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Investigation of a new bis(carboxylate)triazole-based anchoring ligand for dye solar cell chromophore complexes

Alessandro Sinopoli, Fiona A. Black, Christopher J. Wood, Elizabeth A. Gibson* and Paul I. P. Elliott*

A novel anchoring ligand for dye-sensitised solar cell chromophoric complexes, 1-(2,2′-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylic acid (dctzbpy), is described. The new dye complexes [Ru(bpy)2(dctzbpy)][PF6]2 (AS16), [Ir(ppy)2(dctzbpy)][PF6] (AS17) and [Re(dctzbpy)(CO)3Cl] (AS18) were prepared in a two stage procedure with intermediate isolation of their diester analogues, AS16-Et2, AS17-Et2 and AS18-Et2 respectively. Electrochemical analysis of AS16-Et2, AS17-Et2 and AS18-Et2 reveal reduction potentials in the range -1.50 to -1.59 V (vs Fc+/Fc) which are cathodically shifted with respect to that of the model complex [Ru(bpy)2(dcbH2)]2+ (Ered = -1.34 V, dcbH2 = 2,2′-bipyridyl-4,4′dicarboxylic acid). This therefore demonstrates that the LUMO of the complex is correctly positioned for favourable electron transfer into the TiO2 conduction band upon photoexcitation. The higher energy LUMOs for AS16 to AS18 and a larger HOMO-LUMO gap result in blue-shifted absorption spectra and hence reduced light harvesting efficiency relative to their dcbH2 analogues. Preliminary tests on TiO2 n-type and NiO p-type DSSCs have been carried out. In the cases of the Ir(III) and Re(I) based dyes AS17 and AS18 these show inferior performance to their dcbH2 analogues. However, the Ru(II) dye AS16 (η = 0.61 %) exhibits significantly greater efficiency than 1 (η = 0.1 %). In a p-type cell AS16 shows the highest photovoltaic efficiency (η = 0.028 %), almost three times that of cells incorporating the benchmark dye coumarin C343.

Introduction

The application of transition metal complexes, principally those of ruthenium(II), have attracted enormous attention for their application in n-type dye-sensitised solar cells (DSSC).1-4 The relatively long-lived triplet metal-to-ligand charge-transfer (3MLCT) states of these complexes5 allow efficient charge injection into the electrode on which the complex is adsorbed. Innumerable reports have appeared in the literature on the design and modification of the ligand set for these complexes in order to enhance the optical absorption cross-section to increase light harvesting efficiency and the optimise the component of these dye complexes is therefore the ligand on which the 3MLCT state is localised and which anchors the complexes to the electrode. The energy of the lowest-unoccupied molecular orbital (LUMO) of the dye, localised on this ligand then largely determines the excited state oxidation potential which must be correctly positioned relative to the Fermi level of the electrode to favour efficient charge injection, and relative to the electrolyte redox couple to minimise short-circuit reactions. Whilst complexes of ruthenium dominate the literature dyes based on a variety of metals have been evaluated including osmium,7 platinum,8 rhenum,9 iron,10 and iridium11 as well as zinc porphyrins.12 Great strides have also been taken in the optimisation of metal free organic dyes.13, 14

Over thirty years ago, Goodenough and co-workers15 reported the use of 4,4′-dicarboxy-2,2′-bipyridine (dcbH2, Figure 1) as an ambidentate ligand for coordination to Ru(II) and metal oxide semiconductors. Strong electronic coupling between the MLCT excited states of dcbH2-containing Ru compounds and TiO2 has been inferred from femtosecond transient absorption spectroscopy, and the timescales extracted from such data are on the order of < 25 fs.16 To this day dcbH2 remains the most efficient and widely utilised anchoring ligand for applications in DSSCs, however, a number of other carboxylate-based variant ligands have been...
investigated. Heuer et al. reported the design of a new bipyridine based anchoring ligand (4,5-diazafluoren-9-ylidene)malonic acid (dfm, Figure 1) together with its corresponding complex \([\text{Ru(bpy)}_2(\text{dfm})]^2+\) (bpy = 2,2′-bipyridyl). Mishra et al. prepared the complex BCT-1, \([\text{Ru(dctzbpyH}_2)(\text{NCS})_2][\text{NBu}_4]_2\), where the distance between the bpy core of the ligand and its anchoring carboxylate group has been extended by the introduction of a thiophene spacer (dctzbpyH). This increases charge separation upon charge injection and reduces the rate of recombination but also leads to augmentation of the light absorption properties over the corresponding dcbH complex. This yielded an overall conversion efficiency of 6.1% compared with the 4.8% achieved using the archetypal DSSC dye \([\text{Ru(dcbH}_2)(\text{NCS})_2]\). In an attempt to minimise charge recombination rate constant, Abrahamsson et al. introduced a phenyleneethynylene unit between a bpy ligand and the surface anchoring groups (dcpebpy, Figure 1), preparing the corresponding \([\text{Ru(dcpebpy)}_2(bpy)](\text{NCS})_2\) complex. This resulted in a three times smaller recombination rate compared to that for N3.

