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Photophysics and Photochemistry of 1,2,3-Triazole-Based Complexes

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Abstract

The copper-catalysed cycloaddition of alkynes and azides to form 1,2,3-triazoles has emerged as a powerful tool in ligand design and the synthesis of novel transition metal complexes. In this review we focus on the photophysical properties of metal complexes bearing 1,2,3-triazole-based ligands with a particular emphasis on those of d⁶ metals including rhenium(I), iron(II), ruthenium(II), osmium(II) and iridium(III). We also highlight key examples of triazole complexes of platinum(II) and palladium(II) as well as the lanthanides and coinage metals.

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1. Introduction

Kinetically inert d⁶ transition metal complexes such as those of ruthenium(II), iridium(III), rhenium(I) etc. have been of enormous interest in the literature over the past four decades due to the attractive and rich photophysics and photochemistry that they exhibit.[1] These properties make them amenable to application in artificial photosynthesis,[2] solar fuels catalysis,[3] dye-sensitised solar cells (DSSCs),[4] electroluminescent devices,[5, 6] luminescence live-cell imaging,[7, 8] photoinitiated anti-cancer agents and singlet oxygen sensitisation for photodynamic therapy.[9-11] molecular sensors[12] and switches.[13] Key to the successful application of complexes of this type is the tuning of electronic and photophysical properties through efficient ligand design and synthesis. To this day the pyridyl moiety remains one of the most common donor motifs incorporated into chelate ligands for these complexes. More recently ligands based on 1,4-disubstituted-1,2,3-triazoles have been investigated for these applications. With formation through copper(I)-catalysed alkyne/azide cycloaddition (CuAAC)[14, 15] under mild conditions and with wide substrate scope, this has led to an explosion of research activity.

CuAAC chemistry offers significant advantages as a tool in ligand design and has enabled access to rich coordination chemistry. Alkynes and azides are available from commercial suppliers or are readily synthetically accessible from cheap starting materials. Alkyne reagents can be accessed through reliable and robust Sonogashira coupling protocols, however, *in situ* routes have been developed from aldehyde precursors through use of the Bestmann-Ohira reagent.[16, 17] Azides are also easily accessible from amine precursors via a diazonium salt. Convenient one-pot routes to 1,2,3-triazoles in which the azide is formed *in situ* from the corresponding

alkylhalide and sodium azide,[18, 19] or from an arylamine treated with *tert*-butylnitride and trimethylsilylazide have emerged.[20]

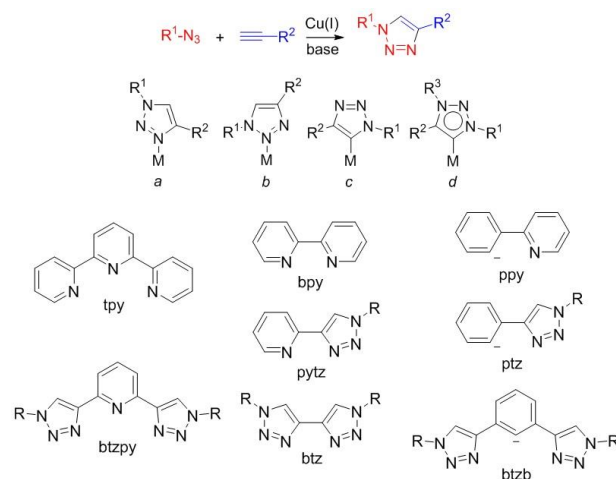


Figure 1. CuAAC reaction for formation of 1,4-disubstituted-1,2,3-triazoles and possible coordination modes of triazole-based ligand (top). Structures and naming of commonly occurring pyridine- and triazole-based ligand motifs appearing in this review (bottom).

For use as a ligand, 1,4-disubstituted-1,2,3-triazoles most obviously possess two lone-pairs available for coordination to a metal ion at the N(3) and N(2) positions (Figure 1 top, *a* & *b* respectively), the former being more basic. The high functional group tolerance of CuAAC reactions enables other donor moieties to be incorporated in either or both of the substituents at the 1- and 4-positions enabling access to a wide range of chelating ligands. The C-H bond at the 5-position is fairly polarised and therefore also enables

cleavage to yield anionic triazolides (c).[21] Alkylation occurs selectively at the N(3) position to form 1,3,4-trisubstituted-1,2,3-triazolium salts in which the 5-position C-H group becomes further activated and acidic enabling access to abnormal mesoionic N-heterocyclic carbene ligands (d).[22]

A number of reviews have appeared on the synthesis and utilisation of the 1,2,3-triazole moiety[23-31] including its coordination[32-34] and organometallic chemistry.[35] In this review we focus on the rich photophysics and photochemistry that has arisen through the use of 1,2,3-triazole-containing ligands. We pay particular attention to complexes of d^6 metal ions such as Re(I), Ru(II), Fe(II), Os(II), Ir(III) containing oligopyridyl ligand analogues (Figure 1 bottom) but also include work on luminescent Pd(II), Pt(II), coinage metal and lanthanide complexes. Throughout the course of the review we will use the ligand shorthand nomenclature given in Figure 1 occasionally using an appended superscript to denote the identity of triazole substituents, R (e.g. pytz^{Ph}).

2. Photophysical properties of d^6 metal triazole-based complexes

It is instructive to first summarise some key aspects of the electronic structure and photophysical properties of metal complexes taking the archetypal d^6 complex $[\text{Ru}(\text{bpy})_3]^{2+}$ as an illustrative example. The highest occupied molecular orbitals (HOMOs) are of predominantly metal d -orbital character (Figure 2a) whilst the lowest unoccupied molecular orbitals (LUMOs) are typically of ligand π^* character. The excited states and transitions for these complexes are often depicted using a Jablonski diagram (Figure 2b). The traditional Jablonski diagram generally assumes a largely isostructural set of ground and excited states and does not take into account changes in the geometry of the complex. It is therefore often more intuitive to describe these states in terms of their potential energy surfaces especially where photochemical reactivity comes into play (Figure 2c).

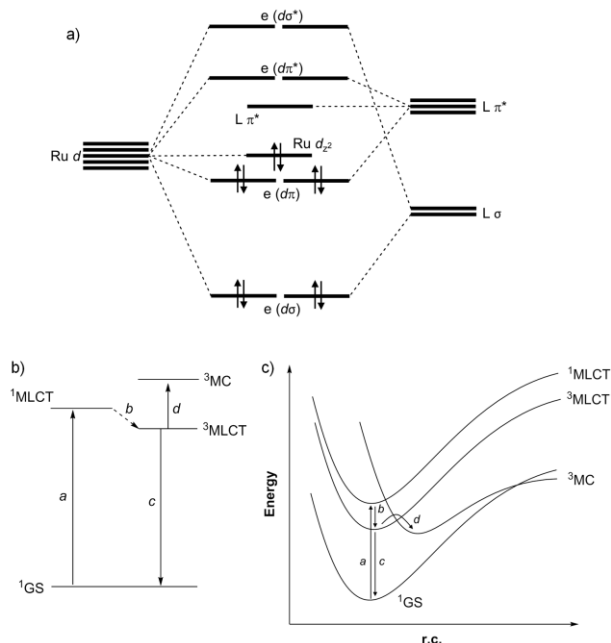


Figure 2. Simplified molecular orbital energy diagram (a), qualitative Jablonski diagram (b) and potential energy surface diagram (c) for ground and excited states for a $[\text{Ru}(\text{bpy})_3]^{2+}$ -type complex.

The lower energy excitation features of the optical absorption spectra are dominated by singlet metal-to-ligand charge-transfer ($^1\text{MLCT}$) character (Figure 2, process a). Intersystem crossing then yields the triplet $^3\text{MLCT}$ state (process b) from which luminescence typical for this class of

complexes derives (process c). Due to the strong spin-orbit coupling associated with the heavy metal centre direct spin-forbidden transitions from the ground state to the $^3\text{MLCT}$ state can commonly be observed at much lower intensity and longer wavelength than the more intense $^1\text{MLCT}$ bands. The $^3\text{MLCT}$ state can also undergo non-radiative deactivation through thermal population of triplet metal-centred (^3MC) states (process d). Characterised by population of a $d\sigma^*$ orbital this involves weakening and elongation of metal-ligand bonds with rapid relaxation to the ground state but can also result in isomerisation and/or ligand loss reactions. As a generalisation, this description of the photophysical processes occurring within ruthenium(II) complexes can be broadly extended to d^6 complexes of rhenium(I) and iridium(III) as well as square-planar d^8 complexes of platinum(II) and palladium(II). Specific differences are discussed where they arise.

2.1 Rhenium(I) complexes

Rhenium(I) tricarbonyl complexes represent a particularly unusual example of metal carbonyls which are emissive in aerated fluid solution. Efforts have principally focused on α,α' -diimine-containing complexes of the type $\text{fac-}[\text{Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3(\text{X})]^{0/+}$, where the diimine ligand $\text{N}^{\wedge}\text{N}$ is commonly 2,2'-bipyridine, 1,10-phenanthroline or derivatives thereof and X is either a halide or neutral N-donor ligand e.g. pyridine. Typically, complexes such as the archetypal $\text{fac-}[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ exhibit a HOMO dominated by a Re $5d$ -orbital (with additional carbonyl π^* contributions as well as p-orbital contributions where X is a halide e.g. Cl or Br) and a diimine π^* -based LUMO. Thus, the lowest energy emissive excited state is of $^3\text{MLCT}$ character. The photophysical properties of analogous Re(I) complexes can be significantly tuned through modification of the structure of the diimine ligand thereby modulating the energy of the LUMO. An additional strong dependence on the identity of the axially coordinated ligand, X, is also observed which varies the energy of the HOMO.

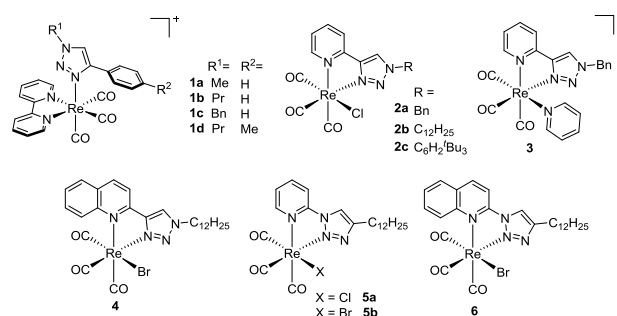


Figure 3. Structure of Re(I) triazole-based complexes.

Table 1. Photophysical data for selected rhenium(I) triazole-based complexes.

Complex	$\lambda_{\text{max}}^{\text{em}} / \text{nm}$	$\phi / 10^{-2}$
1a	543 ^a	not recorded
2a	538 ^b	0.33
2b	522 ^b	0.10
3	496 ^b	3.10
4	582 ^c	0.56
5a	569 ^b	0.19
5b	564 ^b	0.17
6	617 ^b	0.06
$[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$	633 ^b	0.27

a dichloromethane; b acetonitrile; c 98:2 water/DMSO

This synthetic diversity has been exploited by Elliott and co-workers in the preparation of a series of $\text{fac-}[\text{Re}(\text{bpy})(\text{CO})_3(\text{L})]^+$ complexes containing a range of axially coordinated 1,2,3-triazole ligands, L (Figure 3).[19] Complexes **1a-1d** were found to be emissive in aerated dichloromethane

solutions at room temperature, with **1a** displaying an emission maximum of 543 nm and a luminescence lifetime of 482 ns. By contrast, emission from the parent complex $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ measured under identical conditions is reported at 612 nm in dichloromethane, highlighting that replacement of the π -donating chloride with a triazole results in stabilisation of the metal-based HOMO with respect to the LUMO. An emission maximum of 549 nm ($\tau = 466$ ns) for the analogous complex $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ indicates that the 1,2,3-triazole moiety in the axial position has only limited influence on the photophysical properties.

