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1520Investigation of a new bis(carboxylate)triazole-
based anchoring ligand for dye solar cell
chromophore complexes†Alessandro Sinopoli,^a Fiona A. Black,^b Christopher J. Wood,^b Elizabeth A. Gibson*^b
and Paul I. P. Elliott*^a

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 (dctzbp), is described. The new dye complexes [Ru(bpy)₂(dctzbp)] [PF₆]₂ (**AS16**), [Ir(ppy)₂(dctzbp)] [PF₆] (**AS17**) and [Re(dctzbp)(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⁺ (**1**) (*E*_{red} = -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.

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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 to optimise the ground state and excited state oxidation potentials for charge-injection and dye regeneration processes.⁶ A critical component of these dye complexes is therefore the ligand on which the ³MLCT state is localised and which anchors the complexes to the elec-

trode. 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 rhenium,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, Fig. 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

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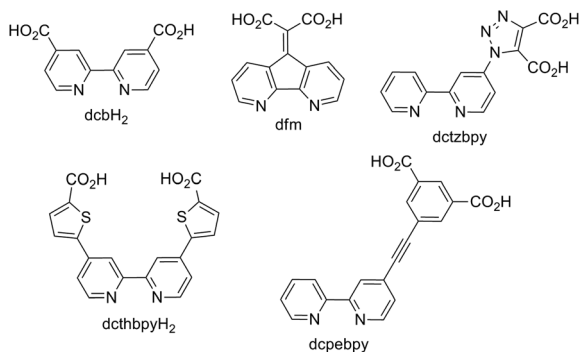


Fig. 1 Structures of selected carboxylate-based DSSC anchoring ligands.

anchoring ligand (4,5-diazafluoren-9-ylidene)malonic acid (**dfm**, Fig. 1) together with its corresponding complex $[\text{Ru}(\text{bpy})_2(\text{dfm})]^{2+}$ (**bpy** = 2,2'-bipyridyl).⁶ Mishra *et al.* prepared the complex **BCT-1**, $[\text{Ru}(\text{dctzbpH}_2)_2(\text{NCS})_2][\text{NBu}_4]_2$, 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 (**dctzbpH₂**).¹⁷ 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 **dcbH₂** complex. This yielded an overall conversion efficiency of 6.1% compared with the 4.8% achieved using the archetypal DSSC dye **N3** ($[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$). In an attempt to minimise the rate constant for charge recombination, Abrahamsson *et al.* introduced a phenylethyne unit between a **bpy** ligand and the surface anchoring groups (**dcpebp**, Fig. 1), preparing the corresponding $[\text{Ru}(\text{dcpebp})(\text{bpy})(\text{NCS})_2]$ complex. This resulted in a recombination rate three times smaller compared to that for **N3**.¹⁸

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^{19–21} and also boronic acid derivatised complexes.²²

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.^{23–30} Pellegrin *et al.* have reported ruthenium(ii)-based sensitisers for p-type DSSC devices with phosphonic acid, thiocarboxylate and catechol derived anchoring groups.²⁹ Ji *et al.* have reported cyclometalated ruthenium complexes of the type $[\text{Ru}(\text{N}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N})]^+$ as sensitisers for p-type DSSCs.²⁸ Addition of a rigid biphenylene 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 triarylamine anchoring groups yielding efficiencies of up to 0.09%.²⁷ Massin *et al.* have also reported carboxylate-appended triarylamine functionalised dyes with a $[\text{Ph}_2\text{C}=\text{C}=\text{Ru}(\text{dppe})_2]$ core (**dppe** = 1,2-bis(diphenylphosphino)ethane).²⁵

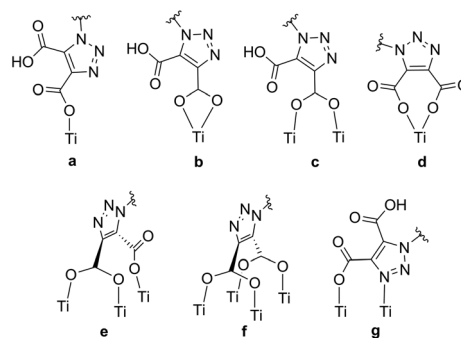


Fig. 2 Selection of the potential TiO_2 anchoring modes that could be adopted by the **dctzbp** ligand.

Through the use of triazole-based “click” chemistry³¹ we report here the design and synthesis of the novel anchoring ligand (2,2'-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylic acid (**dctzbp**, Fig. 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_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_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 Fig. 2), both carboxylate groups (bidentate (**d**), tridentate (**e**), tetradentate (**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 surface oxygen atoms or carboxylate with surface hydroxyl groups can also be envisaged.

We also report the preparation of ruthenium(ii), iridium(iii) and rhenium(i) complexes **AS16-Et₂** to **AS18-Et₂** of the initial diethyl ester of the **dctzbp** ligand and subsequent photo-physical and electrochemical analyses. Further, we report the hydrolysis of these complexes to their corresponding diacids **AS16** to **AS18** (Fig. 3) and pilot studies on their utilisation in DSSC test devices with comparison to corresponding **dcbH₂** complexes **1** to **3**.

