Photophysical properties of new cyclometalated ruthenium complexes and their use in dye sensitized solar cells†

Haware Kisserwan, Amanda Kamar, Tharallah Shoker and Tarek H. Ghaddar*

Received 28th February 2012, Accepted 22nd June 2012
DOI: 10.1039/c2dt30482a

A new class of cyclometalated ruthenium complexes, Ru(C^N^N)(N^N^N′′′)Cl where N^N^N′′′ = 4,4′,4″-tricarboxy-2,2′,6′,2″-terpyridine and C^N^N = substituted 6-phenyl-2,2′-bipyridine, for Dye Sensitized Solar Cells (DSSCs) is proposed. We have investigated the effect of different substituents (R = COOH, thiophen-2-yl, F and OCH3) on the ancillary C^N^N′′′ ligand on the photophysical properties and performance of the six different cyclometalated ruthenium complexes in DSSCs. Using an ionic liquid-based electrolyte, efficiencies up to η = 3.06% have been attained under 1 sun irradiation. Moreover, the T66 based DSSC exhibited a good stability under 1000 W m^-2 light soaking at 60 °C for 24 days, retaining 92.8% of its initial efficiency.

Introduction

The dye sensitized solar cell (DSSC) is a type of solar cell device that attracted the attention of many scientists since the pioneer work of Grätzel and O’Regan in 1991.1 A DSSC is based on the sensitization of titania, a wide band-gap semiconductor, with either organic or inorganic dyes which results in the fabrication of an efficient and low cost solar cell. Recently, DSSC’s efficiencies have reached 12.3% under AM 1.5 sunlight irradiation, using a zinc-porphyrin complex as a sensitizer and a cobalt-based electrolyte system.2 However, two main challenges that are still facing the DSSC device under normal operating conditions, and the DSSC’s efficiency being at the low side (lower than 15%).

Many research groups have been trying to tackle those challenges by optimizing the different components of the DSSC, such as the titanium dioxide film, redox electrolyte, counter electrode and most importantly the sensitizer dye structure.3 We are one of these research groups who have been working on engineering new ruthenium based dyes that address the DSSC’s challenges. Designing ruthenium based dyes that lack the thiocyanate ligand (SCN −), which is considered from long-term chemical stability tests as the weakest part in most ruthenium-based dyes,4,5 is of great interest. In addition, red-shifting the absorption band of the sensitizer and increasing the molar absorption extinction coefficient in the visible and near-IR region may have positive effects on the DSSCs’ efficiencies. As such, thinner titania films can be used in a DSSC that harvest most of the visible light with diminished electron recombination processes than the conventional DSSCs that incorporate dyes with low to mid molar absorption coefficients in conjunction with thick titania films (>10 μm). Recently, a new class of cyclometalated ruthenium complexes that lack the SCN − ligand and have better light harvesting properties than N719 has been introduced by different research groups.4–12 The high interest in this class of ruthenium based dyes is due to their encouraging long term stability measurements and extended absorption in the visible region (down to 800 nm).10

In the present study, we report the synthesis, electronic, optical, and sensitizing properties of new cyclometalated dyes, T65 through T71, Scheme 1. These ruthenium complexes bear a (tctpy = 4,4′,4″-tricarboxy-2,2′,6′,2″-terpyridine) moiety as the anchoring ligand to titanium dioxide and a C^N^N′′′ moiety as the ancillary ligand with different substituents on the three aromatic rings. The selection of the substituents in these dyes was based on the following reasons: (a) the introduction of a thienyl group on the middle pyridyl ring would increase the absorption extinction coefficient of the dye in the visible and near-IR region, as shown by many research groups,8,10,13,14 due to the increase in conjugation, and the large radial extension in bonding because of the presence of the electron rich sulfur hetero-atom. (b) The carboxylic acid group on the terminal pyridyl ligand may act as an additional anchoring group to the TiO2 film, in addition to a neutralization effect of the positive charge present on the ruthenium center. (c) The meta-fluorine and the para-methoxy substituents on the phenyl ring, with respect to the ruthenium center, were selected in order to tune the redox potential of the ruthenium complexes.

Results and discussion

The successful synthesis of the six different C(H)^N^N′ ligands (L65 through L71) was accomplished by multi-step reactions following Krönke methodology, Scheme 1. The complexes...
T65 through T71 were synthesized in a one-pot reaction involving the respective ligand (L65 through L71), Ru(trimethoxy carbonylterpy)Cl3 and N-methylmorpholine in an ethanol–water solvent mixture. In this one-pot reaction the N-methylmorpholine plays the role of a reductant and base, where the ruthenium center gets reduced to RuII during the reaction and the ester groups on the N^N^′^N^′′ get hydrolyzed to the carboxylate form.