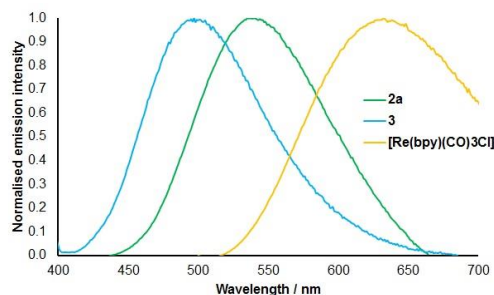


Figure 4. Representative emission spectra for complexes **2a**, **3** and $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ in acetonitrile solutions.

1,2,3-Triazoles have also been extensively utilised within bidentate chelating ligands, the most widely investigated of which are based on 4-(pyrid-2-yl)-1,2,3-triazole (pytz) (Figure 3). Obata *et al.* first reported rhenium(I) coordination complexes of pytz with *fac*- $[\text{Re}(\text{pytz}^{\text{Bn}})(\text{CO})_3\text{Cl}]$ (**2a**) displaying an electronic absorption band with a maximum at 333 nm, slightly higher in energy than that observed for the bpy analogue (371 nm).[36] TD-DFT calculations reveal these electronic transitions to be of HOMO-1 \rightarrow LUMO $^1\text{MLCT}$ character. The LUMO of **2a** is found to be of π^* character, distributed primarily over the pyridyl ring of the pytz^{Bn} ligand and is significantly destabilised relative to that of bpy. This results in a large blue-shift in the emission from **2a** (λ_{max} of 538 nm, $\phi = 3.3 \times 10^{-3}$ in deaerated acetonitrile, $\tau_{77\text{K}} = 8.90$ μs) compared to that for *fac*- $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ ($\lambda_{\text{max}} = 633$ nm, $\phi = 2.7 \times 10^{-3}$, $\tau_{77\text{K}} = 3.17$ μs) (Figure 4). Replacement of the halide ligand by a neutral pyridine donor in **3** results in a blue-shift in emission of 42 nm over that of **2a** with a ten-fold increase in quantum yield.[37]

Polcar *et al.* noted that the replacement of the pyridyl moiety in the pytz framework with quinolinyl (**4**, Figure 3 & Table 1) leads to a red-shift in the emission maximum through stabilisation of the ligand-centred LUMO.[38] Furthermore, the use of inverted 1-(pyrid-2-yl)- and 1-(quinolin-2-yl)-1,2,3-triazole ligands, in which coordination to rhenium occurs through the less basic N(2) atom (**5a** & **6**), results in a further red-shift in the phosphorescence maxima.[38] Similar results have been obtained by Crowley and co-workers who showed that emission from complexes of the regular pytz framework were more sensitive to the coordinating solvents and have faster rates of non-radiative decay over their inverse-pytz analogues.[39] These complexes were shown to be effective photocatalysts for CO_2 reduction with the sterically encumbered **2c** showing a high level of catalytic stability.[40]

Use of the pytz ligand motif has been expanded upon by other workers including the groups of Crowley and Benoist.[41, 42] These groups reported spectroscopic properties of Re(I) tricarbonyl complexes featuring pytz ligands substituted at the 1-position of the triazole ring which generally results in the observation that there is little effect upon the photophysical properties indicating little electronic communication through the triazole ring.

Attachment of a triphenylamine (TPA) moiety to the 5-position of the pyridyl ring in **7** (Figure 5), on the other hand, is observed to lead to a shift in both electronic absorption and emission to lower energy compared to those of the unsubstituted parent complex.[43] Indeed, the lowest excited state in this complex is observed to be of ILCT character involving electron transfer from TPA to pytz-based π^* orbitals. The change in charge transfer character from MLCT as is typically observed in the other Re pytz complexes results in a slight increase in electron density at the metal centre, as confirmed through TRIR spectroscopy which reveals a small negative shift in carbonyl stretching frequencies upon photo-excitation.

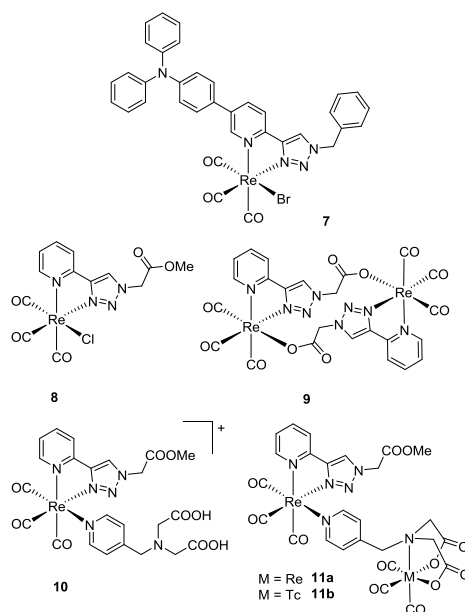


Figure 5. Structures of further rhenium(I) triazole-based complexes.

Boulay *et al.* have shown that simple molecular dimers can be attained when the substituent at the 1-position of the triazole of a coordinated pytz contains carboxyl functionality (Figure 5).[44] The anionic carboxyl terminus readily functions as the axial ligand at an adjacent Re(I) centre, resulting in a luminescent dimer (**9**) whose wavelength of emission is unchanged from the mononuclear parent ester analogue (**8**) but where the quantum yield of phosphorescence is expectedly almost double.

Crowley and co-workers have assembled several Pd(II)-based metallo-supramolecular cages with an appended emissive pyridyltriazole-containing Re(I)-based luminophore analogous to **2a** on the outer or *exo* domain of the molecular cage.[45] This design strategy therefore not only proves to be a successful way in which to access luminescent supramolecular cages but also opens up the possibilities of investigating the biological properties of these architectures through luminescence microscopy or even applying the cages for photocatalysis.

Re(I) tricarbonyl complexes lend themselves to use as biological imaging agents owing to their long-lived phosphorescence, biological stability, low toxicity and the aforementioned ease in which triazole-containing ligands can be functionalised.[8] Several reports, most notably those from the group of Polcar, have made use of the pytz architecture and its close structural analogues in the design of Re(I) complexes towards multi-modal biological imaging agents. These include complexes bearing amides, [46] hexanoylglutamine,[47] short peptides,[48] sugars,[49] azidoalkyl[50] and alkyl moieties appended to the triazole ring.[51] Interestingly, in the case of the latter, the long alkyl chain leads to increased emission intensity in aqueous solutions

due to folding of the chain around the rhenium core providing protection from solvent related quenching interactions.

Complexes of Re(I) are of interest in the field of radiochemistry owing not only to the radioactive isotopes of Re itself ($^{186/188}\text{Re}$) but also to the fact that Re(I) is an excellent mimic of the group 7 congener $^{99\text{m}}\text{Tc}$. Derivatisation of the mononuclear complex **10** (Figure 5) to yield the bimetallic complexes **11a** or **11b** enables access to potentially dual mode medical diagnostic agents through optical $^3\text{MLCT}$ -based emission and γ -ray emission from decay of the $^{99\text{m}}\text{Tc}$ nucleus.[52]

2.2 Iridium(III) Complexes

Luminescent complexes of iridium(III) have been of intense interest in the literature due to their potential application as phosphorescent dopants in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs) and electronic display devices. Of prime importance is the fine tuning of the emission wavelength and hence perceived colour. The control of these properties through modification of ligand structure is therefore of key importance. Thus, the versatility and wide scope of CuAAC chemistry has generated considerable activity in this area.

The archetypal complexes are neutral triscyclometalated complexes such as $[\text{Ir}(\text{ppy})_3]$ (**12**, $\text{ppyH} = 2$ -phenylpyridine, Figure 6) and biscyclometalated complexes of the form $[\text{Ir}(\text{ppy})_2(\text{L}^{\wedge}\text{L}')^{+0}]$ (where $\text{L}^{\wedge}\text{L}'$ is an neutral ancillary ligand such as bpy (**13**) yielding cationic complexes or an anionic ancillary ligand which gives charge neutral complexes). The HOMO of both of these archetypal complex architectures has a large Ir d-orbital contribution but also significant π -aryl donor character. In triscyclometalated complexes the LUMO is localised on the N-donor π -system. In the biscyclometalated systems the LUMO is either located on the cyclometalated ligand N-donor ring or on the ancillary ligand depending on the relative energies of the π^* orbitals of these ligands. Thus, depending on the exact nature of the ligands, emission derives from $^3\text{MLCT}/^3\text{LLCT}$ or $^3\text{MLCT}/^3\text{ILCT}$ states.

Clearly 1,2,3-triazoles can be incorporated into both the cyclometalated or ancillary ligands (or both). The versatility and wide substrate scope of the CuAAC reaction lends itself to the efficient synthesis of a wide range of cyclometalated ligand precursors with a range of aryl substituents. The CuAAC methodology thus enables a facile route to the optoelectronic tuning of the emissive properties of iridium(III) phosphorescent complexes. Cyclometalation of aryl-1,2,3-triazoles was first demonstrated by Schubert and co-workers who reported a series of complexes **14** to **17** (Figure 6).[53] The bpy complex **14** is brightly luminescent ($\lambda_{\text{max}} = 560$ nm, $\phi = 0.45$), more so than its ppy analogue **13** possibly due to the steric shielding of the complex by the large decyl substituents of the triazole rings. Emission is also blue-shifted through perturbation of the bpy-centred LUMO to higher energy. The acetylacetonate complex **16** is only weakly emissive.

The groups of De Cola[54] and Zysman-Colman[55] prepared and investigated a series of complexes based on 4-(2,4-difluorophenyl)-1,2,3-triazole-based ligand precursors. Stabilisation of the Ir(d)-aryl(π) HOMO due to the electron-withdrawing fluorine atoms in complexes **18** and **19** results in emission bands significantly shifted towards the blue region of the visible spectrum compared to that of the non-fluorinated analogue **21** (Figure 7). Additional destabilisation of the LUMO through the inclusion of *t*-butyl substituents onto the bpy ancillary ligand in complexes **20** and **22** leads to sky-blue phosphorescence.[55] Incorporation of π -donating $-\text{NMe}_2$ substituents on to the ancillary ligand in **23** results in a further

slight blue-shift in the emission maximum relative to **20**. Complexes **18** and **20** to **22** have been shown to exhibit electrochemiluminescence through annihilation of electrochemically generated oxidised and reduced radicals of the complexes.[56]

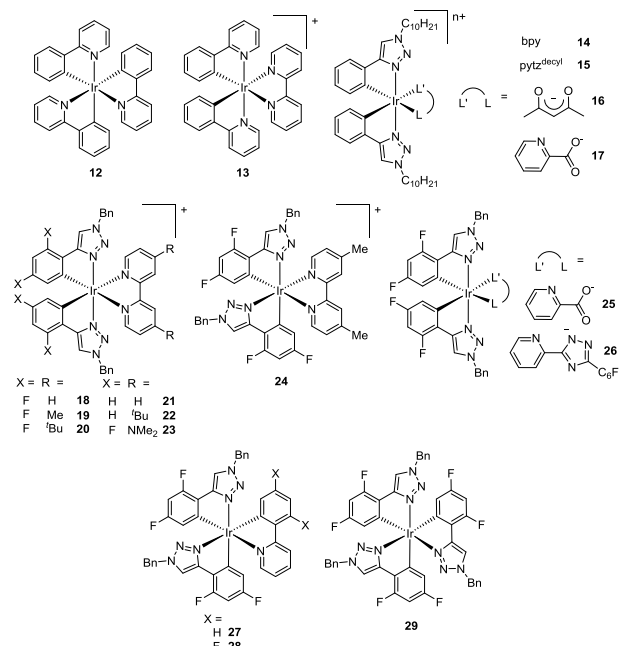


Figure 6. Structures of iridium(III) complexes containing cyclometalated pyridine- and 1,2,3-triazole-based ligands.

