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Original Citation

Scattergood, Paul A., Sinopoli, Alessandro and Elliott, Paul I. (2017) Photophysics and photochemistry of 1,2,3-triazole-based complexes. Coordination Chemistry Reviews. ISSN 0010-8545

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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] electrochromic devices,[5, 6] luminescent live-cell imaging,[7, 8] photoinduced 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-butylnitrite and trimethylsilylazide have emerged.[20]

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

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).
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. pyridyl).

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 [Ru(bpy)]^2+ as an illustrative example. The lower unoccupied molecular orbitals (HOMOs) are of predominantly metal d-orbital character (Figure 2a) whilst the lowest unoccupied metal d-orbital character (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 [Ru(bpy)]^2+ complex.](image)

The lower energy excitation features of the optical absorption spectra are dominated by singlet metal-to-ligand charge-transfer (MLCT) character (Figure 2, process a). Intersystem crossing then yields the triplet 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 MLCT state can commonly be observed at much lower intensity and longer wavelength than the more intense MLCT bands. The MLCT state can also undergo non-radiative deactivation through thermal population of triplet metal-centred (MC) states (process d). Characterised by population of a dπ* 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^6 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 fac-[Re(N=N)₃(CO)₃(X)]^0, where the diimine ligand N=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 fac-[Re(bpy)(CO)Cl] exhibit a HOMO dominated by a Re 5d-orbital (with additional carbon 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 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.](image)

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_max^00 / nm</th>
<th>ϕ / 10^−2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>543</td>
<td>not recorded</td>
</tr>
<tr>
<td>2a</td>
<td>538</td>
<td>0.33</td>
</tr>
<tr>
<td>2b</td>
<td>522</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>496</td>
<td>3.10</td>
</tr>
<tr>
<td>4</td>
<td>582</td>
<td>0.56</td>
</tr>
<tr>
<td>5a</td>
<td>569</td>
<td>0.19</td>
</tr>
<tr>
<td>5b</td>
<td>569</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>617</td>
<td>0.06</td>
</tr>
<tr>
<td>[Re(bpy)(CO)Cl]</td>
<td>633^0</td>
<td>0.27</td>
</tr>
</tbody>
</table>

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 fac-[Re(bpy)(CO)(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 [Re(bpy)(CO)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 (τ = 466 ns) for the analogous complex [Re(bpy)(CO)(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 [Re(bpy)(CO)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-[Re(pyz)(CO)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 → LUMO 3 MLCT character. The LUMO of 2a is found to be of π* character, distributed primarily over the pyridyl ring of the pytz 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, φ = 3.3 x 10^-3) in deaerated acetonitrile, τ_{77K} = 8.90 μs) compared to that for fac-[Re(bpy)(CO)Cl] (λ_max = 633 nm, φ = 2.7 x 10^-3, τ_{77K} = 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]

Policar 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-pyzt analogues.[39] These complexes were shown to be effective photocatalysts for CO₂ reduction with the sterically encumbered 2e 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 Policar, 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 (\(^{186,188}\)) but also to the fact that Re(I) is an excellent mimic of the group 7 congeners \(^{99m}\)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 3MLCT-based emission and \(\gamma\)-ray emission from decay of the \(^{99m}\)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 control of these properties through modification of ligand architectures has a large Ir d orbital c character. In triscyclometalated complexes the LUMO is localised on the N donor ligand and yields charge neutral complexes. The HOMO of both of these archetypal complexes the LUMO is localised on the N-Donor ring or on the ancillary ligand depending on the relative energies of the \(\pi^*\) orbitals of these ligands. Thus, depending on the exact nature of the ligands, emission derives from MLCT/LLCT or \(3\)MLCT/\(2\)LLCT 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 itsppy 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 upon 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(t) 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 \(\tau\)-butyl substituents onto the bpy ancillary ligand in complexes 20 and 22 leads to sky-blue phosphorescence.[55] Incorporation of \(\pi\)-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.](image)