Purification of the different complexes was accomplished using preparative C-18 column with methanol–water solvent mixture as the eluent. The six different cyclometalated complexes (T65 through T71) were characterized by 1H-NMR, APPI-MS, differential pulse voltammetry, steady state and lifetime emission and UV/Vis spectroscopy.

The 1H-NMR spectra (Experimental section and ESI†) confirmed the cyclometallation by the appearance of a doublet signal between 5.6 to 6.1 ppm for the different ruthenium complexes, which is a characteristic signal for the ortho hydrogen atom to the ruthenium center. In addition, the 1H-NMR of the cyclometalated confirmed the sufficient purity of the above complexes to be used as dyes in a DSSC.

The UV/Vis data for T65 through T71 are depicted in Table 1. The UV/Vis absorption spectra of complexes in ethanol show in the visible region two intense absorption peaks around 410–422 nm (ε = 1.35–1.90 × 104 M−1 cm−1) and at 520–554 nm (ε = 1.35–1.86 × 104 M−1 cm−1) with shoulders up to 682 nm such in the case of T66, Fig. 1A. Fig. 1B shows the light harvesting efficiencies (LHE) of the different dyes when anchored on 4 μm thick TiO2 films. A close look at the absorption data of the different complexes shows an interesting effect of substituting the C^N^N^′ at the 4 position with a carboxylic acid group, such as in the case of the different complexes' pairs T65–T66 and T70–T71. As can be seen from Table 1, the absorption extinction coefficients of the complexes with a carboxylic acid moiety at the 4 position (T66 and T71) are higher than their analogs (T65 and T70, respectively) that lack the carboxylic acid substituent by Δε = 2.0–4.6 × 103 M−1 cm−1. In order to gain insight into the electronic structure of the different dyes and to correctly assign the origin of the electronic transitions in the visible region, we performed DFT and TD-DFT calculations using the B3LYP/6-31G* exchange correlation functional with the Los Alamos effective core potential LanL2DZ16 as implemented in the Gaussian03 program package.17 The geometries of the complexes (T65 through T71) were optimized in water using the C-PCM algorithm.18 As an example, the frontier
orbitals of T65 and T66 are shown in Scheme 2, and the TD-DFT excitation transitions in the visible regions for the six complexes are shown in Table 1. The HOMO, HOMO − 1 and HOMO − 2 of all of the complexes have a ruthenium t$_{2g}$ character in addition to some contributions from the N$^\prime$N$^\prime$$^\prime$N$^\prime$$^\prime$ ligand. The LUMO and LUMO + 1 of the complexes that lack the carboxylic acid substituent at the 4 position of the C$^\prime$N$^\prime$N$^\prime$ ligand (T65, T67, T68 and T70) are π* orbitals localized on the N$^\prime$N$^\prime$$^\prime$N$^\prime$$^\prime$ ligand. However, the LUMO + 1 for the complexes with the carboxylic acid substituent at the 4 position of the C$^\prime$N$^\prime$N$^\prime$ ligand (T66 and T71) is a π* orbital localized on the C$^\prime$N$^\prime$N$^\prime$ ligand, and the LUMO and LUMO + 2 are π* orbitals localized on the N$^\prime$N$^\prime$$^\prime$N$^\prime$$^\prime$ ligand. The computed ground-state vertical excitation energies with oscillator strength (f) greater than 0.05 are shown in Table 1. As can be seen, the predicted vertical excitations to the red of 500 nm are mainly MLCT transitions with small contributions from intra-ligand LLCT transitions. However, a close look at these transitions reveals an interesting finding, where T66 and T71 lack a HOMO to LUMO + 1 transition and instead a major contribution from the HOMO to LUMO + 2 is found. Moreover, the calculated oscillator strength for the transitions involving the HOMO to LUMO + 2 contributions in T66 and T71 are higher than that of T65 and T70, respectively. This finding might explain the above mentioned experimental results that a carboxylic acid substituent at the 4 position of the C$^\prime$N$^\prime$N$^\prime$ ligand causes an increase in the molar extinction coefficient of the absorption bands in the visible region.