Whilst carboxylates represent by far the most commonly encountered anchoring moiety DSSC dyes with other anchoring groups have also been investigated. These include phosphonic acid appended copper(I) and ruthenium(II) complexes and also boronic acid derivatised complexes.

In contrast to the wealth of literature on transition metal-based dyes for n-type DSSCs, only a few examples have been reported for NiO p-type cells. Pellegrin et al. have reported ruthenium(II) based sensitisers for p-type DSSC devices with phosphonic acid, thiocarboxylate and catechol derived anchoring groups. Ji et al. have reported cyclometalated ruthenium complexes of the type \([\text{Ru(N}^\circ\text{N})_2(\text{C}^\circ\text{N})]^+\) as sensitisers for p-type DSSCs. Addition of a rigid biphienylene spacer between the carboxylate anchor and the aryl ring of the cyclometalated ligand led to a marked increase in device efficiency (0.05 % compared to 0.009 % with no spacer). Recently Wood et al. reported bis(bidentate) ruthenium(II) based dye complexes bearing electron rich carboxylate derivatised triarylamino anchoring groups yielding efficiencies of up to 0.09 %. Massin et al. have also reported carboxylate-appended triarylamino functionalised dyes with a bis(diphenyolphosphino)ethane backbone (dppe).

Through the use of triazole-based “click” chemistry we report here the design and synthesis of the novel anchoring ligand \((2,2′\text{-bipyridine-3-yl})\text{-1,2,3-triazole-4,5-dicarboxylic acid (dctzbpy, Figure 1). Triazole moieties have been utilised in conjugated polymers and results suggested that the linkage is somewhat electronically insulating. }^{32,33}\) Whilst this might be expected to impair to some extent the rate of charge injection into TiO\textsubscript{2} for an immobilised dye, this could significantly retard recombination reactions thereby enhancing overall photovoltaic efficiency. The designed anchor ligand also presents conformational freedom that would enable multiple possibilities for TiO\textsubscript{2} surface coordination modes to be envisaged. For example, the various possibilities for coordination by one carboxylate group (monodentate (a), bidentate (b) or bridging (c) in Figure 2), both carboxylate groups (bidentate (d), tridentate (e), tetradeionate (f)) or anchoring through the 4-position carboxylate with additional surface coordination of the triazole-N3 atom (g) could result in highly favourable adsorption characteristics. Further anchoring modes through hydrogen bonding between carboxylic acid and

Figure 1. Structures of selected carboxylate-based DSSC anchoring ligands.

Figure 2. Selection of the potential TiO\textsubscript{2} anchoring modes that could be adopted by the dctzbpy ligand.

Figure 3. Structure of complexes AS16-18 and their dcbH\_3 analogues 1-3.
Results & Discussion

The above mentioned ligand, dctzbpy, was prepared by the route described in Scheme 1. We, and others, have previously reported the preparation and reactivity of the bpy derivative 4-azido-2,2’-bipyridyl.34, 35 This azide precursor was subject to reaction with the corresponding diacids to provide the dctzbpy ligand by ~0.4 ppm with the 1H NMR resonances for the H-6 and H-6’ groups can also be envisaged. 

The 1H NMR spectrum of the product shows seven unique environments (Supporting Information) for the protons on the bipyridyl fragment along with two sets of signals for the ethyl groups of the ester moiety. This is consistent with the cycloaddition of the acetylenic fragment to form the triazole and loss of the azido precursor. The 1H NMR spectra due to the overlap of signals (Supporting Information). 

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Cyclic voltammetry traces and summarised electrochemical data are presented in Figure 4 and Table 1 respectively. The complex AS16-Et2 presents a reversible Ru(II)/(III) oxidation at +1.00 V and an irreversible reduction peak at -1.50 V assigned to the dctzbpy reduction. This is followed by two further
reversible reduction peaks assigned to the bpy ligands. A quasi-reversible oxidation is observed at +0.90 V for AS17-Et₂, corresponding to the one-electron Ir(III)/Ir(IV) couple. The first reduction presents as a quasi-reversible process at -1.59 V again assigned to dcbz bpy ligand. Complex AS18-Et₂ is characterised by a quasi-reversible oxidation peak at +1.00 V, in agreement with the potential of other Re(CO)₃(dcb-Et₂)X-based complexes (X = halide).²⁰ It also presents a reversible dcbz-based reduction at -1.56 V. The oxidation potentials for these complexes are similar to those of their corresponding dcbH₂-based analogues consistent with the expectation of a largely metal-based HOMO.²⁰ The dcbz-based reduction potentials (-1.5 to -1.6 V) are more cathodically shifted than that reported for 1 (-1.34 V)²⁰ consistent with a higher energy LUMO as indicated in the spectroscopic data.¹⁷ -¹⁹