Table 2. Summarised emission wavelength data for iridium(III) triazole-based complexes (quantum yield in parentheses).

Complex	$\lambda_{\text{max}}^{\text{em}} / \text{nm} (\phi)$	Complex	$\lambda_{\text{max}}^{\text{em}} / \text{nm} (\phi)$
12	530 (0.40) ^a	32	478, 506 (0.02) ^b
13	580 (0.29) ^a	33	455, 484 (0.02) ^b
14	560 (0.45) ^a	34	600, 635 (0.09) ^b
15	495 (0.29) ^a	35	476, 508 (0.82) ^d
16	435 (0.02) ^a	36	454, 483 (0.28) ^d
17	527 (0.11) ^a	37	532, 568 (0.04) ^d
18	514 (0.73) ^b	38	485 (0.002) ^b
19	497 (0.81) ^b	39	452 (0.0005) ^b
20	498 (0.80) ^b	40	487 (0.003) ^b
21	580 (0.25) ^b	41	461 (0.0003) ^b
22	575 (0.35) ^b	42	495 (0.027)
23	495 (0.47) ^b	43	not observed
24	512 (0.77) ^b	44	500 (0.002) ^e
25	498 (0.012) ^a	45	464, 485 (0.003) ^e
26	440, 462 (0.05) ^a	46	492 (0.007) ^e
27	480, 510 (0.76) ^a	47	493 (0.003) ^e
28	465, 489 (0.50) ^a	48	505 (0.015) ^e
29	392, 418 (-) ^c	49	460, 489 (0.32) ^a
30	477, 507 (0.21) ^a	50	457, 487 (0.31) ^a
31	452, 483 (0.22) ^a	51	458, 487 (0.27) ^a

^a deaerated dichloromethane; ^b deaerated acetonitrile; ^c 77K butyronitrile glass; ^d aerated dichloromethane; ^e deaerated THF

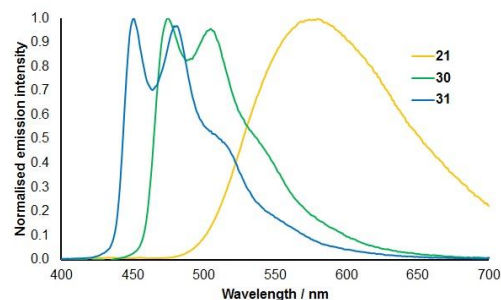


Figure 7. Representative emission spectra for complexes **21**, **30** and **31** in acetonitrile.

The formation of biscyclometalated complexes is usually regioselective in which the metalated aryl rings are *cis* to one another whilst the neutral N-donor rings of the same ligands adopt a mutually *trans* arrangement. Through careful control of reaction temperatures De Cola and co-workers were able to isolate N,N-*cis* and -*trans* isomeric complexes **24** and **19** respectively.[54] **24** was found to exhibit a slightly red-shifted emission spectrum compared to **19** but with comparable quantum yield. When incorporated into polymer light-emitting diode and LEC devices **24** was found to yield greater luminance. The neutral picolinate complex **25** exhibits strongly solvatochromic emission (475 nm in toluene to 534 nm in dimethylformamide) due to the large $^3\text{MLCT}/^3\text{LLCT}$ contributions to the emissive state. The 1,2,4-triazolate complex **26** on the other hand shows true-blue emission with much greater $^3\text{MLCT}/^3\text{ILCT}$ character.

Biscyclometalated complexes have also been incorporated into mesoporous silica materials through templated synthesis.[57] Carbazole-appended analogues of **26** bearing 1,2,4-triazolate ancillary ligands have been used to prepare blue- and green-emitting solution processed OLEDs.[58] When bis[(4-methoxyphenyl)imino]acenaphthene is used as an ancillary ligand biscyclometalated phenyltriazole complexes exhibit panchromatic absorption extending as far as 800 nm.[59] Biscyclometalated aryltriazole iridium(III) complexes have recently been investigated for their use as photosensitisers in DSSC devices achieving some of the highest efficiencies for iridium(III) based dyes relative to benchmark complexes.[17]

Triscyclometalated complexes containing aryltriazole ligands have also been prepared. The heteroleptic complexes **27** and **28** containing a third cyclometalated arylpyridine ligand are both highly luminescent with good quantum yield.[60] The homoleptic complex **29** shows no room temperature emission but exhibits deep blue emission at 77 K. This is presumably a consequence of the high energy of the triazole-centre $^3\text{MLCT}$ state and facile ^3MC population as observed in pyrazole based analogues.[61, 62]

The 1,2,3-triazole ring has also been incorporated into the ancillary ligand of biscyclometalated iridium(III) complexes.[53, 63, 64] In complexes containing pytz-based ancillary ligands such as **30** and **31** (Figure 8) emission spectra exhibit vibronic structure rather than a broad featureless band as observed for bpy-containing analogues. [53, 65, 66] This behaviour is indicative of a large amount of C^N-based intraligand charge transfer (ILCT) in the emissive state. Thus, changing one pyridine in the bpy ligand in $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ for a triazole donor results in the switching of the emissive state from $^3\text{MLCT}/^3\text{LLCT}$ to $^3\text{MLCT}/^3\text{ILCT}$ character. These complexes and analogues of them have been shown to be efficient chemiluminescence agents[67, 68], used in LECs[69] and have been used as live cell luminescence imaging agents.[70] Analogues of **30** with a cyclodextrin appended to the triazole N(1) position[71] show enhanced luminescence and have been utilised as photosensitisers for solar hydrogen production in non-covalent supramolecular assemblies with methylviologen and cyclodextrin derivatised platinum nanoparticles.[72]

Donnelly and co-workers have investigated the use of the more flexible picolyltriazole ancillary ligand containing a methylene spacer between the pyridine and triazole donors which forces coordination through the triazole N(2) position.[73] The ppy and dfppy complexes **32** and **33** exhibit very similar emission spectra to **30** and **31** suggesting that emission derives from the same $^3\text{MLCT}/^3\text{ILCT}$ state. Complex **34** exhibits a significantly red-shifted emission band relative to its ppy and dfppy analogues stemming from the reduced energy of the LUMO associated with the quinoline-based cyclometalated ligands.

The group of Zysman-Colman[74] as well as our own group[75] have studied complexes containing the

symmetrical btz ancillary ligand (**35** to **37**). Emission spectra for these complexes are very similar to their pytz analogues. Therefore in cyclometalated arylpyridine complexes the emissive excited states are independent of the pytz or btz ancillary ligands, a conclusion supported by computational calculations.

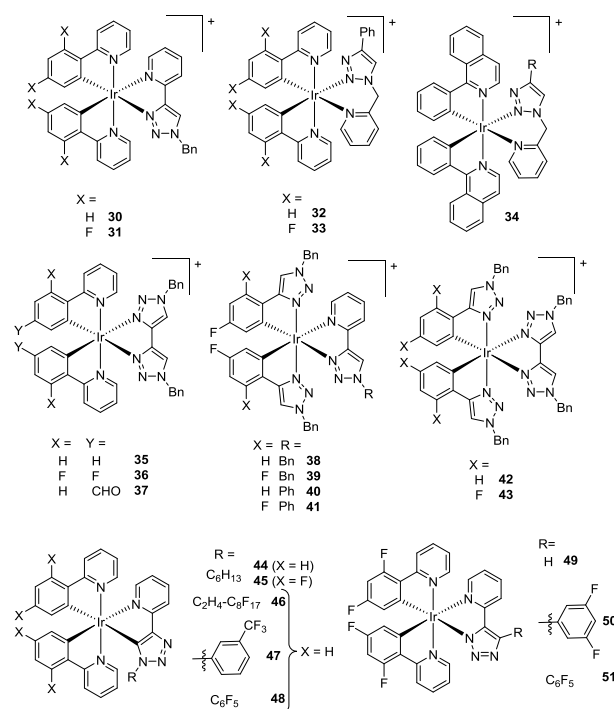


Figure 8. Structures of biscyclometalated iridium(III) complexes with 1,2,3-triazole-based ancillary ligands.

Heteroleptic biscyclometalated complexes in which triazole moieties have been incorporated into both cyclometalated and ancillary ligands have been reported.[76] Complexes **38** to **41** exhibit unstructured emission bands between 450 and 490 nm suggesting a switch back to $^3\text{MLCT}/^3\text{LLCT}$ excited state character with the excited electron localised on the pytz ligand.[77] However, all four complexes have quantum yields below 1 % ascribed to thermal population of non-radiative ^3MC states from emissive $^3\text{MLCT}/^3\text{LLCT}$ states.

The group of Zysman-Colman have reported complexes **42** and **43** containing four triazole rings.[74] **42** is weakly luminescent whilst no emission is observed for **43** likely through facile population of non-radiative ^3MC states. Indeed the complex is not photostable and decomposes through expulsion of the btz ligand.

Swager and co-workers have been able to isolate the triazole complexes **44** to **48** through transmetalation from the copper(I) triazolate formed during the CuAAC reaction.[78] The complexes exhibit emission bands that are similarly positioned to those of pytz complexes **30** and **31** but in which the vibronic coupling is much less resolved indicating a greater $^3\text{LLCT}$ contribution to the emissive excited states.

De Cola and co-workers have reported the neutral triazole complexes **49** to **51** which have very similar emission spectra to that of **31** and in which there is a negligible influence from the substituent on the triazole ring.[79]

2.3 Ruthenium(II) complexes

The ubiquity of bpy and tpy-based ruthenium(II) complexes in the area of photophysics and photochemistry has inevitably led to significant interest in the investigation of their analogous triazole-containing complexes. The homoleptic pytz

complex **52** (Figure 9) is prepared as a mixture of its *fac* and *mer* isomers due to the asymmetry of the ligand. The reduction potential is cathodically shifted by approximately 0.5 V compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ reflecting the higher energy LUMO associated with the pytz-based ligand over that of bpy.[80] In the series of complexes **53** to **55** the $^1\text{MLCT}$ absorption and $^3\text{MLCT}$ emission bands (77 K) are observed to blue-shift on increasing pytz content (Table 3).[81] This is due to the lesser π -acceptor ability of pytz over bpy resulting in increased electron density on the bpy ligands with consequential destabilisation of the LUMO relative to the HOMO. This also results in a quenching of emission presumably due to ^3MC states becoming more accessible. Even at 77 K no emission is observed from the homoleptic complex **55**.