All of the complexes showed weak emission around 800 nm with emission lifetimes ranging between 1.1 and 15.3 ns, however, among the different complexes T68 had the shortest emission lifetime $\tau_{em}$ = 1.1 ns. By comparing the closely related complexes (T65, T67 and T68), T68 owns the weakest σ-donating C$^\prime$N$^\prime$N$^\prime$ ligand among these three complexes, while in the case of T67 the σ-donation of the C$^\prime$N$^\prime$N$^\prime$ ligand is the highest. It is well known that strong σ-donating ligands in general raise the 3MC states of bis-tridentate ruthenium complexes which results in an increase in the energy gap between the 3MC and 3MLCT excited states. As a consequence, the efficiency of the thermally activated crossing processes from the 3MLCT state to the 3MC state decreases, which in turns prolongs the emission lifetime, such as in the case of T67. However, when comparing the different complexes’ pairs T65–T66 and T70–T71, an introduction of the electron-withdrawing carboxyl group at the 4 position of the C$^\prime$N$^\prime$N$^\prime$ results in a stabilization of the N$^\prime$N$^\prime$$^\prime$N$^\prime$$^\prime$ LUMO π* ligand orbitals more than the HOMO π(t$_{2g}$) metal orbital (Scheme 2). Therefore, the energy gap between the 3MC and 3MLCT excited states increase and thus longer emission lifetimes are seen such as in the case of T66 and T71 when compared to T65 and T70, respectively.

The electrochemical properties of the different ruthenium complexes (T65 through T71) were evaluated by differential pulse voltammetry in CH$_3$CN with 0.1 TBAPF$_6$ at a scan rate = 100 mV s$^{-1}$. In order to overcome solubility difficulties of the complexes in CH$_3$CN and to imitate the working environment in a DSSC, a TiO$_2$ film stained with the respective ruthenium complex was used as the working electrode. The $\text{Ru}^\text{III}$ redox potentials of the ruthenium complexes adsorbed on TiO$_2$ films were measured to be between 0.87 and 0.96 V vs. NHE depending on the substituents present on the C$^\prime$N$^\prime$N$^\prime$ ligand. As expected, T68 had the highest oxidation potential due to the presence of the fluorine substituent, whereas, T67 had the lowest oxidation potential due to the electron donating effect of the methoxy group on the ruthenium center. It is worth to mention here that from previous work on T66 the redox potential was evaluated to be $E_{1/2} = 0.65$ V vs. NHE in CH$_3$CN solution.

### Table 1 Measured and calculated spectroscopic data for T65 through T71

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{abs}$, nm ($\varepsilon$, 10$^3$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{em}$, nm ($\tau_{em}$ ns)</th>
<th>TD-DFT excitation energies (nm)</th>
<th>Oscillator strength$^b$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>T65</td>
<td>418 (1.44), 524 (1.50), 570 (sh), 664 (sh)</td>
<td>810 (8.0)</td>
<td>532.5</td>
<td>0.1054</td>
<td>H – 1 to L + 1 (94%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>501.1</td>
<td>0.0547</td>
<td>H – 2 to L + 1 (53%), H to L + 1(21%), H – 1 to L (9%), H to L + 2 (6%)</td>
</tr>
<tr>
<td>T66</td>
<td>418 (1.90), 530 (1.86), 574 (sh), 682 (sh)</td>
<td>801 (14.5)</td>
<td>524.7</td>
<td>0.1044</td>
<td>H – 1 to L + 2 (88%), H-1 to L + 1 (7%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>502.6</td>
<td>0.2137</td>
<td>H – 2 to L + 1 (34%), H to L + 2 (32%) H – 1 to L (15%), H – 2 to L + 2 (11%)</td>
</tr>
<tr>
<td>T67</td>
<td>422 (1.39), 534 (1.45), 664 (sh)</td>
<td>799 (13.6)</td>
<td>535.0</td>
<td>0.0839</td>
<td>H – 1 to L + 1 (90%), H to L + 3 (5%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>520.2</td>
<td>0.1406</td>
<td>H – 1 to L (41%), H to L + 1 (26%) H – 2 to L + 1 (11%), H to L + 4 (7%)</td>
</tr>
<tr>
<td>T68</td>
<td>410 (1.35), 518 (1.35), 556 (sh), 650 (sh)</td>
<td>791 (11.1)</td>
<td>526.5</td>
<td>0.1010</td>
<td>H – 1 to L + 1 (94%)</td>
</tr>
<tr>
<td>T70</td>
<td>410 (1.46), 520 (1.35), 568 (sh), 654 (sh)</td>
<td>803 (8.7)</td>
<td>500.6</td>
<td>0.0790</td>
<td>H – 2 to L + 1 (48%), H to L + 1 (25%) H – 1 to L (14%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>521.2</td>
<td>0.1005</td>
<td>H – 1 to L + 1 (94%)</td>
</tr>
<tr>
<td>T71</td>
<td>410 (1.77), 522 (1.60), 570 (sh), 660 (sh)</td>
<td>812 (9.3)</td>
<td>514.7</td>
<td>0.0991</td>
<td>H – 1 to L + 2 (93%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>494.6</td>
<td>0.1859</td>
<td>H to L + 2 (40%), H – 2 to L + 1 (32%) H – 1 to L (19%)</td>
</tr>
</tbody>
</table>