The isolated and purified complexes AS16-Et₂ to AS18-Et₂ were then refluxed in KOH/acetone and neutralised with HCl to yield the corresponding dctz bpy complexes. The analogous dcbH₂ complexes [Ru(bpy)₂(dcbH₂)][PF₆]²⁻ (1)²⁰, [Ir(ppy)₂(dcbH₂)][PF₆]²⁻ (2)²⁰, and [Re(CO)₃(dcbH₂)Cl] (3)²⁰ were also prepared for comparison. UV-Visible absorption spectra were recorded for all complexes in acetonitrile solutions at room temperature and are presented in Figure 5 with summarised data listed in Table 2.

Table 2. Summarised photophysical data for complexes AS16-18 and their dcbH₂ analogues 1-3 at room temperature in acetonitrile

<table>
<thead>
<tr>
<th>Complex</th>
<th>λₓₓₓₓ nm (ε / dm³ mol⁻¹ cm⁻¹)</th>
<th>λmaxₓₓₓₓ nm</th>
<th>t/ ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>245 (21923), 287 (44481), 308 (26079), 357 (7836), 430 (8807), 475 (9880)</td>
<td>682</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>256 (30778), 289 (24016), 377 (6905)</td>
<td>689</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>252 (10289), 303 (8202), 413 (1826)</td>
<td>725</td>
<td>35</td>
</tr>
<tr>
<td>AS16</td>
<td>242 (15624), 287 (30138), 424 (4642), 456 (5719)</td>
<td>638</td>
<td>34</td>
</tr>
<tr>
<td>AS17</td>
<td>255 (4431), 301 (23330), 364 (7771), 415 (1914)</td>
<td>590</td>
<td>25</td>
</tr>
<tr>
<td>AS18</td>
<td>254 (20024), 297 (15317), 397 (3815)</td>
<td>553</td>
<td>38</td>
</tr>
</tbody>
</table>

The comparison between the dcbH₂ complexes and their dctz bpy analogues shows similar absorption profiles but with a slight blue shift in the lower energy absorptions for complexes AS16-18. All complexes show a strong band at 250-300 nm attributed to π-π* MLCT transitions together with 3MLCT bands of modest intensity (ε ≈ 5000-10000 dm³ mol⁻¹ cm⁻¹) above 400 nm. The blue-shifted absorption bands in the spectra of the dctz bpy complexes suggests that the LUMO is higher in energy than those for the dcbH₂ analogues and that the biscoxytriazole group is less electron withdrawing than the two carboxylate groups bonded directly to the bipyridyl core in dcbH₂. Nevertheless, LUMO is correctly positioned with reference to the TiO₂ Fermi level for favourable charge injection when adsorbed on a photoanode.⁴ These similar absorption patterns will be expected to result in comparable photovoltaic performance for the dyes AS16-18 relative to 1-3.

The complexes AS16-18 exhibit broad emission bands between 550 and 650 nm which are similarly blue-shifted relative to their dcbH₂ analogues, with similar life-times at about 32 ns. This again is indicative that the LUMO of the dctz bpy ligand, and thus that of its complexes, is higher in energy with respect to dcbH₂ thereby leading to the observed destabilisation of 3MLCT T₁ states in these complexes.

In order to gain a more complete understanding of the photophysical and electrochemical properties imparted by the new ligand dctz bpy we turned to density functional theory (DFT) calculations. These calculations were carried out on the free acid carboxylic acid complexes AS16-18, partly to reduce computational cost of the extra alkyl groups of the ester groups, and due to the fact that the spectroscopic absorption properties of the free acid and ester complexes differ little accounting for the experimental absorption spectra. Optimised singlet ground state geometries for the three new dyes AS16-18 and model complexes 1-3 were calculated at the B3LYP level of theory using Stuttgart-Dresden relativistic small-core effective core potentials and basis sets for the metallic elements and 6-311G* basis sets for all other atoms. Molecular orbital energies (Figure 6) and localisations (Figure 7) were then determined in single-point calculations using the COSMO solvation model (ε = 73.5 for acetonitrile). The HOMO has significant metallic d-orbital character in all cases with additional aryl π* character in the case of AS17 and CO π* and Cl p-orbital character for AS18. In all cases the LUMO is dominated by the dctz bpy ligand and is mostly localised over the bpy fragment. For AS16 there is also a minor contribution from the bpy ligands whilst for AS17 and AS18 there is an additional contribution from the dicarboxytriazole moiety.