Through anion recognition interactions with the polarised triazole C-H bond the complex $[\text{Ru}(\text{phen})_2(\text{pytz}^{\text{Me}})]^{2+}$ and its trinuclear analogue with a cyanuric acid tethered core have been shown to be selective sensors for phosphate ions.[82, 83] The pytz-based complex **56** has been evaluated as a sensitiser for DSSC devices. A high power conversion efficiency of 7.8 % was achieved given the comparatively blue-shifted absorption profile with respect to other known bpy-based dyes.[84] Homoleptic Ru(II) tris-pytz complexes have been shown to have antimicrobial activity against MRSA.[85] Analogues of **53** in which *p*-nitrophenylethynyl and *p*-alkoxyphenylethynyl substituents are introduced at the 5-position of the pytz pyridine ring are luminescent in deaerated dichloromethane solutions. The inclusion of the nitro-substituents are found to red-shift and enhance emission intensity over the alkoxy substituted complex through stabilisation of the ligand π^* -based LUMO.[86, 87] Complexes of this type have been grafted into light-harvesting polymers[88] for use as sensitisers for photocatalytic hydrogen evolution.[89] Despite the pytz moiety appearing to lead to quenched emission, complexes such as **57** containing a fluorene group at the triazole N(1) position are emissive in dichloromethane solutions at room temperature. It is possible that this enhancement occurs through an antenna effect sensitised by the fluorene fluorophore.[90]

Complexes of symmetrical btz-based ligands have been reported.[80, 91] For the series of complexes **58** to **60** there is again a blue-shift in $^1\text{MLCT}$ absorption bands as btz content increases, significantly so for the final replacement of bpy by btz in **60** reflecting the much higher energy of the btz ligand LUMO to that of bpy (by ~ 1 eV).[92] It is noteworthy that DFT calculations on this series suggest that whilst the T_1 states of **58** and **59** are of $^3\text{MLCT}$ character, the lowest energy triplet state of **60** is ^3MC in nature. One- and two-electron reduced forms of analogues of **53** and **58** exhibit broad absorption in the near-infrared region of the spectrum through excitation of bpy-centred radical electrons.[93]

Complexes of the triazole-containing analogue of the tpy ligand framework, btzpy, have also been investigated.[94] The $^1\text{MLCT}$ absorption band of the heteroleptic complex **61** is blue-shifted by ~ 40 nm relative to that of $[\text{Ru}(\text{tpy})_2]^{2+}$ underlining the LUMO-destabilising effect of the triazole ring ligand.[95] Mirroring this the 77 K emission spectrum is also shifted to higher energy reflecting the destabilisation of the $^3\text{MLCT}$ state. The homoleptic complex **62** exhibits a $^1\text{MLCT}$ maximum at 394 nm and is non-emissive at 77 K. A metallosupramolecular polymer containing $[\text{Ru}(\text{btzpy})_2]^{2+}$ -like units spaced by a diethynylphenylene π -conjugated unit is however emissive ($\lambda_{\text{max}} = 700$ nm).[96] The switching on of emission likely stems from stabilisation of the $^3\text{MLCT}$ states through conjugation with the spacer with possible equilibrium with $^3\pi\text{-}\pi^*$ states associated with the linker.

Cyclometalated complexes bearing aryltriazole based ligands (Figure 10) have been prepared and characterised.[97] The inclusion of the anionic aryl donor in the ptz complex **63**

results in destabilisation of the HOMO with respect to that of its pytz analogue which has both metallic and aryl π -character. As a result the absorption profile is red shifted relative to that of its isoelectronic analogue **53** and extends beyond 600 nm. A related dinuclear complex **64** has been prepared by reaction of $[\text{Ru}(\text{bpy})_2(\text{dtzbp})]^{2+}$ (dtzbp = 5,5'-bis(1-butyl-1,2,3-triazol-4-yl)-2,2'-bipyridyl) with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. [98] The redox asymmetric product contains RuN_5C and RuN_6 coordination domains for which two oxidation waves are observed at +0.79 and +1.28 V (vs Ag/AgCl) respectively. Upon one-electron oxidation a metal-to-metal charge transfer band can be seen at 1300 nm which then disappears upon removal of a second electron.

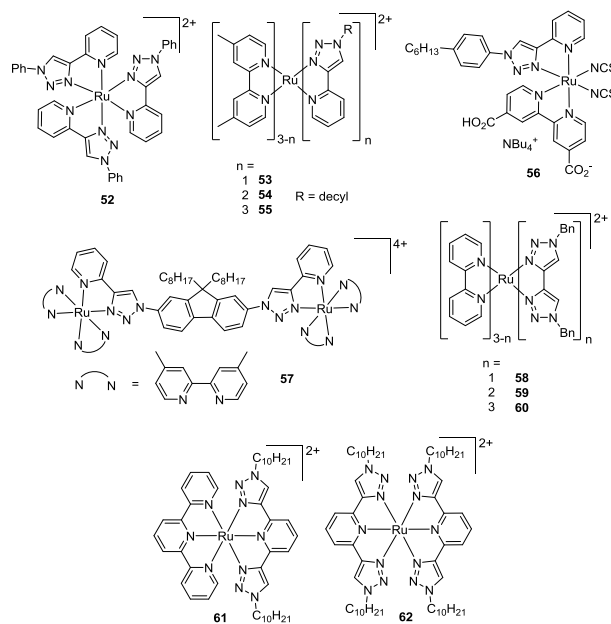


Figure 9. Structures of ruthenium(II) complexes bearing pyridyltriazole, bitriazolyl and bistriazolylpyridine ligands.

Table 3. Summarised photophysical data for Ru(II) triazole-based complexes (wavelengths of lowest energy $^1\text{MLCT}$ absorption maxima and $^3\text{MLCT}$ emission maxima).

Complex	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}}^{\text{max}} / \text{nm}$
$[\text{Ru}(\text{bpy})_3]^{2+}$	452 ^a	610 ^a
52		
53	446 ^b	575 ^c
54	392 ^b	563 ^c
55	384 ^b	not observed
58	446 ^b	565, 610 ^d
59	425 ^b	544, 585 ^d
60	303 ^b	not observed
$[\text{Ru}(\text{tpy})_2]^{2+}$	474 ^a	604 ^c
61	432 ^a	583 ^c
62	394 ^a	not observed
$[\text{Ru}(\text{tpy})(\text{btz})]^{+}$	541 ^a	not observed
73	464 ^a	648 ^a
74	520 ^a	730 ^a
75	480 ^a	650 ^a
76	463 ^a	643 ^c
79	473 ^a	694 ^e

^a acetonitrile, RT; ^b dichloromethane, RT; ^c 77 K *n*-butyronitrile; ^d 77 K 4:1 EtOH:MeOH; ^e deaerated EtOH/MeOH (4:1) at RT

Complexes containing the tridentate cyclometalated ligand framework btzb (Figure 10) have also been investigated as analogues of the better known 1,3-dipyridylbenzene (dpb) complexes.[99] Complexes **65** to **67** are characterised by Ru(II/III)-based oxidations between +0.53 and +0.59 V (vs Ag/AgCl) which are shifted towards more negative potential relative to that of $[\text{Ru}(\text{tpy})_2]^{2+}$ (+1.23 V) due to mixing of

significant π -character of the central anionic aryl ring in the HOMO.[97, 100] Complexes **68** to **70** of this type have also been investigated by Schubert and co-workers for their use as light-harvesting photosensitisers.[101-103] Inclusion of carboxylate moieties in the three 4-pyridyl positions of the tpy ligand gives rise to significant stabilisation of the ligand-centred LUMO such that optical absorption bands extend to 700 nm with high molar extinction coefficients in the visible region (up to 20,000 dm³ mol⁻¹ cm⁻¹).[102] When **68** is utilised in DSSC devices high solar energy conversion efficiencies of up to 4.5 % (compared to 5.2 % for cells prepared using “black dye”) were obtained.[104]

Treatment of **65** with Ag⁺ was found to result in reductive C-C coupling to form **71** in a similar manner to that observed for ruthenium(II) dpb complexes by Sauvage *et al.*[105-107] The UV-visible absorption spectrum of the dinuclear complex is very similar to that of its mononuclear precursor suggesting that in the ground state there is little communication between the two metal centres. An analogous dinuclear complex incorporating a pyrene linker (**72**) has also been reported.[108] Upon one-electron oxidation of **71** a new ligand-to-metal charge transfer band is observed around 730 nm along with an intervalence charge transfer (IVCT) transition observed in the near-IR region of the spectrum (1000 – 2700 nm). Similar IVCT behaviour is observed for **72**. Upon removal of a second electron from **71** and **72** these IVCT bands are observed to disappear.

The bidentate triazolyldene complex **73** has been reported which exhibits a slightly destabilised HOMO relative to that of [Ru(bpy)₃]²⁺ due to the slight anionic charge on the abnormal carbene ligand donor C-atom.[109] The resultant narrowing of the HOMO – LUMO gap results in a slight red-shift in the ³MLCT-based emission band, appearing at 648 nm.

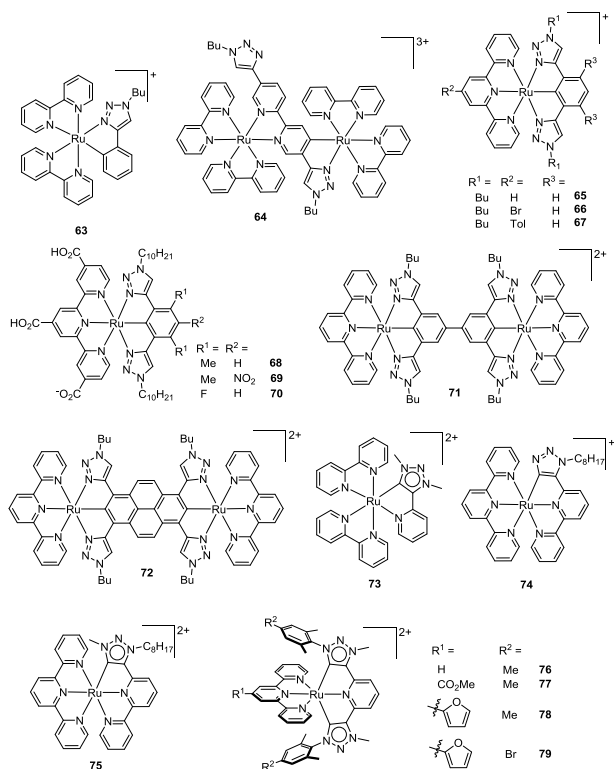


Figure 10. Structures of triazole-based cyclometalated and abnormal N-heterocyclic carbene complexes.