$^a$ Measured in basic aerated methanol and $\lambda_{em}$ = 510 nm. $^b$ Only bands with oscillator strength $f \geq$ 0.05 are listed.
however, when anchored on TiO₂ (present work) the redox potential shifted to $E_{1/2} = 0.89$ V vs. NHE. Berlinguette et al. reported high dependence of the Ru²⁺/³⁺ redox potentials on the medium when conducting cyclic voltammetry measurements on similar cyclometalated ruthenium complexes in different solvent media. Moreover, the extent of protonation of the carboxylic acid groups has a profound effect on the Ru²⁺/³⁺ redox potential of cyclometalated ruthenium complexes as it was shown in a different study by Berlinguette et al. who reported a 0.3 V shift in the Ru²⁺/³⁺ redox potential in DMF towards less positive values for a tris-bidentate cyclometalated ruthenium complex ($\text{Bu}_4\text{N})_3[\text{Ru}(dcbpy)(dcbpyH)(C}^\text{N})]\text{PF}_6$ when compared to the fully protonated form $[\text{Ru}(dcbpyH_2)(C}^\text{N})]\text{PF}_6$ ($dcbpyH_2 = 4,4'$-dicarboxy-2,2'-bipyridine and C}^\text{N} = 2(2,4-difluorophenyl)-pyridine). Therefore, we rationalize the different measured $E_{1/2}$ values for T66 in solution and when anchored on TiO₂ to a similarity between the effect of protonation of the carboxylate groups with H⁺ and their coordination to Ti⁴⁺ sites in the TiO₂ film. Moreover, the $E_{0-0}$ values of the different dyes were estimated to be in the range $E_{0-0} = 1.7$–1.8 eV from the intersection of the corresponding normalized absorption and emission spectra. The approximated oxidation potentials ($E_{ox}^*$) of the six different complexes in their excited states fall between −0.8 and −0.9 V vs. NHE, which are more negative than the conduction band level of nanocrystalline TiO₂ (−0.5 V vs. NHE). Therefore, upon photo excitation of these complexes fast electron injection into TiO₂ is expected.

The photocurrent vs. voltage ($I$) response of cells made with the different cyclometalated complexes (T65 through T71) and N719 as a reference are shown in Fig. 2. The non-volatile
iodide/triiodide electrolyte used (see Table 2) was one which gives a lower voltage but promotes high quantum efficiency of electron injection in low volatility solvent mainly designed for N719. As can be seen from the data shown in Table 2, DSSCs made with T65 to T68 showed similar efficiencies, η = 2.88, 3.05, 2.95 and 3.06%, respectively. Whereas, T70 and T71 showed lower DSSCs’ efficiencies at η = 2.62 and 1.50%, respectively. In order to understand the reasons behind the four different (T65 to T68), yet similar, dyes’ performance in the studied DSSCs, we measured the incident photon to electron conversion efficiency (IPCE) and the electrochemical impedance spectra (EIS) of these cells.

Fig. 3 shows the typical EIS Nyquist plots measured under dark conditions at a forward bias of −0.6 V. The equivalent circuit used to fit the experimental data is shown in Fig. 3 as an inset. Rct is the series resistance due to the transport resistance of the FTO and the electrolyte. Ca and Rct are the chemical capacitance and the charge recombination resistance at the TiO2/electrolyte interface, respectively. Whereas, CPr and RPr are the interface capacitance and charge-transport resistance at the platinum/electrolyte interface, respectively. The larger semicircle at mid frequencies represents the interfacial charge recombination resistance (Rct) at the dyed TiO2/electrolyte interface. From the fitted Rct and Cct values, we calculated similar values for the T65, T66 and T68 cells (Rct = 41, 39 and 41 Ω cm−2 and Cct = 7.9, 7.8 and 7.3 × 10−4 F cm−2 for T65, T66 and T68, respectively), which suggests that the electron recombination rates are very similar in these three cells. However, in the case of T67, a smaller Rct value (Rct = 34 Ω cm−2 for T67) and a higher Cct value (Cct = 8.2 × 10−4 F cm−2) of T65 were calculated. Therefore, we speculate that the reason behind the smaller Voc value measured in the T67 cell is mainly due to an acceleration in the electron recombination processes (Rct: T68–T65–T66 > T67). Such a finding was not of a surprise to us, since we always hypothesized in previous studies that the presence of an electron-rich sp3-hybridized hetero-atom, such as oxygen in the case of T67, accelerates the electron recombination processes at the TiO2/dye/electrolyte interface most probably due to iodine binding to such hetero-atoms.27,28