Frontier molecular orbital energies are provided in Table 3. In agreement with UV-visible absorption and emission data there is a slight destabilization of both HOMO and LUMO orbitals, but to a greater extent for the latter, for AS16-18 relative to those of their dcbH₂ analogues. Thus the HOMO-LUMO gaps for the dctz bpy complexes are an average of 0.12 eV larger than for 1-3 accounting for the experimental spectroscopic data. The ground state frontier molecular orbitals of AS16-18 are thus correctly localised to facilitate optimum charge-transfer directionality with respect to the carboxylate anchor for efficient charge injection when adsorbed onto a photoanode. Moreover, the relative energy of the dctz bpy ligand localised LUMO in complexes AS16-18,
being slightly higher than those of the dcbH₂ analogues 1 to 3, will inevitably be favourably positioned relative to the TiO₂ Fermi level in order to facilitate charge injection into the electrode.

Table 3. Calculated HOMO and LUMO energies for complexes AS16-18 and 1-3.

<table>
<thead>
<tr>
<th>Dye</th>
<th>LUMO / eV</th>
<th>HOMO / eV</th>
<th>HOMO-LUMO / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-7.92</td>
<td>-11.26</td>
<td>3.33</td>
</tr>
<tr>
<td>AS16</td>
<td>-7.68</td>
<td>-11.10</td>
<td>3.42</td>
</tr>
<tr>
<td>2</td>
<td>-5.65</td>
<td>-8.13</td>
<td>2.48</td>
</tr>
<tr>
<td>AS17</td>
<td>-5.41</td>
<td>-8.04</td>
<td>2.63</td>
</tr>
<tr>
<td>3</td>
<td>-3.51</td>
<td>-6.00</td>
<td>2.49</td>
</tr>
<tr>
<td>AS18</td>
<td>-3.30</td>
<td>-5.94</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Figure 6. Calculated molecular orbital energy level diagram for complexes AS16-18 and 1-3.

Figure 7. Optimised geometries and plots of HOMO (top) and LUMO (bottom) orbitals for complexes AS16 to AS18.

Time-dependent DFT (TDDFT) calculations were carried out on the optimised ground state geometries of each complex in order to determine vertical excitation energies and the nature of the lowest energy singlet excited states. Simulated absorption spectra are overlaid with experimental spectra and shown in Figure 8 and reveal that predicted transitions correlate well with the experimental spectra. The excitations to the S₁ state of all complexes are primarily HOMO→LUMO in character, however, they are of low oscillator strength and will therefore contribute little to the observed absorption spectra. Consistent with the enlarged HOMO-LUMO gap in complexes AS16-18 relative to their respective dcbH₂ analogues the S₁ transitions occur at shorter wavelengths. The major transitions observed for all complexes between 350 and 550 nm are primarily of 1MLCT character. Higher energy intense absorptions (240 to 350 nm) are assigned as having predominantly 1LC π→π* character. The ruthenium complex AS16 presents two dominating transitions at 452 (S₅) and 412 (S₆) nm respectively, involving primarily HOMO-2→LUMO+2 1MLCT character. The iridium complex AS17 exhibits one transition at 421 nm (S₄) of mainly HOMO-1→LUMO 1MLCT/1LCT character and two transitions at 394 (S₅) and 393 (S₆) nm with 1MLCT/1LCT and 1MLCT/1LLCT character respectively. The rhenium complex AS18 exhibits a strong transition at 443 nm (S₄) with a predominant composition of HOMO-1→LUMO 1MLCT character.

Figure 8. TDDFT calculated absorption spectra for complexes AS16-18 with experimental spectra overlaid.

The relative positioning of the frontier orbitals in the dctzbpy complexes described would indeed seem to make them amenable to application in the photovoltaic sensitisation of n-type solar cells. We therefore prepared n-type TiO₂-based test DSSC devices utilising complexes AS16 to AS18 along with those of the corresponding dcbH₂ analogues for comparison.

The free dye AS16 and TiO₂-immobilised AS16 were analysed by FTIR spectroscopy and microscopy in an attempt to gain insight into the anchoring mode of the dctzbpy ligand. Unfortunately the data do not enable any definitive conclusions to be drawn.

The principle photovoltaic parameters for the constructed DSSC devices are listed in Table 4. The overall conversion efficiencies η were derived from the equation η = J_scV_ocFF, where J_sc is the short circuit current density, V_oc is the open circuit voltage, and FF is the fill factor. Figure 9 shows the photocurrent-voltage and IPCE traces of the n-type DSSCs based on the new dyes.

The IPCE values are generally below 10% over the visible region of the spectrum except for those of AS16 and 2 (Figure 9). The IPCE profiles reflect the absorption profiles of the corresponding dyes; both AS16 and 1 exhibit IPCE maxima coincident with the region in which the complexes have a
1MLCT-based absorption band between 400-500 nm. All the other complexes have absorption maxima between 370 and 420 nm so their IPCE curves show only the tail of these bands into the visible region.

