of the Ru\(^{II}\) center from 1.20 to 0.89 V vs. the normal...
hydrogen electrode (NHE), Table 1. The presence of the electron rich TPA group would also red-shift the absorption maximum of the dye in the visible and near-IR region due to the increase in conjugation and electron donation ability. Whereas, the electron deficient TFP group would raise the dye’s redox potential when compared to the analogous TPA-based dye, which in turn ensures an efficient regeneration of the oxidized sensitizer by the iodide/triiodide electrolyte system upon electron injection.

The absorption and emission spectra of the four dyes in ethanol is depicted in Fig. 1. The first class of dyes (T133-134) shows an absorption in the visible region extending down to 750 nm ($\lambda_{\text{abs}} = 513$ nm and 508 nm with extinction coefficients $\varepsilon = 9.3$ and $9.9 \times 10^3$ M$^{-1}$ cm$^{-1}$ for T133 and T134, respectively). The T135 and T136 absorption extends down to 820 nm with maxima at $\lambda_{\text{abs}} = 566$ nm and 572 nm and extinction coefficients $\varepsilon = 7.9$ and $6.8 \times 10^3$ M$^{-1}$ cm$^{-1}$, respectively. The same trend was seen in the absorbance measurements done on 6 µm TiO$_2$ films dyed with the different dyes (see Fig. S4 in supporting information), suggesting that the amounts of the five different adsorbed dyes are similar. The lowest energy transitions are attributed to $S_1$ MLCT transitions inferred from TD-DFT calculations (see Table S1 and Fig. S2 in Supporting Information). The four dyes also show emission in the near-IR region, Fig. 1, with intriguing longer lifetimes in Supporting Information. The four dyes also show emission maxima at $\lambda_{\text{em}} = 715, 705, 770$ and 767 nm and emission lifetimes of $\tau_{\text{em}} = 70, 85, 120, 140$ ns, respectively, Fig. 1 and Table 1. Such long emission lifetimes might positively add to the enhancement of electron injection efficiency.

The electrochemical properties of the different ruthenium complexes (T133 through T136) were evaluated by differential pulse voltammetry in dimethylformamide (DMF), Fig. 2. (see also Fig. S1 in the Supporting Information). The Ru$^{III}$ redox potentials of the four dyes were measured to be $E_{1/2} = 1.10, 1.20, 1.00$ and 0.89 vs NHE for T133 through T136, respectively. Table 1. T134 and T137 showed only one redox peak between 0.2 and 1.5 V which is attributed to the oxidation/reduction of the Ru$^{III}$ center. Upon comparing the redox potentials of the four dyes shows that upon the introduction of a third tetratolate ligand a shift of ~ 0.2 V is seen for T135 and T136 when compared to T134 and T133, respectively. As expected, T134 had the highest potential due to the electron donating effect of the TPA group on the ruthenium center. T133 and T136 show in addition to the ruthenium’s redox potential two redox peaks in the scanned potential window which are attributed to the redox active TPA groups.

The derived redox potentials of the dyes’ excited states from both the Ru$^{III}$ redox potential and the optical energy gap ($E_{0.0}$ was calculated from the intersection of the lowest energy MLCT band and the emission band) ranges between $E^{*}\text{ox} = -0.74$ and -0.92 V vs NHE. These values are higher than that of the TiO$_2$ conduction band edge (CB) (~ 0.5 V vs. NHE), and thus upon photo excitation of these complexes fast and efficient electron injection into the TiO$_2$ CB is expected.

Table 1 Spectroscopic and Electrochemical Data of the Dyes

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$E_{1/2}$ vs NHE</th>
<th>$E^{*}\text{ox}$ vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>T133</td>
<td>311 (4.65), 380 (1.11), 513 (0.93)</td>
<td>715 (70)</td>
<td>1.35, 1.25</td>
<td>-0.81</td>
</tr>
<tr>
<td>T134</td>
<td>311 (3.75), 380 (1.02), 508 (0.99)</td>
<td>705 (85)</td>
<td>1.20</td>
<td>-0.74</td>
</tr>
<tr>
<td>T135</td>
<td>337 (3.77), 385 (1.09), 566 (0.79)</td>
<td>770 (120)</td>
<td>1.00</td>
<td>-0.78</td>
</tr>
<tr>
<td>T136</td>
<td>333 (8.63), 388 (1.02), 572 (0.68)</td>
<td>767 (140)</td>
<td>1.35, 1.22, 0.89</td>
<td>-0.92</td>
</tr>
<tr>
<td>N719</td>
<td>306 (4.40), 379 (1.40), 525 (1.35)</td>
<td>755 (9)</td>
<td>1.08</td>
<td>-0.98</td>
</tr>
</tbody>
</table>

* Measured in ethanol. $^b$ Measured in aerated ethanol with $\lambda_{\text{em}} = 532$ nm. $^c$ Measured in DMF with 0.1 M TBAPF$_6$.