Comparing the similar pair of dyes (T70 and T71), T70 showed better performance as a DSSC dye (η = 2.62 and 1.50% for T70 and T71, respectively). We speculate that the extra

Table 2 Redox potentials and DSSCs’ performance of T65 through T71 and N719 dyes

<table>
<thead>
<tr>
<th></th>
<th>E_redox (V)</th>
<th>J_sc (mA cm−2)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
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<tbody>
<tr>
<td>T65</td>
<td>0.90</td>
<td>8.8</td>
<td>535</td>
<td>0.61</td>
<td>2.88</td>
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<tr>
<td>T66</td>
<td>0.89</td>
<td>9.3</td>
<td>535</td>
<td>0.61</td>
<td>3.05</td>
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<tr>
<td>T67</td>
<td>0.87</td>
<td>8.9</td>
<td>528</td>
<td>0.63</td>
<td>2.95</td>
</tr>
<tr>
<td>T68</td>
<td>0.96</td>
<td>8.8</td>
<td>555</td>
<td>0.63</td>
<td>3.06</td>
</tr>
<tr>
<td>T70</td>
<td>0.93</td>
<td>7.8</td>
<td>525</td>
<td>0.64</td>
<td>2.62</td>
</tr>
<tr>
<td>T71</td>
<td>0.94</td>
<td>4.6</td>
<td>539</td>
<td>0.61</td>
<td>1.50</td>
</tr>
<tr>
<td>N719</td>
<td>1.12</td>
<td>12.1</td>
<td>607</td>
<td>0.67</td>
<td>4.93</td>
</tr>
</tbody>
</table>

a Redox potentials of the dyes on TiO2 were measured in CH3CN with 0.1 M TBAPF6 at a scan rate of 100 mV s−1 vs. NHE. & Measured under 100 mW cm−2 simulated AM1.5 spectrum with an active area = 0.126 cm2 and 0.6 M DMPII, 0.05 M LiI, 0.5 M TBP, 0.1 M GuSCN and 0.03 M I2 in MPN as the electrolyte.

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carboxylic acid moieties on the C^N^N' ligand in these two dyes alter the dyes’ adsorption profiles on the TiO_2 film which might influence the electron injection and electron recombination rates to and from the TiO_2 film, respectively. This former effect could be profound especially in the T71 case where the position of the two carboxylic acid moieties at the 4 and 4' position of the C^N^N' ligand act as strong anchoring motifs to the TiO_2 film, thus rendering the efficiency of electron injection from the LUMO which resides on the N^N'-N'-N' ligand. Such a phenomenon would explain the lower photocurrents seen for T70 and T71 (J_{sc} = 7.8 and 4.6 for T70 and T71, respectively) and the lower IPCE’s when compared to T65, Fig. 4. In addition, the differences between the IPCE spectra (Fig. 4) and the LHE spectra (Fig. 1B) for T70 and T71 also suggest that these two dyes have lower electron injection yields than T65 through T68.  

Finally, the lower performance of the different cyclometalated complexes when compared to N719 is mainly attributed to the positive charge that is intrinsic of these complexes. Such a charge is expected to accelerate charge recombination processes at the TiO_2/electrolyte interface as evident in the measured lower R_dt values of these complexes than that of N719 (R_dt = 92 \Omega \text{ cm}^{-2} \text{ for N719}, Fig. 3.  