Through use of ruthenium-catalysed alkyne/azide cycloaddition (RuAAC) Sinn *et al.* were able to prepare the ligand 6-(1-octyl-1,2,3-triazol-5-yl)-2,2'-bipyridyl in which tridentate N[^]N[^]N[^] coordination including to the triazole is not possible. Reaction with [Ru(tpy)(NCMe)₃]²⁺ leads to

cyclometalation to form the triazolide complex **74**. [110] The HOMO of **74** has contributions from the metal as well as the triazolide π -system and is destabilised with respect to that of [Ru(tpy)₃]²⁺ such that absorption bands are shifted to lower energy (Table 3). The complex is also emissive through the destabilisation of ³MC states due to the strong σ -donor character of the triazolide. Upon methylation of the N(3) position of the triazolide with iodomethane the mesoionic triazolyldene complex **75** is produced. As a consequence of the overall charge neutrality of the carbene donor, and poor π -donor properties relative to triazolide, the HOMO is stabilised relative to that of **74** and consequently the absorption and emission maxima are shifted to higher energy. Interestingly, successive protonation and deprotonation of **75** can be utilised to reversibly form the carbene with resultant shifting of the ³MLCT emission band between 730 and 648 nm.

Both the 1,5- (*via* RuAAC)[110] and 1,4-disubstitution (*via* CuAAC)[111] regioisomers of btzpy undergo selective methylation of the triazole N(3)-positions to yield bis(triazolium) salt carbene ligand precursors and subsequent access to complexes **76** to **79**. Due to the strong σ -donor character of the triazolyldene donors and the consequential destabilisation of emission-deactivating ³MC states, long lived phosphorescence from terpyridine based ³MLCT states is observed. Indeed, for **79** an excited state lifetime of 7.9 μ s was determined.[111] Through further derivatisation with inclusion of a carboxylate group on the terpyridine ligand and phosphonate groups on the carbene wing-tip aryl rings, DSSC dyes were prepared with stabilised TiO₂ anchoring and power conversion efficiencies of up to 0.2 %, an order of magnitude larger than in the absence of the phosphonate anchors.[112]

2.4 Iron(II) complexes

The exploration of 1,2,3-triazole complexes of Fe(II) has until very recently been rather minimal. Whilst the Fe(II)-pytz coordination motif has predominantly featured within metallosupramolecular assemblies, model homoleptic complexes of the form [Fe(pytz)₃]²⁺ (Figure 11) have also been reported.[113-115] UV-Vis absorption spectra recorded for the low-spin complexes **80** & **81** show a broad absorbance feature between 300-450 nm, assigned to overlapping Fe-to-pyridine ($\lambda_{\text{max}} \approx 425$ nm) and Fe-to-triazole ($\lambda_{\text{max}} \approx 310$ nm) charge transfer transitions. Comparison with the MLCT absorption band of [Fe(bpy)₃]²⁺ ($\lambda_{\text{max}} \approx 530$ nm) indicates a larger HOMO-LUMO energy gap as a consequence of the poorer π -accepting ability of 1,2,3-triazole over pyridine.

The propanol-substituted [Fe(btzpy)₂]²⁺ complex **82** has been reported by Flood and co-workers.[94] The UV-Vis absorption spectrum exhibits an intense feature at 295 nm associated with ligand-based π - π^* transitions, whilst a broad MLCT band is observed at 443 nm, the latter shifted by *ca.* 4500 cm⁻¹ to higher energy with respect to [Fe(tpy)₂]²⁺ ($\lambda_{\text{max}} = 552$ nm) due to destabilisation of the btzpy-localised LUMO.

Use of Fe(II)-centred photosensitisers within solar energy applications is highly desirable although has been met with little success owing to extremely short-lived ³MLCT excited states.[116, 117] As deactivating ³MC states can be destabilised through the incorporation of strong σ -donors within the ligand set, research efforts have considered the use of carbene donors, with both terdentate bis-2,6-(triazolyldene)pyridine[118] (**83**) and bis(1,2,3-triazol-5-ylidene)[119] (**84**) complexes of Fe(II) having been synthesised. In the latter instance Sundström *et al.* have reported a ³MLCT lifetime of 13 ps, significantly elongated with respect to the [Fe(bpy)₃]²⁺ parent complex ($\tau = 130$ fs).[119]

It is additionally noteworthy that bis(1,2,3-triazol-5-ylidene) ligands have been utilised within low-spin complexes of Fe(III). In **85**, the directionality of photoinduced charge transfer is reversed, being of LMCT in nature. Most impressively, the resultant ²LMCT excited states are emissive at room temperature ($\lambda = 600$ nm) with a lifetime of 100 ps.[120]

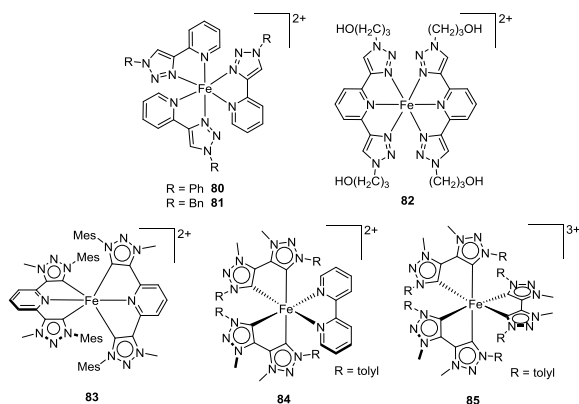


Figure 11. Structures of pytz, btzpy and 1,2,3-triazole-based aNHC complexes of iron.

2.5 Osmium(II) complexes

Examples of osmium(II) complexes bearing 1,2,3-triazole-based ligands are rare. The first reported example was a polymer-tethered complex of the form $[\text{Os}(\text{bpy})_2(\text{pytz})]^{2+}$. When co-polymerised with blue, yellow and red emitting thiazole-based fluorophores, energy transfer between the organic dyes and the complex is observed. A polymer tagged only with the osmium complex was shown to function as a sensitizer for colloidal platinum-mediated hydrogen evolution.[121]

The series of complexes **86** to **88** (Figure 12) have been investigated. Similarly to the photophysical properties exhibited by their ruthenium(II) analogues, increasing btz ligand content leads to a progressive blue-shift in the ¹MLCT and ³MLCT-based absorptions with respect to the absorption profile for $[\text{Os}(\text{bpy})_3]^{2+}$. [122] As before, the shift in the MLCT bands is highly pronounced upon replacement of the final bpy by btz. In contrast to the behaviour observed for the ruthenium analogues the presence of btz in the heteroleptic complexes **86** and **87** does not lead to quenching of emission due to the much larger ligand-field splitting associated with osmium, with emission maxima at 724 and 713 nm respectively. The homoleptic complex **88** is perhaps extremely weakly emissive at room temperature but is brightly phosphorescent at 77 K with emission maxima at 444 and 474 nm. **86** and **87** were utilised in light-emitting electrochemical cell (LEC) devices and shown to yield electroluminescence but gave devices with poor stability.

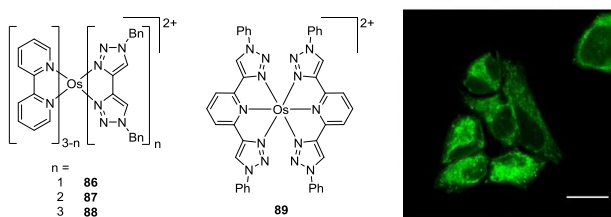


Figure 12. Structures of osmium(II) triazole-based complexes and confocal microscopy image of HeLa cells stained with complex **89**.

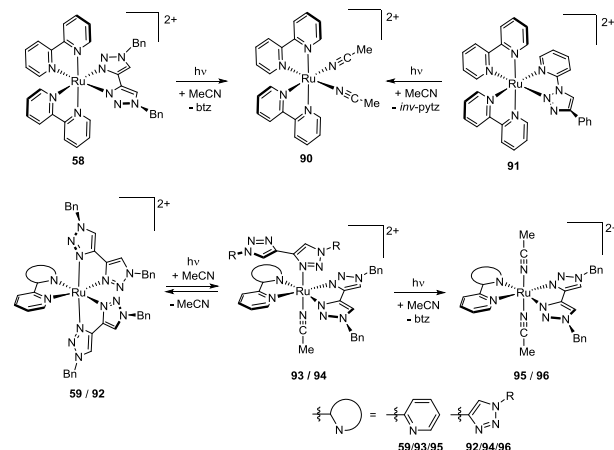
The bistridentate complex **89** has been reported and, unlike its iron(II) and ruthenium(II) analogues, found to be emissive at 595 nm.[123] The emission intensity is strongly affected by the presence of oxygen with a singlet oxygen

quantum yield of 0.57 in acetonitrile solutions. **89** was investigated as a luminescent cellular imaging agent by confocal microscopy and is observed to enter U2OS and HeLa cancer cells with localisation in the mitochondria (Figure 12).

2.6 Photochemistry of 1,2,3-triazole-based d⁶ metal complexes.

As well as enabling the preparation of luminescent complexes 1,2,3-triazole-based ligands have also been shown to allow access to highly novel photochemical reactivity.

Ru(II) complexes of tetradentate tripodal ligands with pyridine and triazole arms have been prepared. Photochemical reactivity in complexes of the form $[\text{Ru}(\text{L})(\text{DMSO})(\text{Cl})]^+$ (where L is a tripodal amine ligand derived from tris(2-pyridylmethyl)amine with 3-*n* pyridyl and *n* triazole arms) can be controlled as a function of triazole content, with a greater number of triazole donors leading to an increase in both the electron density at the metal centre and the strength of the Ru-DMSO bond.[124] Complexes where *n* = 1 and 2 undergo efficient photoinitiated ligand exchange of DMSO for MeCN when irradiated at 396 nm, whereas the rate of photosubstitution is considerably slower when *n* = 3, allowing for the detection of *bis*-solvento DMSO/MeCN and (MeCN)₂ photo-product intermediates by ¹H NMR spectroscopy.[125] Photochemical reactivity has also been reported for $[\text{Ru}(\text{bpy})(\text{L})]^{2+}$ complexes. Whilst steric repulsion leads to photochemistry in the fully pyridyl-containing system (*n* = 0, photochemical quantum yield $\phi_{423} = 2.1 \times 10^{-3}$), successive replacement of pyridyl with triazole donors enhances the rate of photodissociation of an axial arm of the tetradentate ligand and subsequent MeCN coordination. This is most efficient when *n* = 3 with a conversion of 99 % ($\phi_{436} = 0.06$). [126]



Scheme 1. Photochemical reactivity of ruthenium(II) btz complexes in donor solvents.

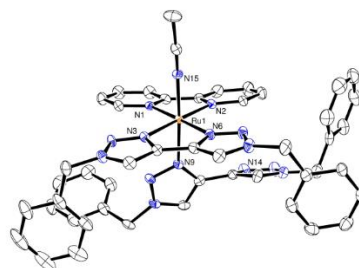


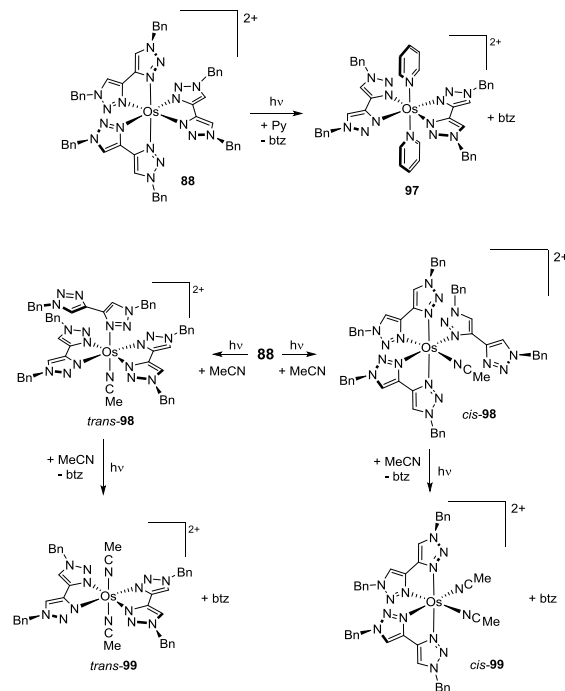
Figure 13. ORTEP plot of the structure of the cation *trans*- $[\text{Ru}(\text{bpy})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ (**93**, ellipsoid at 50 % probability, hydrogen atoms, counterions and solvent removed for clarity).