Table 4. Photovoltaic parameters of tested dyes AS16-18 and 1-3 with N719 as a benchmark comparison in TiO2-based n-type DSSC devices. The electrolyte contained 0.6 M tetrabutylammonium iodide, 0.015 M l3, 0.1 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine in MeCN.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Jsc / mA cm⁻²</th>
<th>Voc / mV</th>
<th>FF / %</th>
<th>η / %</th>
<th>IPCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N719</td>
<td>10.7</td>
<td>779</td>
<td>69</td>
<td>5.76</td>
<td>65</td>
</tr>
<tr>
<td>1</td>
<td>0.39</td>
<td>457</td>
<td>57</td>
<td>0.1</td>
<td>6</td>
</tr>
<tr>
<td>AS16</td>
<td>1.18</td>
<td>662</td>
<td>78</td>
<td>0.61</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>1.44</td>
<td>633</td>
<td>78</td>
<td>0.71</td>
<td>17</td>
</tr>
<tr>
<td>AS17</td>
<td>0.06</td>
<td>485</td>
<td>72</td>
<td>0.02</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.36</td>
<td>495</td>
<td>73</td>
<td>0.13</td>
<td>6</td>
</tr>
<tr>
<td>AS18</td>
<td>0.24</td>
<td>532</td>
<td>73</td>
<td>0.09</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 9. Current-voltage traces for pilot TiO2-based n-type DSSC devices utilising complexes AS16 to AS18 and model dyes 1 to 3 (top) along with IPCE traces for each cell (bottom). The electrolyte contained 0.6 M tetrabutylammonium iodide, 0.015 M l3, 0.1 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine in MeCN.

The obtained photovoltaic efficiencies for complexes AS17 and AS18 are lower than those for their dcbH2 analogues determined under identical conditions. This is not unexpected and attributable to their blue-shifted absorption profiles which would result in lower light harvesting efficiency. Further, whilst the LUMO energies for AS16-18 are expected to be in the correct position relative to the TiO2 Fermi level they are higher in energy than those of 1-3. This might imply less efficient overlap of the LUMO with the TiO2 conduction band and consequently lower electron injection efficiency. The best result for the new dyes is obtained for complex AS16 with an efficiency of 0.61 % (compared to 0.1 % for 1 and 5.76 % for the benchmark dye N719 under the same conditions). AS16 achieved the highest open circuit voltage (0.66 V) which might suggest a longer excited state electron lifetime,8 hence a higher electron density on the TiO2 surface. The efficiency for AS17 was dramatically lower than that of its dcbH2 analogue 2. Indeed, the efficiency of 2 (0.71 %) exceeds that of AS16 with a reasonably strong optical absorption shoulder when adsorbed on TiO2 (Supplementary Information) that matches the band at 450-550 nm apparent in the IPCE trace. The rhenium complexes AS18 and 3, however, showed very similar Jsc, Voc and η values to each other.

Whilst AS16 indeed shows superior performance over its dcbH2 model in the cells test the performance of the other new dyes, especially in the case of AS17, is disappointing and likely stems from the elevated LUMO associated with the dctz bpy anchoring ligand. However, we reasoned that these dyes may yield greater sensitisation efficiency than their dcbH2 analogues in p-type devices for the very same reason.24 We therefore constructed and tested NiO-based p-type cells based on the new dyes and their dcbH2 analogues 1 to 3 along with coumarin C343 as a benchmark comparison. Current-voltage and IPCE plots are provided in Figure 10 with photovoltaic parameters listed in Table 5.

Table 5. Photovoltaic parameters of tested dyes AS16-18 and 1-3 with Coumarin-C343 as a benchmark comparison in NiO-based p-type DSSC devices. The electrolyte contained 0.1 M l3 and 1 M LiI in MeCN.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Jsc / mA cm⁻²</th>
<th>Voc / mV</th>
<th>FF / %</th>
<th>η / %</th>
<th>IPCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C343</td>
<td>0.26</td>
<td>105</td>
<td>37</td>
<td>0.01</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>0.076</td>
<td>58</td>
<td>27</td>
<td>0.0012</td>
<td>2</td>
</tr>
<tr>
<td>AS16</td>
<td>0.69</td>
<td>94</td>
<td>42</td>
<td>0.028</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>0.069</td>
<td>134</td>
<td>40</td>
<td>0.0037</td>
<td>3</td>
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<tr>
<td>AS17</td>
<td>0.14</td>
<td>89</td>
<td>42</td>
<td>0.0052</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>77</td>
<td>45</td>
<td>0.0056</td>
<td>6</td>
</tr>
<tr>
<td>AS18</td>
<td>0.15</td>
<td>79</td>
<td>46</td>
<td>0.0055</td>
<td>6</td>
</tr>
</tbody>
</table>