In order to test the robustness of such cyclometalated complexes under light soaking, we performed a preliminary long-term stability test on a T66 DSSC incorporating a low volatility electrolyte (0.5 M N-methylbenzimidazole, 0.6 M DMPII, 0.05 M LiI and 0.05 M I_2 in MPN). Fig. 5 shows the JV curves of a T66 cell taken during a 24 days period while illuminated with a 100 mW cm^{-2} light intensity using a white LED source at 60 °C. Interestingly, the T66 DSSC’s efficiency dropped only by 7.2% on day 24 (η = 2.63 and 2.44% on days 1 and 24, respectively), mainly due to a drop in the short-circuit current (J_{sc} = 7.0 and 6.3 mA cm^{-2} on days 1 and 24, respectively) while the photo-voltage increased by 20 mV (V_{oc} = 589 and 609 mV on days 1 and 24, respectively). N719 based cells studied under the same conditions showed a 14.3% drop in the efficiency from

![Fig. 4](image1.png)  
**Fig. 4** Relative IPCE spectra of T65 through T71 with (0.6 M DMPII, 0.05 M LiI, 0.5 M TBP, 0.1 M GuSCN and 0.03 M I_2 in MPN) as the electrolyte.

![Fig. 5](image2.png)  
**Fig. 5** Evolution of the photocurrent–voltage (JV) curves of T66 during visible-light soaking (100 mW cm^{-2} simulated AM1.5) at 60 °C. Electrolyte: 0.5 M N-methylbenzimidazole, 0.6 M DMPII, 0.05 M LiI and 0.05 M I_2 in MPN.

η = 4.01% to 3.44% on days 1 and 24, respectively (J_{sc} = 9.7 and 8.2 mA cm^{-2} and V_{oc} = 640 and 650 mV on days 1 and 24, respectively). Such a result, suggests that the use of cyclometalated ruthenium complexes that lack labile mono-dentate ligands is a good strategy for engineering dye complexes that perform well under prolonged operational environment.

**Conclusions**

In conclusion, six different cyclometalated ruthenium complexes, T65 through T71, have been synthesized and the effect of different substituents (R = COOH, thiophen-2-yl, F and OCH_3) on the ancillary C^N^N' ligand has been investigated on the photophysical properties and performance of these complexes in DSSCs. In the case of the T65 through T68 dyes, where the C^N'-N' is a 6'-phenyl-4'-thiophen-2-yl-[2.2']bipyridinyl with different substituents on either the phenyl ring or the 2'-pyridyl groups, similar solar cells’ efficiencies were attained (η = 2.88, 3.05, 2.95 and 3.06%, respectively). However, in the case of the two dyes T70 and T71 where the ancillary C^N'-N' ligand is a 6'-phenyl-2,2'-bipyridine-4-carboxylic acid and 6-phenyl-2,2'-bipyridine-4,4'-dicarboxylic acid, respectively, lower efficiencies were measured (η = 2.62 and 1.50% for T70 and T71, respectively). The lower efficiencies of these two dyes could be attributed to less efficient electron injection rates than the T65 to T68 dyes. Moreover, T66 based DSSC exhibited a good stability under 1000 W m^{-2} light soaking at 60 °C for 24 days, retaining 92.8% of its initial efficiency. Finally, the lower efficiencies of the six studied cyclometalated complexes is attributed to their intrinsic positive charge that might accelerate the electron recombination processes in the DSSC and/or to inefficient dye regeneration by the electrolyte when compared to N719. We are currently engineering new cyclometalated complexes that resemble T66 but with long alkyl-chains, which we expect to slow retardation in the electron recombination.
processes. In addition, we will be investigating these, to be made complexes, with different electrolyte systems that may cause faster dye regeneration than the iodide/triiodide one.

**Experimental**

**Materials and instrumentation**

All organic chemicals were purchased from Sigma-Aldrich and used as supplied. C-18 resin was purchased from YMC (Japan). The N719 dye was purchased from Soloronix (Switzerland). FTO glass “Tec15” was purchased from Pilkington (USA). TiO2 colloids were purchased from Dyesol (Australia). The different di-aryl propenones, the different 1-acytaryl pyridinium iodides, (4,4’’-trimethoxy carbonyl-2,2’’-6,2’’-terpyridine)-RuCl3, and methyl 2-acetyl isonicotinate were prepared according to reported procedures in the literature.

Dye sensitized solar cells were fabricated using standard procedures.

8 The counter electrodes were made through two small holes, previously drilled through the counter electrode, which were then sealed with Surlyn. The electrolyte used was as follows: methoxy alcohol for all of the studied dyes. The counter electrodes were fabricated by applying a 2–3 μm thick TiO2 film, on top of which a 4 μm TiO2 scattering layer (400 nm TiO2 particles) was deposited and reheated at 480 °C for 30 min. A TiCl4 post-treatment was applied to the films following reported procedures in the literature.