Complexes of btz have been shown to exhibit photochemical ligand ejection of a btz ligand to yield solvento species. Complexes of the form $[\text{Ru}(\text{N}^{\wedge}\text{N})_2(\text{btz})]^{2+}$ ($\text{N}^{\wedge}\text{N} = \text{bpy}$ (**58**), phen, dmbpy, dmbpy) undergo surprisingly rapid photochemical ligand ejection of btz in acetonitrile to yield *cis*- $[\text{Ru}(\text{bpy})_2(\text{NCMe})_2]^{2+}$ (**90**, Scheme 1 top).[127] Whilst ligand ejection in ruthenium(II) tris-chelate complexes is a well-known phenomenon, in the absence of steric promotion (through incorporation of substituents adjacent to the N-donor atoms of the ejecting ligand to stabilise ^3MC states) this is often a fairly slow process. As was noted for **58** the introduction of the btz ligand results in a destabilisation of the $^3\text{MLCT}$ state compared to that of $[\text{Ru}(\text{bpy})_3]^{2+}$. This destabilisation of the $^3\text{MLCT}$ presumably results in a lower activation barrier to ^3MC population.

The iridium(III) btz complex $[\text{Ir}(\text{dfptz}^{\text{Bn}})_2(\text{btz})]^+$ (**43**) also undergoes photochemical loss of btz presumably via ^3MC state population from a high energy btz-centred $^3\text{MLCT}$ state.[74] This is intriguing as ^3MC states of analogous $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ complexes are assumed to involve elongation of the mutually *trans* Ir-N bonds to the cyclometalated ligands.

Crowley and co-workers have reported ejection of the inverse-pyztz ligand 4-phenyl-1-(pyrid-2-yl)-1,2,3-triazole (*inv*-pyztz) from the complex $[\text{Ru}(\text{bpy})_2(\text{inv-pyztz})]^{2+}$ (**91**).[39] Interestingly, evidence by NMR spectroscopy of a ligand-loss intermediate of the form $[\text{Ru}(\text{bpy})_2(\kappa^1\text{-inv-pyztz})(\text{NCMe})]^{2+}$ was reported. Kirsh-De Mesmaeker and co-workers have investigated complexes of the form $[\text{Ru}(\text{TAP})_2(\text{N}^{\wedge}\text{N})]^{2+}$ ($\text{TAP} = 1,4,5,8\text{-tetraazaphenanthrene}$, $\text{N}^{\wedge}\text{N} = \text{pytz}^{\text{Bn}}$ or btz^{Bn})[128, 129] which in acetonitrile solution both undergo photochemical ligand ejection. The lack of isobestic points in UV-visible absorption spectra indicate either the competitive dissociation of both TAP and triazole-based ligands or the involvement of intermediate species in these processes.[128]

Bis-bitriazolyl complexes $[\text{Ru}(\text{N}^{\wedge}\text{N})(\text{btz})_2]^{2+}$ ($\text{N}^{\wedge}\text{N} = \text{bpy}$ (**59**), pytz (**92**), Scheme 1 bottom) are observed to undergo photochemical ejection of one of the btz ligands.[130] This process proceeds with an extraordinary concomitant ligand rearrangement to yield the complexes *trans*- $[\text{Ru}(\text{N}^{\wedge}\text{N})(\text{btz})(\text{NCMe})_2]^{2+}$ ($\text{N}^{\wedge}\text{N} = \text{bpy}$ [131] (**95**), pytz [132] (**96**)). Even more remarkably this process proceeds with the observation of metastable ligand-loss intermediates *trans*- $[\text{Ru}(\text{N}^{\wedge}\text{N})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ ($\text{N}^{\wedge}\text{N} = \text{bpy}$ (**93**), pytz (**94**)) which in the case of $\text{N}^{\wedge}\text{N} = \text{bpy}$ can be formed near quantitatively within five minutes of irradiation in an NMR tube and has been crystallographically characterised (Figure 13).[131]



Scheme 2. Photochemical reactivity of $[\text{Os}(\text{btz})_3]^{2+}$ (**88**) in pyridine and acetonitrile solutions.

Due to the larger ligand field splitting for osmium(II) complexes relative to their ruthenium(II) analogues, ^3MC population and ligand ejection from complexes of the form $[\text{Os}(\text{N}^{\wedge}\text{N})_3]^{2+}$ has long been considered extremely inefficient or non-existent. However, our group recently reported the unprecedented photochemical ligand ejection for the complex $[\text{Os}(\text{btz})_3]^{2+}$ (**88**).[133] Whilst thermally inaccessible in bpy-containing heteroleptic analogues, the ^3MC states for **88** are evidently readily populated from a high energy btz-centred $^3\text{MLCT}$ state. In pyridine (py) solutions photolysis of **88** yields *trans*- $[\text{Os}(\text{btz})_2(\text{py})_2]^{2+}$ (**97**, Scheme 2) and a similar concomitant rearrangement to coplanarity of the two remaining bidentate btz ligand to that observed for **59**. In acetonitrile solutions photolysis yields both *cis*- and *trans*- $[\text{Os}(\text{btz})_2(\text{NCMe})_2]^{2+}$ (*cis*- and *trans*-**99**) and proceeds with the observation of the ligand-loss intermediates *cis*- and *trans*- $[\text{Os}(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$ (*cis*- and *trans*-**98**).

3. Platinum(II) and palladium(II) complexes.

Coordination of pytz to Pd(II) and Pt(II) was first reported by the group of Sarkar in 2009.[134] $[\text{Pd}(\text{pytz})\text{Cl}_2]$ complexes (Figure 14) generally exhibit two prominent features in their electronic absorption spectra, with bands in the region 270–285 nm being associated with $\pi\text{-}\pi^*$ pytz-localised IL transitions whilst weaker absorbances at lower energy (360–380 nm) are generally assigned to MLCT transitions[135] with a degree of chloride-to-pytz charge transfer contributions.[136] These features are also typical for $[\text{Pt}(\text{pytz})\text{Cl}_2]$ complexes although shifted to higher energy, with CT transitions between 330–340 nm. The lowest energy CT bands recorded for DMF solutions of $[\text{Pt}(\text{pytz}^{\text{Bn}})\text{Cl}_2]$ ($\lambda = 330$ nm) and $[\text{Pt}(\text{bpy})\text{Cl}_2]$ ($\lambda = 389$ nm)[137] highlight the destabilising influence of the triazole upon the ligand based π^* LUMO. Inclusion of electron-withdrawing and -accepting substituents on the triazole ring (**100a-h**, **101a-h**) has negligible impact upon the CT energy, suggestive of minimal contribution to the frontier orbitals.

The synthesis and subsequent coordination of an isomeric analogue of pytz 2-[(4-phenyl-1,2,3-triazol-1-yl)methyl]pyridine (Tz-CH₂-Py) has been reported, with X-Ray crystal structures revealing coordination to Pd(II) and Pt(II) through the triazole N(2) and pyridyl nitrogen positions to give

a 6-membered chelate ring with pseudo square planar geometry.[138] Comparable electronic transitions to those occurring within the pytz complexes are reported, with ¹MLCT absorption bands at 390 and 287 nm recorded for DMF solutions of **102** and **103** respectively. Urankar *et al.* have also reported a homoleptic dicationic complex of Tz-CH₂-Py (**104c**),[139] with the group of Crowley investigating the structural and photophysical properties of further complexes of this type (**104a-g**) in addition to a corresponding homoleptic [Pd(pytz^R)₂]²⁺ family (**105a-g**).[140] The latter series display electronic absorption spectra largely identical to those of the free ligands, with a recurring band at 280 nm assigned to π - π^* transitions localised across the central pytz fragment. An additional weaker band in the region 360-380 nm (**105a-c**) and at 430 nm (**105e**) is assigned with the aid of DFT calculations as being LMCT in nature.

Aside from the pytz motif, 1,2,3-triazoles have also featured within alternative novel chelating ligand systems such as (1-aryl-1,2,3-triazol-4-yl)phosphole.[141] This triazole-phosphole hybrid exhibits different coordination behaviour towards Pd(II) and Pt(II) to form **106** and **107** with P[^]N chelation and bis-monodentate P-donor coordination respectively. These show significant absorption in the visible region, notably different from the π - π^* transitions of the free ligand which are observed at 370 nm.

Phenyltriazole (ptz) complexes of Pt(II) have been prepared, with those bearing a bulky electron-accepting dimesitylboryl group investigated by Wang *et al.* as blue-emitting phosphors.[142] Complexes **108-111** show strongly overlapping LC and MLCT absorption bands and display weak emission at room temperature in 2-Me-THF between 450-500 nm (ϕ = 0.001-0.160). The position of the dimesitylboryl group greatly influences the photophysical characteristics of the resultant complexes. For **109-111** the emission maxima lie between 453 and 474 nm but is shifted to 500 nm when the B(Mes)₂ group is in the *para* position relative to the triazole ring (**108**). The quantum yields are enhanced in frozen solution and in polymethylmethacrylate (PMMA) thin films with **111** giving efficient bright blue-green emission (λ = 464 nm, ϕ = 0.97, 5 wt% in PMMA). Wang and co-workers have further optimised the ligand architecture featuring a trityl-appended ptz cyclometalated ligand and 1,2,4-triazole ancillary (**112**) which offers increased thermal stability, good processability and efficient blue emission.[143] **112** dispersed in PMMA is brightly phosphorescent (λ = 468 nm, ϕ = 0.95, 10 wt% in PMMA) and yields electroluminescent devices with modest external quantum efficiencies (λ = 477 nm, η = 15.9 %). In the absence of bulky substituents analogues of **112** form excimers which give dual emission almost white in colour.