Results & discussion

The above mentioned ligand, **dctzbp**, 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 thermally driven cycloaddition with one equivalent of diethyl acetylenedicarboxylate in refluxing toluene to furnish the diester diethyl-1-(2,2'-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxy-



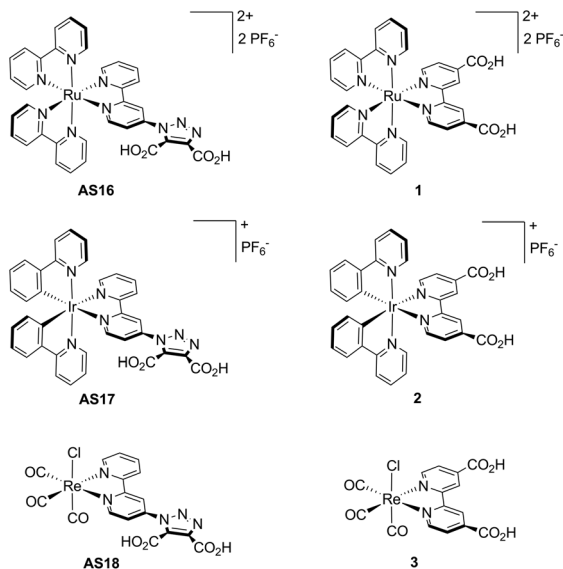
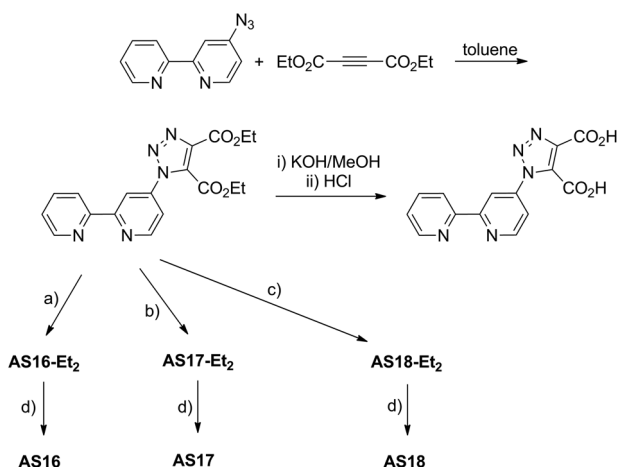


Fig. 3 Structure of complexes AS16–18 and their dcbH₂ analogues 1–3.



Scheme 1 Synthesis of the target 1-(2,2'-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylic acid ligand and complexes AS16 to AS18: (a) (i) [Ru(bpy)₂Cl₂], EtOH, reflux, (ii) NH₄PF₆, MeOH; (b) (i) [Ir(ppy)₂Cl₂], CH₂Cl₂/MeOH, reflux, (ii) NH₄PF₆, MeOH; (c) [Re(CO)₅Cl], toluene, reflux; (d) (i) KOH/acetone, HCl, (ii) NH₄PF₆.

late. Cycloaddition was confirmed by infrared spectroscopy with the disappearance of the azide stretch corresponding to the starting material (2115 cm⁻¹) and the appearance of new CO stretching bands for the carboxylate substituents on the triazole ring (1735 cm⁻¹). The ester groups then underwent hydrolysis to the corresponding carboxylic acids in refluxing dilute KOH in methanol before neutralising with HCl.

The ¹H NMR spectrum of the product shows seven unique environments (ESI⁺) for the protons on the bipyridyl fragment along with two sets of signals for the ethyl groups of the ester moieties. This is consistent with the cycloaddition of the acetylene to form the triazole and loss of magnetic equivalence of

the two carboxylate groups. The resonances for the triazole-appended pyridine ring appear at δ 8.85, 8.67 and 7.61 and are shifted as a result of the cycloaddition relative to those of the azide starting material (δ 8.69, 8.15 and 7.34).³⁵

Routes to ruthenium, iridium and rhenium dcbH₂ complexes [Ru(bpy)₂(dcbH₂)](PF₆)₂ (AS16), [Ir(ppy)₂(dcbH₂)](PF₆) (AS17, ppyH = 2-phenylpyridine) and [Re(CO)₃(dcbH₂)Cl] (AS18) respectively were investigated involving direct reaction of the acid form of the ligand with precursor complexes, however, isolation of the corresponding complexes proved problematic. Isolation of complexes of the intermediate diester ligand, AS16-Et₂, AS17-Et₂ and AS18-Et₂, followed by hydrolysis was deemed to give better results. Thus, two-step syntheses starting from [Ru(bpy)₂Cl₂], [Ir(ppy)₂Cl]₂ and [Re(CO)₅Cl] were carried out. Firstly, the above mentioned starting metal precursor complexes were reacted together with dcbH₂ (Scheme 1) followed by anion metathesis with NH₄PF₆ to yield the desired diester complexes.

As a consequence of the asymmetry of the dcbH₂ ligand the [Ru(bpy)₂] and [Ir(ppy)₂] fragments in AS16-Et₂ and AS17-Et₂ do not possess the C₂ symmetry present in 1 and 2. Hence, each bpy and ppy ligand in AS16-Et₂ and AS17-Et₂ respectively is magnetically unique resulting in complicated ¹H NMR spectra due to the overlap of signals (ESI⁺). The ¹H NMR spectrum of AS18-Et₂ exhibits dcbH₂ signals shifted to higher field in comparison with the free diester ligand by ~0.4 ppm with the resonances for the H-6 and H-6' position appearing at δ 9.21 and 9.06 respectively.