![Figure 7. Representative emission spectra for complexes 21, 30 and 31 in acetonitrile.](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\lambda_{\text{max}} / \text{nm} (\phi))</th>
<th>Complex</th>
<th>(\lambda_{\text{max}} / \text{nm} (\phi))</th>
</tr>
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<tbody>
<tr>
<td>12</td>
<td>530 (0.40)</td>
<td>32</td>
<td>478, 56 (0.02)</td>
</tr>
<tr>
<td>13</td>
<td>580 (0.29)</td>
<td>33</td>
<td>455, 484 (0.02)</td>
</tr>
<tr>
<td>14</td>
<td>560 (0.45)</td>
<td>34</td>
<td>600, 635 (0.09)</td>
</tr>
<tr>
<td>15</td>
<td>495 (0.29)</td>
<td>35</td>
<td>476, 508 (0.82)</td>
</tr>
<tr>
<td>16</td>
<td>435 (0.02)</td>
<td>36</td>
<td>454, 483 (0.28)</td>
</tr>
<tr>
<td>17</td>
<td>527 (0.11)</td>
<td>37</td>
<td>532, 568 (0.04)</td>
</tr>
<tr>
<td>18</td>
<td>514 (0.73)</td>
<td>38</td>
<td>485 (0.002)</td>
</tr>
<tr>
<td>19</td>
<td>497 (0.81)</td>
<td>39</td>
<td>452 (0.0005)</td>
</tr>
<tr>
<td>20</td>
<td>498 (0.80)</td>
<td>40</td>
<td>487 (0.003)</td>
</tr>
<tr>
<td>21</td>
<td>580 (0.25)</td>
<td>41</td>
<td>461 (0.003)</td>
</tr>
<tr>
<td>22</td>
<td>575 (0.35)</td>
<td>42</td>
<td>495 (0.27)</td>
</tr>
<tr>
<td>23</td>
<td>495 (0.47)</td>
<td>43</td>
<td>not observed</td>
</tr>
<tr>
<td>24</td>
<td>512 (0.77)</td>
<td>44</td>
<td>500 (0.002)</td>
</tr>
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<td>464, 485 (0.003)</td>
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<td>492 (0.007)</td>
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<td>505 (0.015)</td>
</tr>
<tr>
<td>29</td>
<td>392, 418 (-)</td>
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<td>30</td>
<td>477, 507 (0.21)</td>
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<td>457, 487 (0.31)</td>
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<tr>
<td>31</td>
<td>452, 483 (0.22)</td>
<td>51</td>
<td>458, 487 (0.27)</td>
</tr>
</tbody>
</table>

\(a\) deaerated dichloromethane; \(b\) deaerated acetonitrile; \(c\) 77K butyronitrile glass; \(d\) aerated dichloromethane; \(e\) deaerated THF

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Scattergood, Sinopoli & Elliott, Photophysics of 1,2,3-triazole complexes
The formation of bисcyclometalated 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 3MLCT/ILCT contributions to the emissive state. The 1,2,4-triazolate complex 26 on the other hand shows true-blue emission with much greater 3MLCT/ILCT character.

Bисcyclometalated complexes have also been incorporated into mesoporous silica materials through templated synthesis.[57] Carbazole-appended analogues of 26 bearing 1,2,4-triazole ancillary ligands have been used to prepare blue- and green-emitting solution processed OLEDs.[58] When bis{(4-methoxyphenyl)imino}acenaphthenes is used as an ancillary ligand bисcyclometalated phenyltriazole complexes exhibit panchromatic absorption extending as far as 800 nm.[59] Bисcyclometalated 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 other cyclopentadienyl complexes.[60]

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 3MLCT 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 bисcyclometalated 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 [Irppy(2)(bpy)] + for a triazole donor results in the switching of the emissive state from 3MLCT/ILCT to 3MLCT/ILCT character. These complexes and analogues of them have been shown to be efficient chemiluminescences[67, 68], used in LECs[69] and have been used as live cell luminescence imaging agents.[70]

Analogues of 30 with a cycloexetrin 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 cycloexetrin derivatised platinum nanoparticles.[72]

Donnelly and co-workers have investigated the use of the more flexible picylitriazole 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 3MLCT/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.

Heteroleptic bисcyclometalated 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 3MLCT/ILCT 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 3MLCT/ILCT 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 photosstable and decomposes through expulsion of the btz ligand.

Swager and co-workers have been able to isolate the triazole complexes 44 to 48 through transmetallation from the copper(I) triazole 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 3LLCT contribution to the emissive excited states.