DSSCs employing a 12 µm thick TiO$_2$ layer plus a 4 µm scattering layer (300 nm) were fabricated using the four different dyes in addition to a DSSC employing the N719 dye for comparison. The TiO$_2$ films were stained by the respective dye solution (0.3 mM) in ethanol for 18 h without any additives. An electrolyte solution (EL1) made of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (MPI), 0.1 M guanadinium thiocyanate (GuNCS), 0.05 M LiI, 0.03 M I$_2$ and

![Fig. 1 Absorption and emission spectra ($\lambda_{\text{em}} = 532$ nm) of T133 (dotted-black), T134 (dashed-green), T135 (dashed-dotted-blue) and T136 (dashed-dotted-dotted-violet) in ethanol.

![Fig. 2: Differential pulse voltammograms (0.1 M Bu$_4$NPF$_6$, DMF) for T133 to T136.](image)
0.5 M 4-tert-butylpyridine (TBP), in methoxypropanonitrile (MPN), was used in these studies. The photocurrent vs voltage ($I(V)$) responses of the above mentioned cells are shown in Fig. 3 and summarized in Table 2. The lower fill factors (FF) and open circuit voltages ($V_{oc}$) of the studied cells when compared to values in the literature are mainly due to the geometry of the cells studied (1 x 1 cm). The T133 through T136 based cells afforded good performances except for T136, with short-circuit photocurrents $J_{sc} = 13.1, 12.0, 13.0$ and 6.7 mA cm$^{-2}$, $V_{oc} = 620, 622, 495$ mV, FF = 0.65, 0.67, 0.66 and 0.65 and efficiencies $\eta = 5.3, 5.0, 5.3$ and 2.2 $\%$, respectively, under simulated AM1.5 G solar illumination at 100 mW cm$^{-2}$. In the case of N719, the cell showed a slightly higher performance with $J_{sc} = 14.6$ mA cm$^{-2}$, $V_{oc} = 637$ mV, FF = 0.67 and $\eta = 6.2\%$.

The measured incident photon to electron conversion efficiency (IPCE) spectra of the T133 through T136 and N719 based cells are shown in Fig. 4. As can be seen, T133 and T134 show similar IPCE values to N719 but blue shifted by 20 and 25 nm, respectively, which is consistent with their UV/vis spectra. From the IPCE, integrated current and IV measurements one can conclude that T133 and T134 show similar electron injection and dye regeneration to N719.

Moreover, the higher $J_{sc}$ value shown by T133 when compared to T134 is mainly attributed to the former’s better light absorption (5 nm red shift). As for T135, the IPCE spectrum shows lower IPCE% values but red shifted by ~ 20 nm when compared to N719. When using EL1 as the electrolyte system, T136 shows much lower IPCE% values than N719 with a similar red shift as T135 (this will be discussed at a later stage). The IPCE spectrum of T135 highlights the better absorption nature of T135 than N719 in the near-IR, however, the measured lower photo-current of T135 could be attributed to its lower absorption extinction coefficient.

In order to understand the above mentioned results (lower efficiency of T136 than N719), we performed electrochemical impedance spectroscopy (EIS) measurements on the five different assembled cells at $V_{oc}$ under different light intensities. EIS spectra were analyzed using an established equivalent-circuit that interprets the different interfaces in a DSSC through a transmission line model. The Fig. 5 shows a plot of the chemical capacitance values at the TiO$_2$/electrolyte interface ($C_i$), for the different cells extracted from the EIS experiments, versus the corrected applied voltage ($\nu E_F - E_{F,redox}$)$_{cor.}$ where $\nu E_F$ is the electron quasi-Fermi energy level in the TiO$_2$ film and $E_{F,redox}$ is the electrolyte redox Fermi level, (the applied voltage is corrected for voltage drop due to the total series resistance, $R_s$). The $C_i$ values for the five cells show an exponential behavior as a function of the corrected applied voltage, where this is due to the trap energy distribution below the conduction band edge.

Considering that the five different cells have the same trap energy distribution (since the TiO$_2$ film is identical in all cells) and the same electrolyte solution is used in these cells, the observed shifts in the ($\nu E_F - E_{F,redox}$)$_{cor.}$ towards higher or lower values could be attributed to an upward or downward shifts in the conduction band edge, respectively. The observed shifts $\Delta (\nu E_F - E_{F,redox})_{cor.}$ compared to N719 lies between +10 and -10 mV for the four tetrazolate based dyes, Fig. 5, which is within our data experimental errors. As such, we can assume that there is no significant shift in the conduction band edge in the five different cells. However, the plots of the charge recombination resistance at the TiO$_2$/electrolyte interface ($R_n$) versus ($\nu E_F - E_{F,redox}$)$_{cor.}$ show some differences between the five DSSCs, Fig. 6. DSSCs that incorporate T133 through T135 show slightly

### Table 2: Performance of T133 through T136 and N719 Dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T133</td>
<td>13.1</td>
<td>620</td>
<td>0.65</td>
<td>5.3</td>
</tr>
<tr>
<td>T134</td>
<td>12.0</td>
<td>620</td>
<td>0.67</td>
<td>5.0</td>
</tr>
<tr>
<td>T135</td>
<td>13.0</td>
<td>622</td>
<td>0.66</td>
<td>5.3</td>
</tr>
<tr>
<td>T136</td>
<td>6.7</td>
<td>495</td>
<td>0.65</td>
<td>2.2</td>
</tr>
<tr>
<td>N719</td>
<td>14.6</td>
<td>637</td>
<td>0.67</td>
<td>6.2</td>
</tr>
</tbody>
</table>

*Measured under 100 mW cm$^{-2}$ simulated AM1.5 spectrum with an active area = 0.126 cm$^2$. Electrolyte EL1: 0.6 M DMPII, 0.05 M LiI, 0.5 M TBP, 0.1 M GuSCN and 0.03 M I$_2$ in MPN.