The final dyes AS16 to AS18 can be readily accessed by hydrolysis with KOH in acetone and subsequent neutralisation. Due to solubility issues, however, and the fact that key properties are expected to differ little after hydrolysis electrochemical characterisation is reported for the more soluble esters AS16-Et₂ to AS18-Et₂.

Cyclic voltammetry traces and summarised electrochemical data are presented in Fig. 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 dcbH₂ 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 be dcbH₂ ligand. Complex AS18-Et₂ is

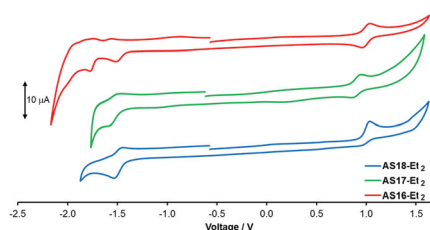


Fig. 4 Cyclic voltammetry traces for complexes AS16-Et₂, AS17-Et₂ and AS18-Et₂ vs. Fc⁺/Fc = 0.0 V.

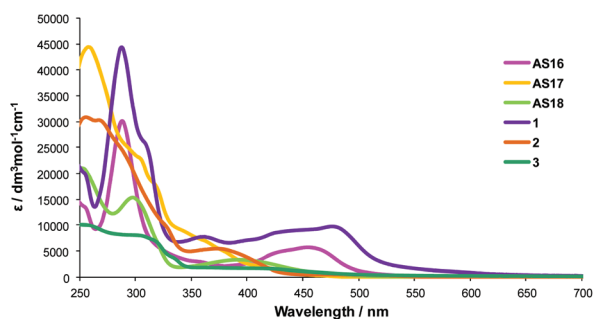


Table 1 Summarised electrochemical data for complexes **AS16–Et₂** to **AS18–Et₂** at room temperature acetonitrile vs. $Fc^+/Fc = 0.0$ V

Dye	E_{ox}/V	E_{red}/V
AS16–Et₂	1.00	−1.50
AS17–Et₂	0.90	−1.59
AS18–Et₂	1.00	−1.56

characterised by a quasi-reversible oxidation peak at +1.00 V, in agreement with the potential of other $Re(CO)_3(dcb-Et_2)X$ -based complexes ($X = \text{halide}$).³⁶ It also presents a reversible detsbpy-based reduction at −1.56 V. The oxidation potentials for these complexes are similar to those of their corresponding $dcbH_2$ -based analogues consistent with the expectation of a largely metal-based HOMO.^{29,36,37} The detsbpy-based reduction potentials (−1.5 to −1.6 V) are more cathodically shifted than that reported for **1** (−1.34 V)²⁹ 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 detsbpy complexes. The analogous $dcbH_2$ complexes $[Ru(bpy)_2(dcbH_2)][PF_6]_2$ (**1**),²⁹ $[Ir(ppy)_2(dcbH_2)][PF_6]$ (**2**)²⁰ and $[Re(CO)_3(dcbH_2)(Cl)]$ (**3**)¹⁷ were also prepared for comparison. UV-Visible absorption spectra were recorded for all complexes in acetonitrile solutions at room temperature and are presented in Fig. 5 with summarised data listed in Table 2.

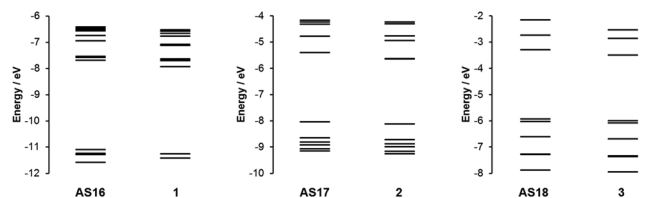
**Fig. 5** UV-visible absorption spectra for complexes **AS16–18** and **1–3** in acetonitrile solutions.**Table 2** Summarised photophysical data for complexes **AS16–18** and their $dcbH_2$ analogues **1–3** at room temperature in acetonitrile

Complex	λ^{abs}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)	λ_{max}^{em}/nm	τ/ns
1	245 (21 923), 287 (44 481), 308 (26 079), 357 (7836), 430 (8807), 475 (9880)	682	32
	256 (30 778), 289 (24 016), 377 (6905)	689	33
	252 (10 289), 303 (8202), 413 (1826)	725	35
AS16	242 (15 624), 287 (30 138), 424 (4642), 456 (5719)	638	34
	255 (44 311), 301 (23 330), 364 (7771), 415 (1914)	590	25
AS18	254 (20 204), 297 (15 317), 397 (3815)	553	38

The comparison between the $dcbH_2$ complexes and their detsbpy 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 $\pi-\pi^*$ ¹LC transitions together with ¹MLCT bands of modest intensity ($\epsilon \approx 5000-10\,000 dm^3 mol^{-1} cm^{-1}$) above 400 nm. The blue-shifted absorption bands in the spectra of the detsbpy complexes suggests that the LUMO is higher in energy than those for the $dcbH_2$ analogues and that the biscarboxytriazole group is less electron withdrawing than the two carboxylate groups bonded directly to the bipyridyl core in $dcbH_2$. Nevertheless, LUMO is correctly positioned with reference to the TiO_2 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 $dcbH_2$ analogues, with similar life-times at about 32 ns. This again is indicative that the LUMO of the detsbpy ligand, and thus that of its complexes, is higher in energy with respect to $dcbH_2$ thereby leading to the observed destabilisation of ³MLCT T_1 states in these complexes.