The AS16 based cell exhibits the highest overall efficiency of all metal complex sensitised p-type cells (0.028 % compared to 0.01 % for C343) and the highest IPCE of 17 %. As might be expected due to the dctz bpy anchoring ligand being less electron withdrawing than dcbH2 the performances of cell using AS16 and AS17 exceed those of 1 and 2 respectively. Indeed, 1 and 2 seem to be desensitisers of NiO in these cells with the current generated below 450 nm most likely stemming from photolysis of the l3' electrolyte as previously noted by Nattestad et al.39 Cells utilising AS18 and 3 yield near identical performance parameters.
Conclusions

We have designed and prepared a new anchoring ligand, 1-(2,2’-bipyridin-4-yl)-1,2,3-triazole-4,5-dicarboxylic acid, and its ruthenium, iridium and rhenium complexes. New ruthenium(II), iridium(III) and rhenium(I)-based dyes, AS16 to AS18 respectively, have been compared with their dcbH₂ analogues. Spectroscopic and theoretical results suggest the LUMO of the dctz bpy ligand is higher in energy than that of dcbH₂. Whilst correctly positioned for charge injection upon photoexcitation the resultant blue shift in optical absorption bands results in inferior light harvesting properties. Whilst improved photovoltaic performance is observed for AS16 this leads to a reduction in the photovoltaic efficiency the other dyes in n-type DSSCs when compared to their dcbH₂ analogues. In p-type cells the ruthenium(II) and iridium(III)-based dyes AS16 and AS17 display superior performance over their dcbH₂ counterparts. Indeed, AS16 is shown to yield three times the efficiency of the benchmark dye coumarin 343. The work therefore offers insights into new anchor ligand systems. The newly reported ligand has potential for further development for dye complexes in NiO-based p-type DSSC devices especially in which a less electron withdrawing anchoring ligand is desirable, and in other applications including dye sensitised electrochemical cells for solar catalysis and biological luminescent imaging.

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Experimental Section

General methods

Chemicals were purchased from Aldrich and Acros, iridium and ruthenium were purchased from Precious Metal Online (Australia) and used as received. All complexation reactions were carried out under nitrogen. 4-Azido-2,2’-bipyridine, \([\text{Ir}(ppy)_2(dcbH_2)]PF_6\); 1, \([\text{Ru}(ppy)_2\text{Cl}_2]\); 24 \([\text{Ir}(ppy)_2\text{Cl}]_2\); 20 \([\text{Ru}(ppy)_2(dcbH_2)]PF_6\); (1), 18 \([\text{Ir}(ppy)_2(dcbH_2)]\); (2), 20 \([\text{Re}(CO)_3\text{Cl}(dcbH_2)]\) (3), 17 were all prepared according to literature procedures. 1H NMR and 13C NMR spectra were recorded on a Bruker Avance 400 MHz instrument. Mass spectrometry data were collected on a Bruker Micro Q-TOF instrument. UV-Visible absorption spectra were recorded on a Varian Cary 300 spectrophotometer and corrected emission spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Luminescent lifetime measurements were carried out using an Edinburgh Instruments Mini-Tau spectrometer.

Electrochemistry

For the cyclic voltammetry a EmStat3 electrochemical interface (Palm Sens, Netherlands) was employed, voltammograms were plotted on PSTrace software (Palm Sens, Netherlands). Cyclic...
voltammetry was carried out in a single compartment three electrode electrochemical cell under nitrogen atmosphere. Glassy carbon, platinum and Ag/AgCl were used respectively as working, counter and reference electrodes. The potential of the tested electrode was measured versus ferrocinium/ferroceane standard internal reference (FeCp+/FeCp). The electrolyte used for the cyclic voltammetry measurements was 0.1 M TBAPF6 in acetonitrile, prior to measurements all the solutions were degassed with nitrogen and during measurements a nitrogen blanket was maintained over the solution. The data were then plotted as current vs voltage.

Dye sensitised solar cell fabrication

FTO glass was used as current collector (TCO30-10, 3 mm thick glass substrate with a 10 Ω/sq). For TiO2-based anodes cleaned and dried FTO electrodes were immersed into a 40 mM aqueous TiCl4 solution at 70 °C for 30 minutes and washed with pure water and ethanol and dried. A layer of nanocrystalline TiO2 paste (Solaronix Ti-Nanoxide SP-T) was used as electrolyte in the TiO2-based n-type cells whereas an electrolyte containing 0.1 M I2 and 1 M LiI in acetonitrile was applied and sintered until the film thickness was 2.5 μm. The films were sintered for 30 minutes and additional layers of precursor solution were deposited as before. Following this a light scattering layer (Solaronix Ti-Nanoxide R/SP) was applied in the same way and the films were sintered at 500 °C for 30 minutes. After a second treatment with TiCl4, the films were sintered for a final time as before. After cooling to 80 °C, the TiO2 electrodes were immersed into a 0.5 mM dye solution in acetonitrile overnight in the dark.