9 These films were then reheated at 480 °C for 30 min. Dyeing was accomplished using 0.3 mM solutions in ethyl alcohol for all of the studied dyes. The counter electrodes were fabricated by applying a 2–3 μm thick TiO2 film, on top of which a 4 μm TiO2 scattering layer (400 nm TiO2 particles) was deposited and reheated at 480 °C for 30 min. A TiCl4 post-treatment was applied to the films following reported procedures in the literature.

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11 Additional processes. In addition, we will be investigating these, to be made complexes, with different electrolyte systems that may cause faster dye regeneration than the iodide/triiodide one.
Preparation of 6-phenyl-2,2′-bipyridine, L68. 

1H-NMR (CDCl₃, 300 MHz), δ (ppm): 7.17–7.21 (m, 3H), 7.34–7.38 (m, 1H), 7.45 (d, 1H, J = 5.1), 7.71 (d, 1H, J = 3 Hz), 7.84–7.90 (m, 2H), 8.17 (m, 2H), 8.61–8.64 (m, 2H), 8.72 (d, 1H, J = 4.2 Hz). 

13C-NMR (CDCl₃, 75 MHz), δ (ppm): 115.6–115.8 (d, 116.4, 121.5, 124.0, 125.7, 127.1, 128.4, 128.8–128.9 (d), 135.4, 136.9, 141.7, 143.3, 149.1, 156.0, 156.3, 156.4, 162.1, 165.1. MS (APPI): m/z = 333.0 [M + H⁺]⁺ calculated for C₂₂H₁₄FN₃S, 333.4.

Preparation of T65 through T71

0.27 mmol of the corresponding ligand (L65 through L71) and (4,4′,4″-trimethoxy carbonyl-2,2′,6,6′-terpyridine)RuCl₃ (0.16 g, 0.27 mmol) were dissolved in ethanol–H₂O (5 : 1 v/v, 60 ml) followed by the addition of N-methylmorpholine (20 ml). The mixture was then refluxed under Ar for 48 h. The solvent was then evaporated under reduced pressure. The obtained dark solid was dissolved in water containing excess tetra-butyl ammonium hydroxide and applied to a preparative C18-column. The compound was purified by a gradient elution with water/methanol 100% : 0% to 60% : 40%. Concentrating the solvent that contains the major band under reduced pressure and acidifying to pH 3.0 with 0.1 M HCl resulted in a dark precipitate. The solid was filtered to yield a dark violet crystalline solid, which was dried under vacuum at 80 °C for 24 h. The mono-protonated form of the different ruthenium complexes were obtained by adding the corresponding mono equivalents of tetra-butyl ammonium hydroxide (TBAOH) in methanol, stirred under N₂ for 1 h and then dried under vacuum at 80 °C for 24 h.

T65.2B. 

1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.92 (t, 24H), 1.30 (m, 16H), 1.56 (m, 16H), 3.33 (m, 16H), 5.67 (dd, 1H, J₁ = 7.5 Hz, J₂ = 0.9 Hz), 6.52 (td, 1H, J₁ = 6.0 Hz, J₂ = 0.9 Hz), 6.77 (td, 1H, J₁ = 6.0 Hz, J₂ = 0.9 Hz), 7.14 (m, 1H), 7.36 (dd, 1H, J₁ = 5.1 Hz, J₂ = 3.9 Hz), 7.49–7.54 (m, 5H), 7.73 (dd, 1H, J₁ = 5.1 Hz, J₂ = 0.9 Hz), 7.92–7.95 (m, 2H), 8.12 (dd, 1H, J₁ = 3.9 Hz, J₂ = 0.9 Hz), 8.51 (d, 1H, J₁ = 1.2 Hz), 8.73 (d, 1H, J₁ = 8.1 Hz), 8.79 (d, 1H, J₁ = 1.2 Hz), 8.96 (d, 2H, J₁ = 0.6 Hz), 9.22 (s, 2H). MS (APPI): m/z = 1262.8 [M – Cl⁻]⁻ calculated for C₹₀H₄₂N₉O₅RuS, 1262.7.

T66.3B. 

1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.96 (t, 36H), 1.42 (m, 24H), 1.64–1.69 (m, 24H), 3.33 (m, 24H), 5.64 (d, 1H, J = 7.2 Hz), 6.51 (t, 1H, J = 7.5 Hz), 6.77 (t, 1H, J = 7.2 Hz), 7.39 (dd, 1H, J₁ = 4.8 Hz, J₂ = 3.6 Hz), 7.52–7.62 (m, 6H), 7.74 (d, 1H, J = 4.5 Hz), 7.79 (d, 1H, J = 7.5 Hz), 8.14 (d, 1H, J = 2.7 Hz), 8.53 (s, 1H), 8.78 (s, 1H), 8.97 (s, 2H), 9.06 (s, 1H), 9.23 (s, 2H). MS (APPI): m/z = 1548.0 [M – Cl⁻]⁻ calculated for C₉₂H₅₂N₁₀O₅Ru₂S, 1548.1.