In order to gain a more complete understanding of the photophysical and electrochemical properties imparted by the new ligand detsbpy 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 moieties, and due to the fact that the spectroscopic absorption properties of the free acid and ester complexes differ little suggesting that they are electronically very similar. 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 (Fig. 6) and localisations (Fig. 7) were then determined in single-point calculations using the COSMO solvation model ($\epsilon = 37.5$ 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 detsbpy ligand and is mostly localised over the bpy fragment. For **AS16** there is also a minor contribution

**Fig. 6** Calculated molecular orbital energy level diagram for complexes **AS16–18** and **1–3**.

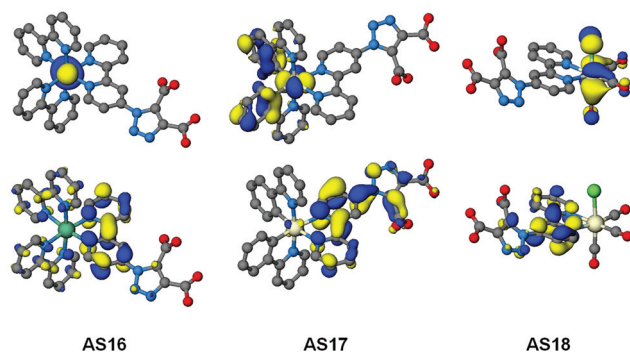


Fig. 7 Optimised geometries and plots of HOMO (top) and LUMO (bottom) orbitals for complexes AS16 to AS18.

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 dctzbp 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 dctzbp 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 the TiO₂ Fermi level in order to facilitate charge injection into the electrode.

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 Fig. 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

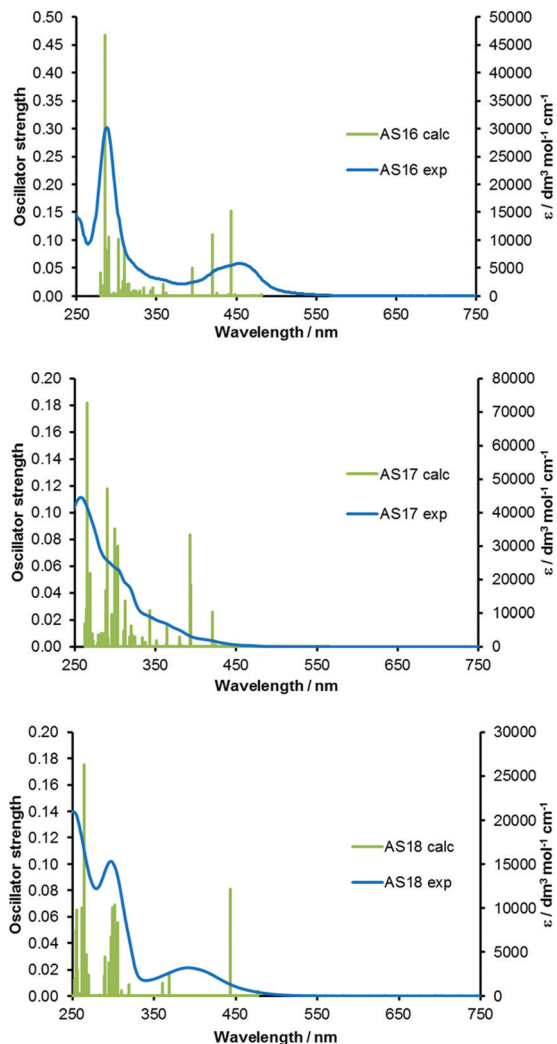


Fig. 8 TDDFT calculated absorption spectra for complexes AS16–18 with experimental spectra overlaid.

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

Dye	LUMO/eV	HOMO/eV	HOMO–LUMO/eV
1	–7.92	–11.26	3.33
AS16	–7.68	–11.10	3.42
2	–5.65	–8.13	2.48
AS17	–5.41	–8.04	2.63
3	–3.51	–6.00	2.49
AS18	–3.30	–5.94	2.64

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 (S₈) 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/¹LLCT character and two transitions at 394 (S₅) and 393 (S₆) nm with ¹MLCT/¹ILCT and ¹MLCT/¹LLCT character respectively. The rhenium complex AS18 exhibits a strong transition at 443 nm (S₂) with a predominant composition of HOMO–1 → LUMO ¹MLCT character.

The relative positioning of the frontier orbitals in the dctzbp 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 dctzbp 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 $\eta = J_{sc}V_{oc}FF$, where J_{sc} is the short circuit current density, V_{oc} is the open circuit voltage, and FF is the fill factor. Fig. 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** (Fig. 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.

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,³⁸ 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 (ESI[†]) that matches the band at 450–550 nm apparent in the IPCE trace. The rhenium complexes **AS18** and **3**, however, showed very similar J_{sc} , V_{oc} and η values to each other.