The NIO films were prepared by using an F108–templated precursor solution containing NiCl2 (1 g), Pluronic® co-polymer (0.01 M) and 20% dectzbpy. The solution was heated to reflux temperature for 4h, after that the solution was neutralised with HCl 2M. A white solid crushed out, collected by filtration and dried under reduced pressure. (134.84 mg, yield 85%) The Pt catalyst was deposited on the FTO glass, coating with 10 μL cm−2 of H2PtCl6 solution (5 mM ethanol solution), air dried and heated at 400 °C for 15 minutes. The dye-covered TiO2 or Nio electrodes and Pt-counter electrodes were assembled into a sandwich-type cell and sealed with a Surllyn hot-melt gasket of 60 μm thickness. A solution of 0.5 M TBP, 0.015 M I2, 0.6 M TBAI and 0.1 M GuSCN in acetonitrile was used as electrolyte in the TiO2-based n-type cells whereas an electrolyte containing 0.1 M I2 and 1 M LiI in acetonitrile was used for p-type cells.

Computational methods

DFT calculations were carried out using the NWChem 6.3 software package,42 B3LYP hybrid functional (20 % Hartree–Fock) method has been used for calculations,53,44 Stuttgart relativistic small core ECP46 for transition metals and 6-311G**46 basis sets for all other atoms. Molecular geometries and molecular orbitals pictures were realised using the cpp1 graphical software. For all the studied complexes, the ground state geometries were first optimised and molecular orbital energies determined. TDDFT calculations on optimised structures in CH3CN by using the COSMO solvation model,48 built in NWChem software, were used to obtain the electronic spectra and molecular orbital energy levels.

Synthesis of diethyl-1-(2,2’-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylate

4-Azido-2,2’-bipyridine (0.1 g, 0.51 mmol) and diethyl acetylenedicarboxylate (0.16 g, 0.76 mmol) was dissolved in toluene (15 mL). The solution was allowed to stir at 70°C for 24 h. The solvent was removed under vacuum and the product was recrystallised from DCM and hexane to yield a white solid. (175 mg, yield 93%) 1H NMR (400 MHz, CDCl3): δ: 8.85 (d, J = 5.28 Hz, 1H, py-H); 8.67 (d, J = 2.08 Hz, 1H, py-H); 8.65 (d, J = 4.44 Hz, 1H, py-H); 8.45 (d, J = 7.92 Hz, 1H, py-H); 7.83 (td, J = 7.72, J = 1.72 Hz, 1H, py-H); 7.61 (dd, J = 5.28, J = 2.16 Hz, 1H, py-H); 7.43 (ddd, 1H, J = 7.52, J = 4.77, J = 1.00, py-H); 4.47 (q, J = 7.12, 2H, C2H2-CH2); 4.46 (q, J = 7.12, 2H, CH2-CH2); 1.14 (t, J = 7.12 Hz, 3H, CH3); 1.35 (t, J = 7.16 Hz, 3H, CH3-CH2).

Synthesis of 1-[2,2’-bipyridine-4-yl]triazole-4,5-dicarboxylic acid

1-[2,2’-bipyridine-4-yl]triazole-4,5-ethyldicarboxylate (0.1 g, 0.51 mmol) was dissolved in 25 mL of NaOH 0.1M and heated to reflux temperature for 4h, after that the solution was neutralised with HCl 2M. A white solid crushed out, collected by filtration and dried under reduced pressure. (134.84 mg, yield 85%) 1H NMR (400 MHz, DMSO-d6): δ: 8.26 (d, J = 5.24, 1H, py-H); 8.77 (d, J = 4.72, 1H, py-H); 8.61 (d, J = 1.36, 1H, py-H); 8.54 (d, J = 7.96, 1H, py-H); 8.15 (t, J = 7.64, 1H, py-H); 7.81 (d, J = 5.20, J = 1.72, 1H, py-H); 7.64 (t, J = 5.48, 1H, py-H).

HRMS (ESI) m/z calcd for C14H12N4O4 311.0654, found 310.0582 (M+H)+

Synthesis of [Ru(bpy)2(diethyl-1-(2,2’-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylate)][PF6]2

100 mg of Ru(bpy)2Cl2 were dissolved in EtOH (20 mL) together with 113 mg of dectzbpy. The solution was heated to reflux temperature overnight, under N2 in the dark. The solvent was removed under reduced pressure and the resulting solid dissolved in MeOH, an excess of NH4PF6 was added and an orange crystalline solid was collected by filtration. The solid was columned on silica gel with MeCN:H2O:KNO3 7:1:0.5 as eluent. The main gloving fraction was then dried, redissolved in acetonitrile and filtered. The filtrate was dried and redissolved in a minimum amount of methanol, NH4PF6 was added, an orange solid crashed and it was collected by filtration. (168.1 mg, yield 76%)
Synthesis of [Ir(ppy)2(diethyl-1-(2,2'-bipyrid-4-yl)-1,2,3-triazole-4,5-ethyldicarboxylate)]PF6 AS17

