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Review

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 d^6 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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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; dmby, 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-azaacetylamide; py, pyridine; LC, ligand-centred.

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1. Introduction

Kinetically inert d^6 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 anticancer agents and singlet oxygen sensitisation for photodynamic therapy [9–11], molecular sensors [12] and switches [13]. Key to

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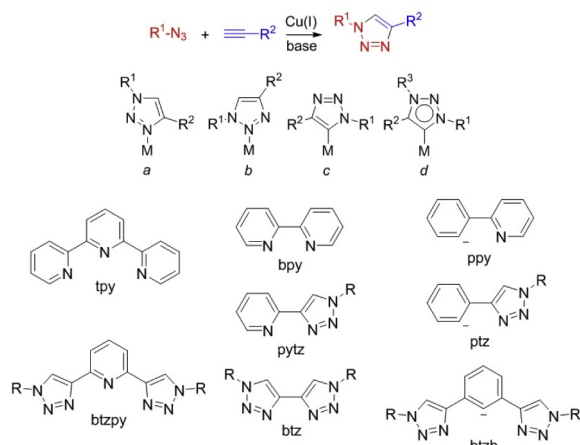


Fig. 1. CuAAC reaction for formation of 1,4-disubstituted-1,2,3-triazoles and possible coordination modes of triazole-based ligand (top). Structures and naming of commonly occurring pyridine- and triazole-based ligand motifs appearing in this review (bottom).

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 (Fig. 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 (Fig. 1 bottom) but also include work on luminescent Pd

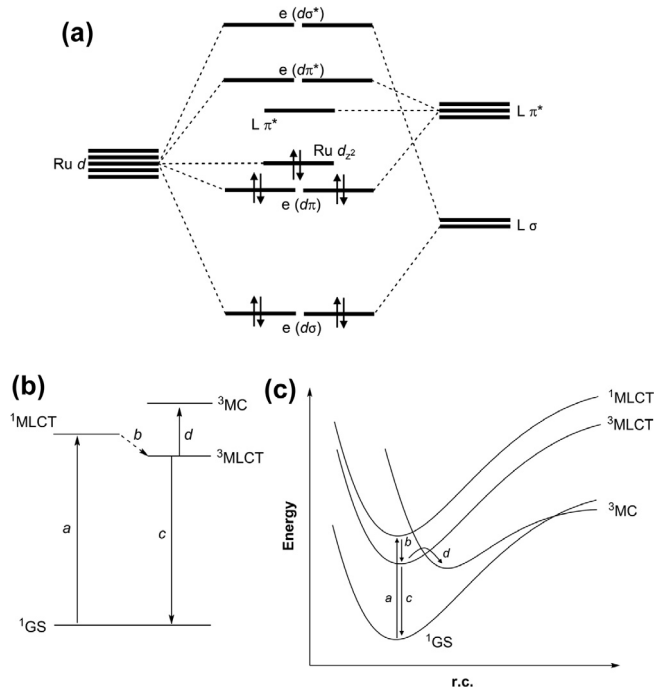


Fig. 2. Simplified molecular orbital energy diagram (a), qualitative Jablonski diagram (b) and potential energy surface diagram (c) for ground and excited states for a $[Ru(bpy)_3]^{2+}$ -type complex.

(II), Pt(II), coinage metal and lanthanide complexes. Throughout the course of the review we will use the ligand shorthand nomenclature given in Fig. 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 $[Ru(bpy)_3]^{2+}$ as an illustrative example. The highest occupied molecular orbitals (HOMOs) are of predominantly metal d-orbital character (Fig. 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 (Fig. 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 (Fig. 2c).

The lower energy excitation features of the optical absorption spectra are dominated by singlet metal-to-ligand charge-transfer (1MLCT) character (Fig. 2, process a). Intersystem crossing then yields the triplet 3MLCT 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 3MLCT state can commonly be observed at much lower intensity and longer wavelength than the more intense 1MLCT bands. The 3MLCT 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

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