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 I₂, 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine in MeCN

Dye	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/mV	FF/%	$\eta/\%$	IPCE/%
N719	10.7	779	69	5.76	65
1	0.39	457	57	0.1	6
AS16	1.18	662	78	0.61	15
2	1.44	633	78	0.71	17
AS17	0.06	485	72	0.02	3
3	0.36	495	73	0.13	6
AS18	0.24	532	73	0.09	5

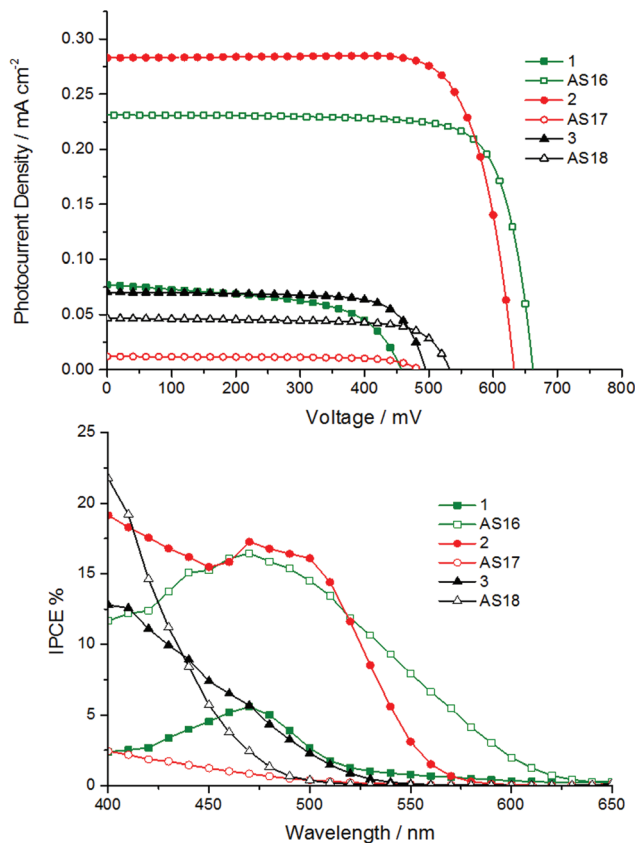


Fig. 9 Current–voltage traces for pilot TiO₂-based n-type DSSC devices utilising complexes **AS16** to **AS18** and model dyes **1** to **3** (top) along with IPCE traces for each cell (bottom). The electrolyte contained 0.6 M tetrabutylammonium iodide, 0.015 M I₂, 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine in MeCN.

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 dctzbp 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 Fig. 10 with photovoltaic parameters listed in Table 5.

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 dctzbp anchoring ligand being less electron withdrawing than dcbH₂ the performances of cells 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 I₃[−] electrolyte as previously noted by Nattestad *et al.*³⁹ Cells utilising **AS18** and **3** yield near identical performance parameters.



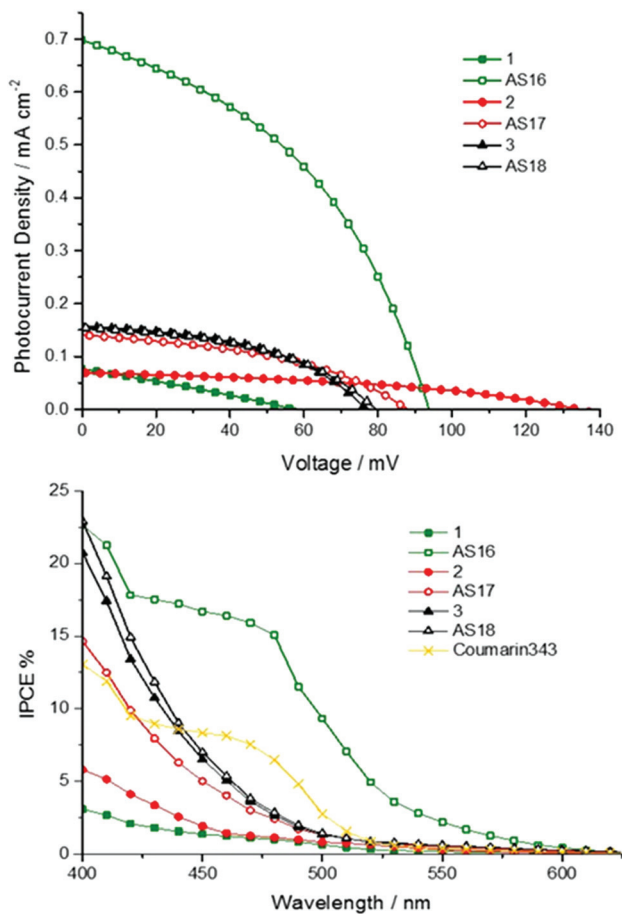


Fig. 10 Current–voltage traces for pilot NiO-based p-type DSSC devices utilising complexes **AS16** to **AS18** and model dyes **1** to **3** (top) along with IPCE traces for each cell (bottom). The electrolyte contained 0.1 M I₂ and 1 M LiI in MeCN.