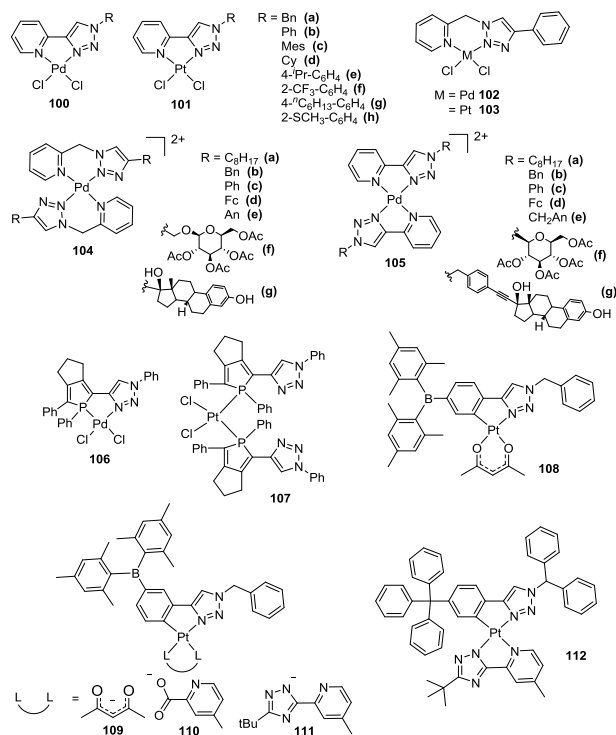


Figure 14. Structures of pytz-derived complexes of Pd(II) and Pt(II) and triazole-phosphole hybrids.

Coordination of btzpy to Pt(II) (Figure 15) has been demonstrated by the groups of Yam[144] and DeCola.[145] Electronic absorption spectra of these complexes contain strong IL π - π^* bands in the region 250-340 nm accompanied by transitions of lesser extinction coefficient between 350-500 nm assigned as being predominantly MLCT in nature. Indeed, for complexes of this type the HOMO is commonly localised on the metal centre with small contributions from the ancillary ligand, whereas the LUMO is mostly pyridine based. Consequently, variation of the alkynyl substituents in **114a-d** can be utilised in the fine tuning of MLCT absorption energy. Consistent with most other N[^]N[^]N Pt(II) chloride complexes, **113** is non-emissive at room temperature. However, owing to the σ -donating alkynyl ligands destabilising luminescence-quenching ³MC states, **114a-d** display weak emission in CH₂Cl₂ solutions (λ = 582-597 nm) at room temperature which is reasonably long-lived at 77 K (1.6-2.2 μ s).

The inclusion of CN⁻ ligands in **115c** and **115d** not only raises the energy of d-d states but also reduces the electron density at the metal centre, facilitating short Pt⁺-Pt contacts and the formation of emissive aggregates. Photoluminescence from thin films of **115c** (λ = 560 nm, τ = 1.67, 0.58 μ s, ϕ = 0.055) and **115d** (λ = 570 nm, τ = 0.09, 0.24 μ s, ϕ = 0.260) at room temperature is assigned to metal-metal-to-ligand charge transfer (MMLCT) within aggregated species.[145] **115a** and **115b** display dual emission at 77 K from both monomeric and aggregated species, with the monomers identified by long-lived structured emission features in the blue-green region (λ = 420, 445, 470 nm, τ = 40 μ s for **115a**; λ = 420, 450, 470 nm, τ = 33 μ s for **115b**). **115a** additionally shows excited state excimeric emission (λ = 685 nm, τ = 15 μ s) whereas **115b** undergoes formation of emissive ground state aggregates (λ = 605 nm, τ = 1.64, 11 μ s).

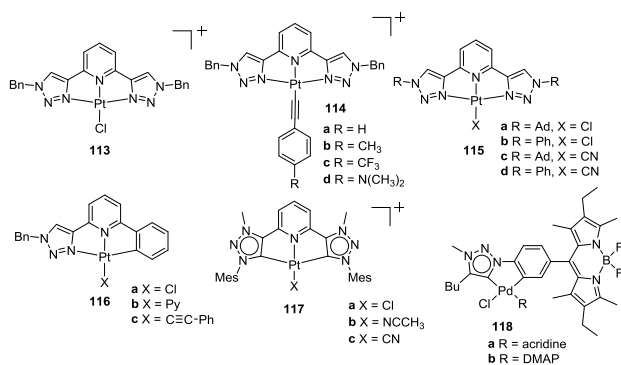


Figure 15. Structures of tridentate triazole-based platinum(II) complexes and platinum(II) triazolyldene complexes.

Strassert and co-workers have made use of a triazole-containing terdentate cyclometalate (TzPyPh) in order to achieve room temperature luminescence in Pt(II) complexes **116a-c**.^[146] Emission spectra exhibit structured vibrational progressions which are attributed to metal-perturbed ligand-centred states. Employment of a σ -donating alkynyl ligand (**116c**) gives red-shifted emission ($\lambda = 510$ nm, $\tau = 2.22$ μ s, $\phi = 0.35$) compared to that of **116b** which makes use of a neutral pyridine donor ($\lambda = 500$ nm, $\tau = 0.42$ μ s, $\phi = 0.02$).

Hwang *et al.* have recently reported the first known examples of bis(triazolyldene)pyridine coordination to Pt(II).^[147] **117a-c** show moderately intense and overlapping absorption bands in the UV region, with those around 225–245 nm ascribed to metal-perturbed intra-ligand transitions whilst those at lower energy are of mixed MLCT/ILCT character. These complexes are emissive in MeCN solutions, with **117a** ($\lambda = 504$ nm, $\tau = 6.93$ μ s) and **117b** ($\lambda = 494$ nm, $\tau = 1.68$ μ s) giving broad bands whilst that of **117c** is more structured with $\lambda_{\text{max}} = 490$ and 522 nm ($\tau = 5.58$ μ s). Solid samples of **117b** additionally display vapochromic attributes, with emission transformed from green ($\lambda = 530, 493(\text{sh})$ nm) to sky-blue ($\lambda_{\text{max}} = 513, 482$ nm) when exposed to THF vapours for example.

BODIPY-functionalised triazolyldene complexes of Pd(II) (**118**) have very recently been reported by Albrecht.^[148] The complex exhibits BODIPY-derived photoluminescence ($\lambda \approx 540$ nm) allowing for monitoring of the exchange of emission-quenching acridine ligands with DMAP by fluorescence spectroscopy.

4. Coinage metal complexes

Triazole-based ligands have been utilised to prepare a range of complexes, clusters and polymers of coinage metals that exhibit photoluminescence. Gold(I) complexes commonly adopt a linear 2-coordinate geometry, which is susceptible to metallophilic association bound via ground states.^[149–151] Gold(I) complexes can also exist in 3- and 4-coordinate geometries.^[152] Open-core coordination patterns for gold complexes tend to suffer photoluminescence quenching, however a small number of examples of emissive gold(I) complexes are known in the literature.^[153] Recently Shi and co-workers presented the synthesis and characterization of a fluorescent N-fused triazole-gold complex (**119**, Figure 16).^[154] The studied gold complex showed a similar Stokes shift with respect to the free ligand implying fluorescence with very little MLCT character.

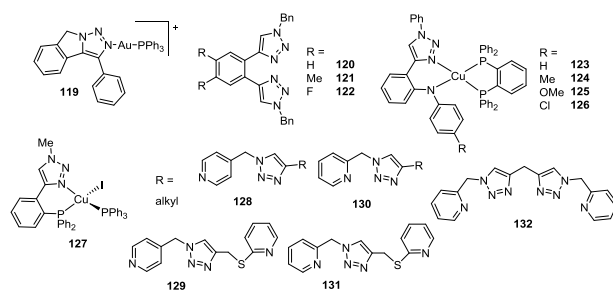


Figure 16. Triazole-based coinage metal complexes and ligands for copper(I) complexes, clusters and coordination polymers.

Eisenberg and co-workers have described a series of tetranuclear Cu(I) clusters of the form $[\text{Cu}_4\text{I}_4(\text{L})_2]$ where L is represented by ligands **120** to **122**.^[155] The clusters adopt a distorted “step-type” geometry with the triazole acting as both chelating and bridging ligands to Cu(I) ions. All the systems exhibited luminescence in the solid state with emission maxima between 495 (**121**) and 524 nm (**120**). Emission is assigned as deriving primarily from $^3\text{LC } \pi \rightarrow \pi^*$ with possible admixing with $^3\text{MLCT}$, halide-to-ligand $^3\text{XLCT}$ and cluster-centred ^3CC character. The group have also reported copper(I) complexes of amido-triazolato ligands (**123** to **126**) for application in OLEDs.^[156] Emission spectra were recorded in THF and benzene and all the complexes exhibit emission maxima in the region of 630 nm with quantum yields up to 0.022. There is a small effect of the aryl R substituent on the energy of the HOMO resulting in small shifts in emission spectra at 77 K. The 4-(2-(diphenylphosphanyl)phenyl)-1,2,3-triazole complex **127** is emissive at $\lambda_{\text{max}} = 500$ nm with a high emission quantum efficiency of 0.97 with long lifetime (177 μ s in 2-Me-THF at 77 K) compared to the other reported complexes.^[157]

The triazole based ligands **128** to **132** have been utilised by Hor and co-workers for the preparation of a range of complexes, clusters and coordination polymers using Zn(II), Co(II), Cu(I/II) metal ions.^[158–162] The copper(I) containing materials were typically observed to show photoluminescence deriving from ligand-centred states and in some cases MLCT and CC-based states.

5. Lanthanide complexes.

Whilst Ln(III) complexes are well known as phosphors, displaying long-lived luminescence across a wide spectral region from the UV to near-IR, they suffer from very weak f-f electronic transitions and low molar extinction coefficients. Therefore, the luminescent excited states must be sensitised through the use of ligands with high absorption cross-sections or through the tethering of d-block metal complexes which serve as light-absorbing antenna. With regards to the former strategy, tricapped trigonal prismatic btzpy complexes of Eu(III) of the form $[\text{Eu}(\text{L})_3]^{3+}$ have been reported.^[94, 163] UV excitation into the $n\text{-}\pi^*/\pi\text{-}\pi^*$ absorption bands of the ligand sensitises narrow line-like $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0\text{--}4$) europium-based emission, with λ_{em} at 580, 595, 617, 650 and 695 nm.

Chandrasekhar and Chandrasekar have developed a synthetic route towards π -conjugated phenyl-linked back-to-back btzpy molecules which serve as ditopic ligands (Figure 17).^[164] A decrease in ligand fluorescence intensity at 381 nm accompanied by the appearance of $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0\text{--}4$) emission bands as **133** is titrated with $\text{Eu}(\text{NO}_3)_3$ is suggestive of the formation of complexes of the type $[\text{Eu}(\text{133})_3](\text{NO}_3)_3$.