De Cola and co-workers have reported the neutral triazolate 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 ppy
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 [Ru(bpy)]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 MLCT absorption and 1 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 1MC 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 [Ru(phen)2(pytz)2]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 sensitisier 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) tripyz complexes have been shown to have antimicrobial activity against MRSA.[85] Analogues of 53 in which p-nitrophenylethyl and p-alkoxophenylethyl 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 alkoxysubstituted complex through stabilisation of the ligand ππ*-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 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 Ti states of 58 and 59 are of 1 MLCT character, the lowest energy triplet state of 60 is 1MC 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 MLCT absorption band of the heteroleptic complex 61 is blue-shifted by ~40 nm relative to that of [Ru(tpy)]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 MLCT state. The homoleptic complex 62 exhibits a 1 MLCT maximum at 394 nm and is non-emissive at 77 K. A metallosupramolecular polymer containing [Ru(btzpy)]2+-like units spaced by a diethynylphenylene π-conjugated unit is however emissive ($\lambda_{emax} = 700$ nm).[96] The switching on of emission likely stems from stabilisation of the 3 MLCT states through conjugation with the spacer with possible equilibrium with ππ* states associated with the linker.

Cycloolatated 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 ptz 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 [Ru(bpy)(dtzpy)]2+ (dtzpy = 5,5′-bis(1-butyl-2,3-triazol-4-yl)-2,2′-bipyridyl) with [Ru(bpy)(Cl)2].[98] The redox asymmetric product contains RuN-C and RuN 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 MLCT absorption maxima and 3 MLCT emission maxima).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{abs} / \text{nm}$</th>
<th>$\lambda_{emax} / \text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)]2+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>452</td>
<td>610</td>
</tr>
<tr>
<td>53</td>
<td>446</td>
<td>575</td>
</tr>
<tr>
<td>54</td>
<td>392</td>
<td>563</td>
</tr>
<tr>
<td>55</td>
<td>384</td>
<td>not observed</td>
</tr>
<tr>
<td>58</td>
<td>446</td>
<td>565, 610</td>
</tr>
<tr>
<td>59</td>
<td>425</td>
<td>544, 585</td>
</tr>
<tr>
<td>60</td>
<td>303</td>
<td>not observed</td>
</tr>
<tr>
<td>[Ru(tpy)]2+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>474</td>
<td>604</td>
</tr>
<tr>
<td>62</td>
<td>432</td>
<td>583</td>
</tr>
<tr>
<td>[Ru(tpy)(btzpy)+]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>464</td>
<td>648</td>
</tr>
<tr>
<td>74</td>
<td>520</td>
<td>730</td>
</tr>
<tr>
<td>75</td>
<td>480</td>
<td>650</td>
</tr>
<tr>
<td>76</td>
<td>463</td>
<td>643</td>
</tr>
<tr>
<td>79</td>
<td>473</td>
<td>694</td>
</tr>
</tbody>
</table>

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

Complexes containing the tridentate cycloolatated ligand framework btz (Figure 10) have also been investigated as analogues of the better known 1,3-dipyridylbenzene (dbp) complexes.[99] Complexes 65 to 67 are characterised by Ru(II/III)-based oxidation between +0.53 and +0.59 V (vs Ag/AgCl) which are shifted towards more negative potential relative to that of [Ru(tpy)]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 triazolylidene 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 MLCT-based emission band, appearing at 648 nm.

![Figure 10. Structures of triazole-based cyclometalated and abnormal N-heterocyclic carbene complexes.](image)