50 mg of [Ru(bpy)3(dentzpy)2]PF6 was dissolved in 8 mL 1M KOH/acetonitrile 1:1 and heated to reflux temperature for 12 hours. After cooling the acetone was removed under vacuum and the solution was neutralised with 1M HCl. The solution was concentrated and a solid crashed out. The solid was collected by filtration, redissolved in a minimal amount of methanol and NH4PF6 was added, newly a yellow solid crashed and it was collected by filtration. (32.1 mg, yield 68%)

Synthesis of [lr(ppy)]2[diethyl-1-(2,2’-bipyrindine-4-yl)triazole-4,5-dicarboxylate]PF6 AS18-Et2

107 mg of [lr(ppy)]2Cl dimer were dissolved in DCM:MeOH 2:1 (12 mL) together with 77 mg of dentzpy and 53 mg of AgPF6. The solution was heated to reflux temperature overnight, under N2 in the dark. The solvent was removed under reduced pressure and the resulting solid dissolved in DCM and filtered on celite pad. The solvent was removed again and the solid recrystallised from acetonitrile/ethanol. A pale yellow solid was collected by filtration and columned with 10% MeOH in DCM. (149.3 mg, yield 74%)

Synthesis of Re(CO)5(diethyl-1-(2,2’-bipyrindine-4-yl)-1,2,3-triazole-4,5-dicarboxylate)Cl AS18-Et2

100 mg of [Re(CO)5]Cl and 113 mg of dentzpy were dissolved in 25 mL of toluene and heated at 70 °C for 12 hours. After cooling the volume was reduced under reduced pressure and a yellow solid crashed out, it was collected by filtration and dried with diethyl ether. (155.8 mg, yield 84%)

1H NMR (100 MHz, CD3CN) δ: 9.21 (d, J = 5.96, 1H, bpy-H); 9.06 (dd, J = 5.38, 3J = 0.70, 1H, bpy-H); 8.70 (d, J = 2.10, 1H, bpy-H); 8.47 (d, J = 8.18, 1H, bpy-H); 8.23 (dt, J = 2.73, 1H, bpy-H); 7.87 (dd, J = 6.08, J = 2.34, 1H, bpy-H); 7.69 (dt, J = 6.49, J = 1.22, 1H, bpy-H); 4.44 (q, J = 7.13, 2H, CH2-CH3); 4.41 (q, J = 7.02, 2H, CH2-CH3); 1.38 (t, J = 7.13, 3H, CH3-CH3); 1.27 (t, J = 6.98, 3H, CH3-CH3).

1H NMR (400 MHz, CD3CN) δ: 9.21 (d, J = 5.96, 1H, bpy-H); 9.06 (dd, J = 5.38, 3J = 0.70, 1H, bpy-H); 8.70 (d, J = 2.10, 1H, bpy-H); 8.47 (d, J = 8.18, 1H, bpy-H); 8.23 (dt, J = 2.73, 1H, bpy-H); 7.87 (dd, J = 6.08, J = 2.34, 1H, bpy-H); 7.69 (dt, J = 6.49, J = 1.22, 1H, bpy-H); 4.44 (q, J = 7.13, 2H, CH2-CH3); 4.41 (q, J = 7.02, 2H, CH2-CH3); 1.38 (t, J = 7.13, 3H, CH3-CH3); 1.27 (t, J = 6.98, 3H, CH3-CH3).
HRMS (ESI) m/z calcd for C_{32}H_{27}ClN_3O_5Re 671.0352, found 689.0694 (M+NH_4)^+.

Synthesis of Re(CO)_3[1H-2,2'-bipyridine-4-yl][triazole-4,5-ethyldicarboxylate]Cl AS18

50 mg of [Re(CO)_3(detzbpy)Cl] was dissolved in 8 mL 1M KOH/acetone 1:1 and heated to reflux temperature for 12 hours. After cooling the acetone was removed under vacuum and the solution was neutralised with 1M NaOH. The solution was concentrated and a yellow solid crashed out. The solid was collected by filtration. (30.7 mg, yield 67%)

1H NMR (400 MHz, DMSO-d_6): 6.84 (d, J = 5.44, 1H, bpy-H); 8.44 (d, J = 8.17, 1H, bpy-H); 8.22 (t, J = 7.78, 1H, bpy-H); 7.97 (dd, J = 6.81, 1H, bpy-H); 7.63 (t, J = 6.1, 1H, bpy-H); 7.15 (d, J = 2.25, 1H, bpy-H); 6.14 (dd, J = 6.95, J = 2.64, 1H, bpy-H).

13C{1H} Low solubility, NMR not recorded.

References