T67.2B. 

1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.91 (t, 24H), 1.30 (m, 16H), 1.56 (m, 16H), 2.74 (s, 3H), 3.33 (m, 16H), 5.95 (d, 1H, J = 7.8 Hz), 6.70 (t, 1H, J = 7.8 Hz), 7.01 (m, 1H), 7.16 (d, 1H, J = 3.9 Hz), 7.25 (dd, 1H, J₁ = 5.1 Hz, J₂ = 3.9 Hz), 7.36 (d, 4H, J = 1.2 Hz), 7.59 (d, 1H, J = 7.5 Hz), 7.61 (dd, 1H, J₁ = 5.1 Hz, J₂ = 1.2 Hz), 7.73 (td, 1H, J₁ = 8.4 Hz, J₂ = 1.5 Hz), 7.99 (dd, 1H, J₁ = 4.8 Hz, J₂ = 1.5 Hz).
0.9 Hz), 8.41 (d, 1H, J = 1.5 Hz), 8.55 (d, 1H, J = 8.1 Hz), 8.61 (d, 1H, J = 1.2 Hz), 8.79 (s, 2H), 9.06 (s, 2H). MS (APPI): m/z = 1292.8 [M − Cl]− calculated for C71H86N7O8RuS, 1292.7.

**T68.2TBA.** 1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.99 (t, 24H, J = 7.8 Hz), 6.45 (48H), 1.36 (m, 32H), 1.65 (m, 32H), 3.35 (m, 24H), 5.60 (1H, J = 7.5 Hz), 7.11 (m, 1H, J = 7.5 Hz), 7.42 (3H, J = 5.7 Hz), 7.48 (d, 2H, J = 6.0 Hz, J2 = 1.8 Hz), 7.84–7.93 (m, 2H), 8.19 (d, 1H, J = 8.1 Hz), 8.71 (s, 1H, J = 9.4 Hz, 8.91 (s, 1H, J = 9.3 Hz), 7.2 Hz, 9.19 (s, 2H). MS (APPI): m/z = 1222.8 [M − H− – TBA − Cl]− calculated for C70H90N7O8Ru, 1220.7.

**T70.3TBA.** 1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.99 (m, 36H), 1.36 (m, 24H), 1.65 (m, 32H), 3.35 (m, 24H), 5.60 (d, 1H, J = 7.8 Hz), 6.45 (48H, 1H, J = 7.6 Hz), 6.73 (t, 1H, J = 7.5 Hz), 7.11 (m, 1H, J = 7.5 Hz), 7.42 (3H, J = 5.7 Hz), 7.48 (d, 2H, J = 6.0 Hz, J2 = 1.8 Hz), 7.84–7.93 (m, 2H), 8.19 (d, 1H, J = 8.1 Hz), 8.71 (s, 1H, J = 9.4 Hz, 8.91 (s, 1H, J = 9.3 Hz), 7.2 Hz, 9.19 (s, 2H). MS (APPLI): m/z = 1222.8 [M − H+ − TBA − Cl]− calculated for C70H90N7O8Ru, 1220.7.

**T71.4TBA.** 1H-NMR (MeOD + 0.1% KOD, 300 MHz), δ (ppm): 0.99 (m, 48H), 1.36 (m, 32H), 1.65 (m, 32H), 3.35 (m, 32H), 5.62 (d, 1H, J = 7.5 Hz, J2 = 0.9 Hz), 6.46 (td, 1H, J = 8.7 Hz, J2 = 0.9 Hz), 6.73 (td, 1H, J = 7.2Hz, J2 = 1.2 Hz), 7.42–7.49 (m, 6H), 7.84 (d, 1H, J = 7.5 Hz), 8.71 (d, 1H, J = 0.9 Hz), 8.92 (d, 2H, J = 9.3 Hz, J2 = 1.2 Hz), 9.19 (s, 2H). MS (APPI): m/z = 1508.1 [M − H+ − TBA − Cl]− calculated for C69H125N9O10Ru, 1508.0.

**Acknowledgements**

This work was supported by the University Research Board (URB) at the American University of Beirut (AUB), the Lebanese National Council for Scientific Research (LNCSC), and the Munib and Angela Masri Institute of Energy and Natural Resources.

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