For aqueous solutions of $[\text{Eu}(\text{134})_3]^{3+}$ and $[\text{Tb}(\text{134})_3]^{3+}$ the lifetimes of phosphorescence are on the order of 1.06 ms and 0.81 ms respectively with corresponding quantum yields in MeCN of 0.024 and 0.70. The impressive efficiency in the latter instance is attributed to excellent energy-matching between the first triplet state of btzpy and the

emissive 5D_4 state of the Tb(III) core. In the Eu(III) case, the 5D_0 state is much lower in energy, with higher lying states (e.g. 5D_1 , 5D_2) also capable of being sensitised by energy transfer from btzpy, thereby facilitating non-radiative decay processes prior to population of the emissive 5D_0 level. Ligand **134** was derivatised in order to append small amino acid residues (**135a-d**) with subsequent formation of complexes with both europium and terbium. [Eu(**135**) $_3$] $^{3+}$ and [Tb(**135**) $_3$] $^{3+}$ display similar electronic absorption profiles, with bands centred at 312 nm and 234 nm being assigned to $n \rightarrow \pi^*$ transitions on the btzpy core and $\pi \rightarrow \pi^*$ transitions associated with the pendant phenyl rings respectively. Upon UV excitation of the btzpy moiety Ln(III)-centred emission is observed, with the spectra of [Eu(**135**) $_3$] $^{3+}$ being identical to that described above whereas [Tb(**135**) $_3$] $^{3+}$ displays narrow bands at 490, 545, 585 and 621 nm, assigned to $^5D_4 \rightarrow ^7F_J$ ($J = 6-3$) transitions. The role of btzpy in sensitising the emission is eloquently confirmed through excitation spectra, the profiles of which match the ligand-based features observed in electronic absorption spectra.[165]

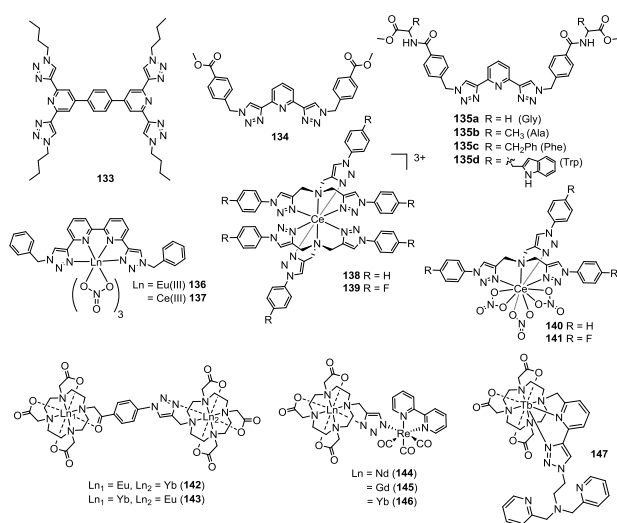


Figure 17. Structures of btzpy-derived ligands and Ln(III) complexes

Emissive btzpy-containing Ln(III) complexes have lent themselves to numerous practical applications such as templating agents for ‘star-branched’ polymers,[166] components within self-assembling healable metallogeles[167] or for bioimaging[168], the latter facilitated by their long emission lifetimes, large Stokes shift and the scope for incorporation of biologically relevant substrates at the triazole moiety through ‘click’ chemistry. Fletcher and co-workers carried out preliminary cellular imaging studies with complexes of the form [Ln(btzpy Bn) $_3$] $^{3+}$ where Ln = Eu(III), Tb(III), Dy(III), Sm(III). All complexes are phosphorescent, with the identity of the metal allowing for good colour tunability with the most intense bands for Dy(III) and Sm(III) observed at 575 and 600 nm respectively. The Ln(III) btzpy Bn complexes were found to be too large for cellular penetration, but were observed to coat the surface of lung cancer cells as observed through confocal microscopy.[168]

1,2,3-Triazoles have additionally featured in diimine-containing ligands designed for lanthanide chelation, such as 6,6'-bis-(1-benzyl-1,2,3-triazol-4-yl)-2,2'-bipyridine (btzbp) and its resultant complexes of Eu(III) (**136**) and Ce(III) (**137**) recently investigated by Nash and co-workers.[169] X-ray crystallography reveals btzbp to complex Ce(III) in a tetradentate fashion, with the remaining coordination sites occupied by nitrate to give the 10-coordinate [Ce(btzbp)(NO $_3$) $_3$] (**137**). UV-Vis absorption spectra reveal a broad transition centred at 332 nm, assigned by the authors to a

4f \rightarrow 5d transition of Ce(III). Whilst no emission was reported for the Ce complex, the Eu analogue exhibits characteristic phosphorescence with a lifetime of 1.62 ms. Ce(III) has also been complexed by 1,2,3-triazole moieties contained within tripodal ligands. Sambri *et al.* have utilised a ‘triple click’ reaction to prepare a small number of tris([1-aryl-1,2,3-triazol-4-yl]methyl)amine (L) tetradentate ligands.[170] The ligand where aryl is phenyl forms both homoleptic [Ce(L) $_2$](ClO $_4$) $_3$ (**138**) and heteroleptic [Ce(L)(NO $_3$) $_3$] (**140**) complexes, both of which were found to be emissive in acetonitrile solution giving a broad band centred at 456 nm ($\tau = 10$ ns; $\phi = 0.010$) for **140** and a red-shifted band at 486 nm ($\tau = 21$ ns; $\phi = 0.015$) for the homoleptic species **138**. The emissive state is described as being of Ce 4d \rightarrow 5f character from the lowest $^2D_{3/2}$ excited state.[171] When the ligand aryl substituents are 4-fluorophenyl groups, the emission for complexes **139** and **141** is observed to blue-shift by 68 and 40 nm respectively compared to their non-fluorinated analogues.

The 1,2,3-triazole fragment has been incorporated within DOTA- and DO3A-based ligand motifs where its positioning upon a pendant arm serves to not only occupy a coordination site of a high valent lanthanide but also to facilitate the attachment of substrates, including those with a luminescence sensitising role, to the ligand architecture through ‘click’ chemistry.[172] The group of Faulkner have utilised 1,2,3-triazoles in the linking of two DOTA-based Ln(III) binding sites giving an architecture which displays dual emission when both Eu(III) and Yb(III) are complexed (**142** and **143**, Figure 17).[173] A similar strategy has been employed in utilising a pendant ‘click’ derived triazole in stabilising Ln(III) coordination through interaction with the N(3) position whilst simultaneously axially coordinating through N(1) to a bipyridine-containing Re(CO) $_3$ complex (**144** to **146**).[174] In this assembly, the d-block complex serves as a light absorbing antenna, sensitising lanthanide luminescence through Dexter energy transfer to metal centres including Yb(III) and Nd(III). DO3A-based Tb(III) complex **147** is brightly emissive but suffers quenching on binding a Cu(II) ion to the dipicolylamine receptor. The adduct [**147**-Cu] $^{2+}$ was found to be a switch-on luminescent sensor for aqueous sulphide ions relevant to waste water environmental pollution.[175]

6. Triazole-based sensors for metal ions

The wide substrate scope and synthetic versatility of CuAAC reactions has made this approach an attractive route to the modular design of photoresponsive molecular sensors for metal ions. Bis-triazolyl coumarin glucoside **148** (Figure 18) responds to Ag(I) with increased emission intensity with λ_{max} ranging from 425 to 475 nm.[176] The bis-triazole-BODIPY sensor **149** selectively binds Ag(I) ions with a binding constant of 8.3×10^6 M $^{-1}$ with emission at $\lambda_{em} = 510$ nm.[177] The methylanthracene triazole-tetraazacyclodecane **150** can form a complex with Cu(II) ions which quenches the ligand fluorescence ($\lambda_{max} = 415$ and 435 nm). [178] The photochromic triazole-conjugated spiropyran **151** changes colour upon Cu(II) complexation, showing a new absorption peak at 571 nm. [179] The amino acid functionalised bis-triazolyl hexose derivative **152** efficiently detects Cu(II)/cyanide by quenching/switch-on of the ligand emission ($\lambda_{max} = 375$ nm). Emission is quenched on addition of the metal ion and emission is then switched-on with addition of cyanide through metal-scavenging.[180] The triazolyl anthracene-based fluorophore **153** undergoes fluorescence quenching in the presence of Cu(II) ions ($\lambda_{max} = 400, 422$ and 458 nm).[181] 2-Anthryltriazolyl ligands of the form shown for **154** undergo fluorescence enhancement upon Zn(II) coordination together with red-shifting the λ_{max} from 420 nm to 455 nm.[182] 2,1,3-Benzothiadiazole-triazole-linked glycoconjugates **155** selectively bind to Ni(II) quenching the

fluorescence of the ligand ($\lambda_{\text{max}} = 515 \text{ nm}$). [183] The triazolyl alkoxy Fischer carbene tungsten complex **156** displays considerable chelation-enhanced fluorescence upon binding with Pb(II), Zn(II) and Cu(II). [184]

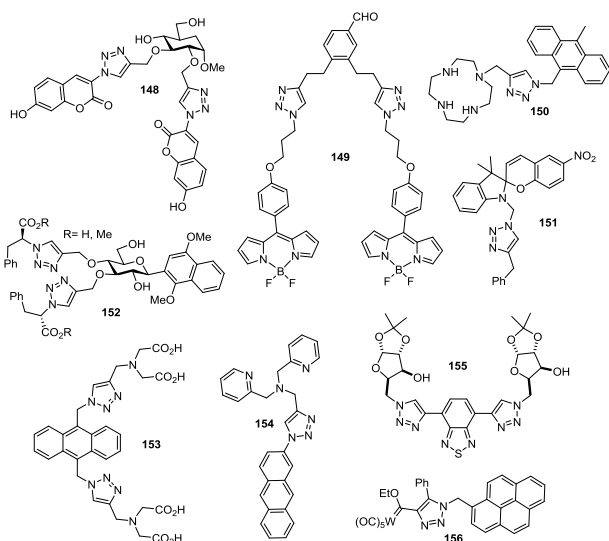


Figure 18. Structures of selected triazole-derived photoresponsive molecular sensors for metal ions.

7. Conclusions and Outlook

Triazole based CuAAC ‘click’ chemistry has evolved as a highly versatile and robust tool for ligand design for transition metal complexes. Not only does the wide substrate scope enable a huge array of ligand architectures to be realised and expansive coordination space to be explored but yields photoactive complexes with highly tunable and fascinating photophysical and photochemical properties. As well as enabling access to highly efficient luminophores for application as phosphorescent dopants in electroluminescent devices and novel dye systems for dye-sensitised solar cells ruthenium(II) and osmium(II) complexes have also been shown to exhibit novel photochemical reactivity resulting in the unprecedented unambiguous spectroscopic identification of ligand loss intermediates.

The future is therefore bright with enormous potential for further fascinating discoveries and developments involving the application of CuAAC derived complexes in materials science and in enabling the exploration of unusual photoreactive excited state phenomena.

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Abbreviations

DMSO, dimethylsulphoxide; TD-DFT, time-dependent density functional theory; ILCT, intraligand charge transfer; TRIR, time-resolved infra-red; LLCT, interligand charge transfer; THF, tetrahydrofuran; Bn, benzyl; Ph, phenyl; dfppyH, 2-(2,4-difluorophenyl)pyridine; phen, 1,10-phenanthroline; MRSA, Methicillin-resistant staphylococcus aureus; DFT, density functional theory; aNHC, abnormal N-heterocyclic carbene; ORTEP, Oak Ridge Thermal Ellipsoid Plot; dmbpy, 4,4'-dimethyl-2,2'-bipyridine; dmobpy, 4,4'-dimethoxy-2,2'-bipyridine; dfptz^{Bn}, 1-benzyl-4-(2,4-difluorophenyl)-1H-1,2,3-triazole; NMR, nuclear magnetic resonance; DMF, N,N-

dimethylformamide; IL, intraligand; CT, charge transfer; Mes, mesityl; Cy, cyclohexyl; Pr, propyl; Fc, ferrocenyl; An, anthracenyl; Ac, acetyl; Ad, adamantyl; DMAP, 4-(dimethylamino)pyridine; Sh, shoulder; Gly, glycine; Ala, alanine; Phe, phenylalanine; DOTA, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid; DO3A, 1,4,7-tris(carboxymethylaza)cyclododecane-10-azaacetylamine.

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