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Fig. 3 (A) Photocurrent–voltage characteristics of DSSCs sensitized with dyes: N719 (solid-red) and T133 (dotted-black), T134 (dashed-green), T135 (dashed-dotted-blue) and T136 (dashed-dotted-dotted-violet) with electrolyte EL1. (B) Dark currents of the corresponding cells.

Fig. 4 IPCE% and integrated current spectra of N719 (solid-red) and T133 (dotted-black), T134 (dashed-green), T135 (dashed-dotted-blue) and T136 (dashed-dotted-dotted-violet) assembled cells with electrolyte EL1.
smaller $R_{ct}$ values than N719 (where a smaller $R_{ct}$ value indicates faster electron recombination from the TiO$_2$ to the electrolyte solution or oxidized dye, and thus lower $V_{oc}$ values). However, the T136 based DSSC shows much smaller $R_{ct}$ values than N719, which suggests fast electron recombination processes at the dyed TiO$_2$/electrolyte interface and in turn causes the low $V_{oc}$ value of 495 mV. These results are also consistent with the dark currents measured for the respective cells, Fig. 3 B.

Open circuit voltage decay (OCVD) experiments were conducted to probe the electron recombination processes. Fig. 7 shows the effective electron lifetime ($\tau_n$) obtained from OCVD measurements,\textsuperscript{25} in addition to the $\tau_n$ values derived from the EIS experiments (from EIS $\tau_n = R_{ct}C_p$). Electron lifetimes obtained from the two different techniques (OCVD and EIS) are in good agreement. The $\tau_n$ values for the T133 through T135 based cells are only ~1.7 times shorter than that of N719. However, T136, and as inferred by all of the performed measurements, shows a much shorter $\tau_n$ than N719 by ~52 times.

Therefore, the slight lower performance of T133 to T135 than N719 is due to the blue-shift in the absorption spectra of T133 and T134 and slightly faster electron recombination processes, whereas that of T135 is due to the latter reason and its low absorption extinction coefficient. However, the much lower efficiency of T136 when compared to T133-T135 and N719 is mainly due to accelerated electron recombination processes. The accumulated electrons in the TiO$_2$ can either recombine with the oxidized dye upon electron injection or to the electrolyte system. The former mechanism becomes significant when the oxidized dye is not sufficiently regenerated by the electrolyte redox system.\textsuperscript{25} In addition, the dye structure can have profound effects on the electron recombination processes, where it was shown by different research groups that depending on the molecular structure of the dye binding to iodine\textsuperscript{26} or even iodide\textsuperscript{27} can take place and affect the DSSC performance negatively or positively, respectively. In order to pinpoint the reason behind such increased electron recombination kinetics in the case of T136, we used a different electrolyte system (EL2: 2.0 M 1,3-dimethylimidazolium iodide (DMI), 0.1 M GuNCS, 0.05 M LiI, 0.03 M I$_2$ and 0.5 M TBP in MPN) that we and other groups\textsuperscript{14} use for dyes that possess redox potentials below 1.0 eV vs NHE and might be inefficiently regenerated with electrolyte systems with low iodide concentrations such as in EL1. Indeed, with EL2 (compared to EL1) T136 shows an increase in efficiency from 2.2 % to 5.3% with higher values of $J_{sc} = 12.8$ mA.cm$^{-2}$ and $V_{oc} = 630$ mV than that with EL1, Fig. 8.
In addition, T136 shows a comparable electron lifetime to the other dyes when EL2 is used as the corresponding electrolyte, (see Fig. S5 in the Supporting Information). Therefore, it would be safe to conclude that in the case of T136 the lower performance shown with EL1 than with EL2 might be due to an inefficiency in its regeneration by EL1. However, at this point one cannot be sure if this is due to T136 lower redox potential than the other three dyes or to its different molecular structure when anchored on TiO2.

Conclusions

In summary, we have successfully designed and synthesized a new class of ruthenium based dyes using bis- and tris-tetrazolate ligands that show interesting photophysical and electrochemical properties. Good DSSCs efficiencies were attained with these new dyes and will show interesting photophysical and electrochemical properties. Using long aliphatic chains, on such more manipulative ligands than a thiocyanate is, extending the conjugation in these ligands might increase the absorption extinction coefficient and thus attain better light harvesting ability.

Acknowledgments

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Notes and references

New Ru$^{II}$ complexes bearing bis- and tris-tetrazolate ligands, and their application as efficient sensitizers in Dye-sensitized Solar Cells are presented.