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 N²N¹N coordination including to the triazole is not possible. Reaction with [Ru(tpy)(NCMe)]³⁺ leads to cyclometalation to form the triazole complex 74.[110] The HOMO of 74 has contributions from the metal as well as the triazole π-system and is destabilised with respect to that of [Ru(tpy)]³⁺ 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 triazole. Upon methylation of the N(3) position of the triazole with iodomethane the mesoionic triazolylidene complex 75 is produced. As a consequence of the overall charge neutrality of the carbene donor, and poor π-donor properties relative to triazole, 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 MLCT 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 triazolylidene 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 μs was determined.[111] Through further derivatisation with inclusion of a carbonate 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(btzpy)]³⁺ (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 (λₘₐₓ ≈ 425 nm) and Fe-to-triazole (λₘₐₓ ≈ 310 nm) charge transfer transitions. Comparison with the MLCT absorption band of [Fe(bpy)]²⁺ (λₘₐₓ ≈ 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)]³⁺ 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)]:[83] (λₘₐₓ = 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-(triazolylidene)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)]²⁺ parent complex (τ = 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 (λ = 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 [Os(bpy)(pytz)]n+. 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 sensitisier 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 [Os(bpy)]n+. 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 tetradeutate tripod ligands with pyridine and triazole arms have been prepared. Photocatalytic reactivity in complexes of the form [Ru(L)(DMF)(Cl)]+ (where L is a tripod amine ligand derived from tristr(pyridylmethyl)amine with 3-π 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-DMF 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)- photo-product intermediates by 1H NMR spectroscopy.[125] Photocatalytic reactivity has also been reported for [Ru(bpy)(L)]n complexes. Whilst steric repulsion leads to photochemistry in the fully pyridyl-containing system (n = 0), photochemical quantum yield Φ323 = 2.1 × 10−3, successive replacement of pyridyl with triazole donors enhances the rate of photodissociation of an axial arm of the tetradeutate ligand and subsequent MeCN coordination. This is most efficient when n = 3 with a conversion of 99% (Φ336 = 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- [Ru(bpy)(c^2-btz)(c^-btz)(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 [Ru(N\(^2\)N)\(_2\)(btz)]\(^2+\) (N\(^2\)N = bpy), phen, dmbpy, dmobpy) undergo surprisingly rapid photochemical ligand ejection of btz in acetonitrile to yield cis-[Ru(bpy)\(_3\)](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 \(^3\)MC 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 \(^3\)MLCT state compared to that of [Ru(bpy)\(_3\)]\(^2+\). This destabilisation of the \(^3\)MLCT presumably results in a lower activation barrier to \(^3\)MC population.

The iridium(III) btz complex [Ir(dpz)\(_2\)(btz)]\(^+\) (43) also undergoes photochemical loss of btz presumably via \(^3\)MC state population from a high energy btz-centred \(^3\)MLCT state.[74] This is intriguing as \(^3\)MC states of analogous [Ir(C\(^2\)N)\(_2\)(N\(^2\)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-pytz ligand 4-phenyl-1-(pyrid-2-yl)-1,2,3-triazole (inv-pytz) from the complex [Ru(bpy)\(_3\)](inv-pytz)]\(^2+\) (91).[39] Interestingly, evidence by NMR spectroscopy of a ligand-loss intermediate of the form [Ru(bpy)\(_3\)](\(\kappa^1\)-inv-pytz)(NCMe)\(_2\)]\(^2+\) was reported. Kirsh-De Mesmaeker and co-workers have investigated complexes of the form [Ru(TAP)\(_2\)](N\(^2\)N)]\(^2+\) (TAP = 1,4,5,8-tetraazaazepanthenzrene, N\(^2\)N = pytz\(_{95}\) or btz\(_{128}\),[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 [Ru(N\(^2\)N)(btz)]\(^2+\) (N\(^2\)N = bpy (59), pytz (92), Scheme 1 bottom) are observed under photochemical ejection of one of the btz ligands.[130] This process proceeds with an extraordinary concomitant ligand rearrangement to yield the complexes trans-[Ru(N\(^2\)N)(btz)(NCMe)]\(^2+\) (N\(^2\)N = bpy [131] (95), pytz [132] (96)). Even more remarkably this process proceeds with the observation of metastable ligand-loss intermediates trans-[Ru(N\(^2\)N)(\(\kappa^1\)-btz)(\(\kappa^1\)-btz)(NCMe)]\(^2+\) (N\(^2\)N = bpy (93), pytz (94)) which in the case of N\(^2\)N = bpy can be formed near quantitatively within five minutes of irradiation in an NMR tube and has been crystallographically characterised (Figure 13).[131]