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 I₂ and 1 M LiI in MeCN

Dye	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/mV	FF/%	$\eta/\%$	IPCE/%
C343	0.26	105	37	0.01	8
1	0.076	58	27	0.0012	2
AS16	0.69	94	42	0.028	17
2	0.069	134	40	0.0037	3
AS17	0.14	89	42	0.0052	5
3	0.16	77	45	0.0056	6
AS18	0.15	79	46	0.0055	6

The results for **AS16** are generally encouraging in terms of dye development but are disappointing when considered in comparison to the benchmark **N719**. With further ancillary ligand development in combination with the new ligand it may be possible to arrive at much higher efficiency n-type sensitisers. Complexes of the new anchoring ligand **dctzbp** may also find potential applications in p-type cells since the data show that the ruthenium(II)-based dye **AS16** results in an efficiency three times that of the benchmark standard dye coumarin-C343. When combined with other ligands about a metal

centre with greater electron withdrawing character this anchoring ligand provides potential for the development of far more efficient p-type sensitisers. Complexes based on the ligands described here may also find utility as photochemical solar fuel catalysts adsorbed on semiconductor nanoparticles.⁴⁰ As the complexes here are luminescent and the carboxylate groups can be utilised for bioconjugation complexes bearing the **dctzbp** core structure could also be used in biological imaging applications.⁴¹

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 **dctzbp** 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 for 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 C343. 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.

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,³⁴ [Ru(bpy)₂Cl₂],²⁴ [Ir(ppy)₂Cl]₂,²⁰ [Ru(bpy)₂(**dcBH₂**)] [PF₆]₂ (**1**),¹⁸ [Ir(ppy)₂(**dcBH₂**)] [PF₆] (**2**),²⁰ [Re(CO)₃(Cl)(**dcBH₂**)] (**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/ferrocene standard internal reference ($\text{FeCp}_2^+/\text{FeCp}_2$). 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 $10 \Omega \text{ sq}^{-1}$). 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 coated on the FTO glass plates by doctor blade technique, using a round mask (5 mm diameter, 0.25 cm² area) made by adhesive tape (3M Magic). The film was dried for 5 minutes on a hotplate and a second layer of TiO₂ was 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® copolymer F108 (1 g), distilled water (3 g) and ethanol (6 g) and the excess was removed by doctor blade. The film was sintered at 450 °C for 30 minutes and additional layers of precursor solution were applied and sintered until the film thickness was *ca.* 1.5 μm.

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 Surlyn 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,^{43,44} Stuttgart relativis-

tic small core ECP⁴⁵ for transition metals and 6-311G*⁴⁶ basis sets for all other atoms. Molecular geometries and molecular orbitals pictures were realised using the ccp1 graphical software. For all the studied complexes, the ground state geometries were first optimized and molecular orbital energies determined. TDDFT calculations⁴⁷ 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, ³J = 5.28 Hz, 1H, py-H); 8.67 (d, ³J = 2.08 Hz, 1H, py-H); 8.65 (d, ³J = 4.44 Hz, 1H, py-H); 8.45 (d, ³J = 7.92 Hz, 1H, py-H); 7.83 (td, ³J = 7.72, ⁴J = 1.72 Hz, 1H, py-H); 7.61 (dd, ³J = 5.28, ⁴J = 2.16 Hz, 1H, py-H); 7.43 (ddd, 1H, ³J = 7.52, ⁴J = 4.77, ⁵J = 1.00, py-H); 4.47 (q, ³J = 7.12, 2H, CH₂-CH₃); 4.46 (q, ³J = 7.12, 2H, CH₂-CH₃); 1.41 (t, ³J = 7.12 Hz, 3H, CH₂-CH₃); 1.35 (t, ³J = 7.16 Hz, 3H, CH₂-CH₃).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ: 159.45, 158.90, 158.61, 154.21, 150.91, 149.38, 143.36, 139.38, 137.12, 132.45, 124.69, 121.24, 117.37, 114.59, 63.93, 62.09, 14.20, 13.77.

HRMS (ESI) *m/z* calcd for C₁₈H₁₇N₅O₄ 367.1280, found 368.1359 (M + H)⁺.

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 0.1 M and heated to reflux temperature for 4 h, after that the solution was neutralised with HCl 2 M. 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: 8.96 (d, ³J = 5.24, 1H, py-H); 8.77 (d, ³J = 4.72, 1H, py-H); 8.61 (d, ⁴J = 1.36, 1H, py-H); 8.54 (d, ³J = 7.96, 1H, py-H); 8.15 (t, ³J = 7.64, 1H, py-H); 7.81 (d, ³J = 5.20, ⁴J = 1.72, 1H, py-H); 7.64 (t, ³J = 5.48, 1H, py-H).

¹³C{¹H} NMR (100 MHz, DMSO-d₆) δ: 160.67, 158.62, 155.34, 152.77, 150.66, 148.55, 144.94, 139.97, 139.14, 134.14, 125.4, 121.45, 120.7, 116.84.

HRMS (ESI) *m/z* calcd for C₁₄H₉N₅O₄ 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 AS16-Et₂

100 mg of Ru(bpy)₂Cl₂ were dissolved in EtOH (20 mL) together with 113 mg of dectzbp. 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%).

¹H NMR (400 MHz, CD₃CN) δ: 8.79 (d, ³J = 2.02, 1H, bpy-H); 8.55–8.49 (m, 5H, bpy-H); 8.12–8.05 (m, 5H, bpy-H); 7.96 (d, ³J = 6.15, 1H, bpy-H); 7.83 (d, ³J = 5.32, 1H, bpy-H); 7.78 (d, ³J = 5.53, 1H, bpy-H); 7.76–7.69 (m, 3H, bpy-H); 7.55 (dd, ³J = 6.15, ³J = 2.20, 1H, bpy-H); 7.48–7.39 (m, 5H, bpy-H); 4.43 (q, ³J = 7.16, 2H, CH₂-CH₃); 4.31 (q, ³J = 7.07, 2H, CH₂-CH₃); 1.37 (t, ³J = 7.12, 3H, CH₂-CH₃); 1.11 (t, ³J = 7.03, 3H, CH₂-CH₃).

¹³C{¹H} NMR (100 MHz, CD₃CN) δ: 159.54; 159.10; 157.74; 156.97; 156.96; 156.93; 156.92; 156.88; 156.87; 156.83; 156.05; 153.52; 152.00; 151.94; 151.91; 151.83; 151.65; 143.10; 140.54; 138.19; 138.10; 138.09; 137.94; 128.41; 127.78; 127.74; 127.70; 127.62; 125.12; 125.08; 124.48; 124.43; 122.04; 119.67; 63.75; 62.25; 13.40; 13.04.

HRMS (ESI) *m/z* calcd for [C₃₈H₃₃N₉O₄Ru]²⁺ 390.5860, found 390.5864 (M)²⁺.

Synthesis of [Ru(bpy)₂(1-[2,2'-bipyridine-4-yl]triazole-4,5-ethyl-dicarboxylic acid)]PF₆ AS16

50 mg of [Ru(bpy)₂(detzbp)](PF₆)₂ was dissolved in 8 mL 1 M 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 1 M 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 red solid crashed and it was collected by filtration. (35.5 mg, yield 75%).

¹H NMR (400 MHz, CD₃CN) δ: 8.76 (d, ³J = 2.08, 1H, bpy-H); 8.55–8.46 (m, 5H, bpy-H); 8.13–8.03 (m, 5H, bpy-H); 7.92 (d, ³J = 6.12, 1H, bpy-H); 7.83–7.70 (m, 5H, bpy-H); 7.61 (d, ³J = 6.12, ⁴J = 2.2, 1H, bpy-H); 7.51–7.40 (m, 5H, bpy-H).

¹³C{¹H} NMR (100 MHz, CD₃CN) δ: 159.68, 159.63, 159.21, 157.86, 157.03, 156.99, 156.94, 156.90, 156.88, 156.46, 156.23, 154.69, 152.38, 151.89, 151.86, 151.84, 151.82, 151.81, 151.62, 143.42, 138.08, 138.03, 138.00, 137.96, 128.03, 127.73, 127.72, 127.66, 127.65, 124.75, 124.43, 124.40, 124.31, 121.72, 120.59.

Synthesis of [Ir(ppy)₂(diethyl-1-(2,2'-bipyrid-4-yl)-1,2,3-triazole-4,5-dicarboxylate)]PF₆ AS17-Et₂

107 mg of [Ir(ppy)₂Cl]₂ dimer were dissolved in DCM:MeOH 2:1 (12 mL) together with 77 mg of detzbp 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/ether. A pale orange solid was collected by filtration and columned with 10% MeOH in DCM. (149.3 mg, yield 74%).

¹H NMR (400 MHz, CD₃CN) δ: 8.81 (d, ³J = 1.70, 1H, bpy-H); 8.54 (d, ³J = 8.04, 1H, bpy-H); 8.20–8.13 (m, 2H, bpy-H); 8.08 (d, ³J = 8.14, 2H, ppy-H); 8.02 (dd, ³J = 5.78, ⁴J = 0.78, 1H, bpy-H);

7.86 (td, ³J = 7.35, ⁴J = 0.84, 2H, ppy-H); 7.82 (d, ³J = 7.62, 2H, ppy-H); 7.72 (dd, ³J = 5.52, ³J = 0.81, 1H, ppy-H); 7.65 (dd, ³J = 6.09, ⁴J = 2.17, 1H, bpy-H); 7.63 (dd, ³J = 5.96, ⁴J = 0.81, 1H, bpy-H); 7.56 (t, ³J = 6.30, 1H, bpy-H); 7.09–7.02 (m, 4H, ppy-H); 6.96–6.90 (m, 2H, ppy-H); 6.29 (dd, ³J = 7.75, ⁴J = 0.88, 1H, ppy-H); 6.26 (dd, ³J = 7.63, ⁴J = 0.74, 1H, ppy-H); 4.42 (q, ³J = 6.95, 2H, CH₂-CH₃); 4.31 (qd, ³J = 7.10, ⁴J = 1.15, 2H, CH₂-CH₃); 1.36 (t, ³J = 7.10, 3H, CH₂-CH₃); 1.10 (t, ³J = 7.10, 3H, CH₂-CH₃).