Due to the larger ligand field splitting for osmium(II) complexes relative to their ruthenium(II) analogues, \(^3\)MC population and ligand ejection from complexes of the form [Os(N\(^2\)N)]\(^2+\) has long been considered extremely inefficient or non-existent. However, our group recently reported the unprecedented photochemical ligand ejection for the complex [Os(btz)]\(^2+\) (88).[133] Whilst thermally inaccessible in bpy-containing heteroleptic analogues, the \(^3\)MC states for 88 are evidently readily populated from a high energy btz-centred \(^3\)MLCT state. In pyridine (py) solutions photolysis of 88 yields trans-[Os(btz)(py)]\(^2+\) (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-[Os(btz)(NCMe)]\(^2+\) (cis- and trans-99) and proceeds with the observation of the ligand-loss intermediates cis- and trans-[Os(\(\kappa^1\)-btz):\(\kappa^1\)-btz(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] [Pd(pytz)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 \(\pi-\pi^*\) 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 [Pt(pytz)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 [Pt(pytz)Cl\(_2\)] (\(\lambda = 330 \text{ nm}\)) and [Pt(bpy)Cl\(_2\)] (\(\lambda = 389 \text{ nm}\)][137] highlight the destabilising influence of the triazole upon the ligand based \(\pi^*\) 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 Pd(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 ptz complexes are reported, with \( ^3 \)MLCT 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 \([\text{Pd}^{2+}\text{ptz}\text{]}\)]\(^2+\) 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 \( \pi-\pi^* \) transitions localised across the central ptz fragment. An additional weaker band in the region 360-380 nm (105a-e) and at 430 nm (105e) is assigned with the aid of DFT calculations as being LMCT in nature.

Aside from the ptz motif, 1,2,3-triazoles have also featured within alternative novel chelating ligand systems such as \( 1\)-ary1-1,2,3-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 \( \pi-\pi^* \) 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 (\( \phi = 0.001 - 0.160 \)). 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 (\( \lambda = 464 \text{ nm}, \phi = 0.97, 5 \text{ wt\% in PMMA} \)). Wang and co-workers have further optimised the ligand architecture featuring a triyl-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 (\( \lambda = 468 \text{ nm}, \phi = 0.95, 10 \text{ wt\% in PMMA} \)) and yields electroluminescent devices with modest external quantum efficiencies (\( \lambda = 477 \text{ nm}, \eta = 15.9 \% \)). In the absence of bulky substituents analogues of 112 form excimers which give dual emission almost white in colour.

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**Figure 14.** Structures of ptz-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 \( \pi-\pi^* \) 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 \( \sigma \)-donating alkynyl ligands destabilising luminescence-quenching \( ^3 \)MC states, 114a-d display weak emission in CH2Cl2 solutions (\( \lambda = 582-597 \text{ nm} \)) at room temperature which is reasonably long-lived at 77 K (1.6-2.2 \( \mu \text{s} \)).

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 (\( \lambda = 560 \text{ nm}, \tau = 1.67, 0.58 \mu \text{s}, \phi = 0.055 \)) and 115d (\( \lambda = 570 \text{ nm}, \tau = 0.09, 0.24 \mu \text{s}, \phi = 0.260 \)) 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 (\( \lambda = 420, 445, 470 \text{ nm}, \tau = 40 \mu \text{s} \) for 115a; \( \lambda = 420, 450, 470 \text{ nm}, \tau = 33 \mu \text{s} \) for 115b). 115a additionally shows excited state excimeric emission (\( \lambda = 685 \text{ nm}, \tau = 15 \mu \text{s} \)) whereas 115b undergoes formation of emissive ground state aggregates (\( \lambda = 605 \text{ nm}, \tau = 1.64, 11 \mu \text{s} \)).
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 alkylnyl ligand (116c) gives red-shifted emission (λ = 510 nm, τ = 2.22 μs, φ = 0.35) compared to that of 116b which makes use of a neutral pyridine donor (λ = 500 nm, τ = 0.42 μs, φ = 0.02).

Hwang et al. have recently reported the first known examples of bis(triazolylidene)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 (λ = 504 nm, τ = 6.93 μs) and 117b (λ = 434 nm, τ = 1.68 μs) giving broad bands whilst that of 117c is more structured with λ_{max} = 490 and 522 nm (τ = 5.58 μs). Solid samples of 117b additionally display vapochromic attributes, with emission transformed from green (λ = 530, 493(sh) nm) to sky-blue (λ_{max} = 513, 482 nm) when exposed to THF vapours for example.

BODIPY-functionalised triazolylidene complexes of Pd(II) (118) have very recently been reported by Albrecht.[148] The complex exhibits BODIPY-derived photoluminescence (λ ≈ 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.