¹³C{¹H} NMR (100 MHz, CD₃CN) δ: 167.35, 167.24, 159.48, 158.15, 157.72, 154.72, 152.48, 150.99, 149.52, 149.49, 149.43, 144.40, 144.09, 143.97, 140.50, 139.62, 138.78, 138.72, 131.80, 131.59, 131.44, 130.49, 130.44, 129.26, 125.37, 124.98, 124.95, 123.66, 123.54, 123.08, 122.82, 122.76, 120.10, 120.01, 119.98, 63.81, 62.24, 13.39, 12.97.

HRMS (ESI) *m/z* calcd for [C₄₀H₃₃N₇O₄Ir]⁺ 867.2230, found 867.2228 (M)⁺.

Synthesis of [Ir(ppy)₂(1-[2,2'-bipyridine-4-yl]triazole-4,5-ethyl-dicarboxylate)]PF₆ AS17

50 mg of AS17-Et₂ was dissolved in 8 mL 1 M 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 1 M 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%).

¹H NMR (400 MHz, CD₃CN) δ: 8.46 (d, ³J = 6.56 Hz, 1H, bpy-H); 8.11 (td, ³J = 6.28, ⁴J = 1.24 Hz, 1H, bpy-H); 8.07 (t, ³J = 5.64 Hz, 2H, ppy-H); 8.00 (bs, 1H, bpy-H); 7.97 (dd, ³J = 4.3, ⁴J = 0.8 Hz, 1H, bpy-H); 7.89–7.84 (m, 2H, ppy-H); 7.81 (d, ³J = 6.08 Hz, 2H, ppy-H); 7.71 (d, ³J = 4.72 Hz, 1H, bpy-H); 7.65 (d, ³J = 4.6 Hz, 1H, ppy-H); 7.63 (d, ³J = 5.16 Hz, 1H, ppy-H); 7.47 (td, ³J = 5.24, ⁴J = 0.72 Hz, 1H, bpy-H); 7.09–7.02 (m, 5H, bpy-H&ppy-H); 6.97–6.9 (m, 3H, ppy-H); 6.31 (dd, ³J = 6.06, ⁴J = 0.6 Hz, 1H, ppy-H); 6.28 (dd, ³J = 6.04, ⁴J = 0.52 Hz, 1H, ppy-H).

¹³C{¹H} NMR (100 MHz, CD₃CN) δ: 167.63, 167.49, 157.16, 156.23, 151.26, 150.45, 149.14, 149.11, 144.28, 144.06, 139.99, 139.88, 139.86, 139.84, 139.21, 139.16, 138.36, 138.33, 131.91, 131.67, 131.65, 131.51, 130.31, 130.27, 130.23, 128.11, 124.82, 124.78, 124.33, 123.4, 123.37, 122.32, 122.3.

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

100 mg of [Re(CO)₃Cl] and 113 mg of detzbp 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 diethylether. (155.8 mg, yield 84%).

¹H NMR (400 MHz, CD₃CN) δ: 9.21 (d, ³J = 5.96, 1H, bpy-H); 9.06 (dd, ³J = 5.38, ³J = 0.70, 1H, bpy-H); 8.70 (d, ³J = 2.10, 1H, bpy-H); 8.44 (d, ³J = 8.18, 1H, bpy-H); 8.23 (dt, ³J = 7.95, 1.52, 1H, bpy-H); 7.78 (dd, ³J = 6.08, ³J = 2.34, 1H, bpy-H); 7.69 (dt, ³J = 6.49, ³J = 1.22, 1H, bpy-H); 4.44 (q, ³J = 7.13, 2H, CH₂-CH₃);



4.41 (q, $^3J = 7.02$, 2H, $\text{CH}_2\text{-CH}_3$); 1.38 (t, $^3J = 7.13$, 3H, $\text{CH}_2\text{-CH}_3$); 1.27 (t, $^3J = 6.98$, 3H, $\text{CH}_2\text{-CH}_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN) δ : 197.63, 197.47, 189.26, 159.55, 157.96, 157.87, 154.73, 154.65, 153.25, 144.91, 140.59, 140.22, 131.79, 128.29, 124.65, 121.86, 119.36, 63.94, 62.24, 13.40, 13.07.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}_5\text{O}_7\text{Re}$ 671.0352, found 689.0694 ($\text{M} + \text{NH}_4$) $^+$.

Synthesis of $\text{Re}(\text{CO})_3(1\text{-}[2,2'\text{-bipyridine-4-yl}] \text{triazole-4,5-ethyldi-carboxylate})\text{Cl AS18}$

50 mg of $[\text{Re}(\text{CO})_3(\text{detzpy})\text{Cl}]$ was dissolved in 8 mL 1 M 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 1 M 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, $\text{DMSO-}d_6$) δ : 8.94 (d, $^3J = 5.44$, 1H, *bpy-H*); 8.44 (d, $^3J = 8.17$, 1H, *bpy-H*); 8.22 (t, $^3J = 7.78$, 1H, *bpy-H*); 7.97 (d, $^3J = 6.81$, 1H, *bpy-H*); 7.63 (t, $^3J = 6.61$, 1H, *bpy-H*); 7.15 (d, $^3J = 2.25$, 1H, *bpy-H*); 6.14 (dd, $^3J = 6.95$, $^4J = 2.64$, 1H, *bpy-H*).

$^{13}\text{C}\{^1\text{H}\}$ Low solubility, NMR not recorded.

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