Eisenberg and co-workers have described a series of tetranuclear Cu(I) clusters of the form [Cu₄L₄]⁺ wherein 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 3LCT π→π* with possible admixing with 3MLCT halide-to-ligand 3XLCT 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 λ_{max} = 500 nm with a high emission quantum efficiency of 0.97 with long lifetime (177 μs in 2-Me-THF at 77 K) compared to the other reported complexes.[157]

The triazol 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(II)/III) 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, triapped trigrimal prismatic btpy complexes of Eu(III) of the form [EuL₃]^{3+} have been reported.[94, 163] UV excitation into the n-π*/π-π* absorption bands of the ligand sensitises narrow line-like 3D_{0} → 3F_{J} (J = 0-4) europium-based emission, with λ_{em} at 580, 595, 617, 650 and 695 nm. Chandrasekhar and Chandrasekhar have developed a synthetic route towards π-conjugated phenyl-linked back-to-back btpy molecules which serve as ditopic ligands (Figure 17).[164] A decrease in ligand fluorescence intensity at 381 nm accompanied by the appearance of 3D_{0} → 3F_{J} (J = 0-4) emission bands as 133 is titrated with Eu(NO₃)₃ is suggestive of the formation of complexes of the type [{Eu(133)}₃(NO₃)₉]⁺.

For aqueous solutions of [Eu(134)]^{3+} and [Tb(134)]^{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 btpy and the
emissive $^5D_0$ state of the Tb(III) core. In the Eu(III) case, the $^7D_{0}$ state is much lower in energy, with higher lying states (e.g. $^7D_{1}$, $^7D_{2}$) also capable of being sensitised by energy transfer from btzpy, thereby facilitating non-radiative decay processes prior to population of the emissive $^7D_{0}$ 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)]$^{3+}$ and [Tb(135)]$^{3+}$ display similar electronic absorption profiles, with bands centred at 312 nm and 234 nm being assigned to n→π* transitions on the btzpy core and π→π* 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)]$^{3+}$ being identical to that described above whereas [Tb(135)]$^{3+}$ 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](image)

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 metallo-gels[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)$_{3}$N$_{3}$] 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 375 and 600 nm respectively. The Ln(III) btzpy$^{3+}$ 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-phenyl-1,2,3-triazol-4-yl)-2,2′-bipyridine (btzpy), and its resultant complexes of Eu(III) (136) and Ce(III) (137) recently investigated by Nash and co-workers.[169] X-ray crystallography reveals btzpy to complex Ce(III) in a tetradentate fashion, with the remaining coordination sites occupied by nitrate to give the 10-coordinate [Ce(btzpy)(NO$_3$)$_{5}$](137). UV-Vis absorption spectra reveal a broad transition centred at 332 nm, assigned by the authors to a 4f→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 homoletic [Ce(III)]([NO$_3$]$_3$) (138) and heteroleptic [Ce(III)][NO$_3$] (140) complexes, both of which were found to be emissive in acetonitrile solution giving a broad band centred at 456 nm (τ = 10 ns; Φ = 0.010) for 140 and a red-shifted band at 486 nm (τ = 21 ns; Φ = 0.015) for the homoleptic species 138. The emissive state is described as being of Ce 4d→5f character from the lowest $^4D_{2}$ 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)$_5$ 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 $\lambda_{\text{max}}$ 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 x10$^{4}$ M$^{-1}$ with emission at $\lambda_{\text{em}}$ = 510 nm.[177] The methylanthracene triazole-tetraazacyclododecane 150 can form a complex with Cu(II) ions which quenches the ligand fluorescence ($\lambda_{\text{max}}$ = 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 ($\lambda_{\text{max}}$ = 375 nm). Emission is quenched on addition of the metal ion and emission is then switched-on with addition of cyanide through metal-sensitising ligands.[180] The triazolyl anthracene-based fluorophore 153 undergoes fluorescence quenching in the presence of Cu(II) ions ($\lambda_{\text{max}}$ = 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 $\lambda_{\text{max}}$ 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 (λ_max = 515 nm).[183] The triazolyl alkox 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.

Acknowledgements

The authors thank the University of Huddersfield (P.A.S & P.I.P.E) and the Qatar Environmental & Energy Research Institute, Hamed Bin Khalifa University (A.S.) for supporting this work.

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; aHNC, abnormal N-heterocyclic carbone; ORTEP, Oak Ridge Thermal Ellipsoid Plot; dmppy, 4,4’-dimethyl-2,2’-bipyridine; dmnpbpy, 4,4’-dimethoxy-2,2’-bipyridine; dftpz,[a] 1-benzyli-(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(carboxymethylazela)ycyclododecane-10-azaacetilamide.

References
