

Review

# Coordination complexes exhibiting room-temperature phosphorescence: Evaluation of their suitability as triplet emitters in organic light emitting diodes

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**Abbreviations:** acac, acetylacetonate; BCP, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; binap, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; bpy, 2,2'-bipyridine; Brphen, 4,5-bromo-1,10-phenanthroline; bt, bis(2-phenylbenzothiazolato-*N,C3'*); btp, bis(2-(2'-benzo[4,5-*a*]thienyl)pyridinato-*N,C3'*); CBP, 4,4'-*N,N'*-dicarbazole-biphenyl; clpby, 4'-(4-chlorophenyl)-6'-phenyl-2,2'-bipyridine; cp, cyclopentadienyl; cpbpy, 4'-(4-carboxyphenyl)-6'-phenyl-2,2'-bipyridine; dbbpy, 4,4'-dibutyl-2,2'-bipyridine; dbm, dibenzolymethanate; dbp, 2,9-di-*n*-butyl-1,10-phenanthroline; dcpe, bis(dicyclohexylphosphino)ethane; dmphen, 2,9-dimethyl-1,10-phenanthroline; dmbpy, 4,4'-dimethyl-2,2'-bipyridine; dpm, dipivaloylmethanate; dpp, 1,3-diphenyl-1,3-propandionate; dppe, bis(diphenylphosphino)ethane; dppf, 1,1'-bis(diphenylphosphino)ferrocene; dppm, bis(diphenylphosphino)methane; dppn, 1,8-bis(diphenylphosphino)naphthalene; dppp, bis(1,3-bis(diphenylphosphino))propane; dpt-NH<sub>2</sub>, 4-amino-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole; en, 1,2-diaminoethane; ephen, 5,6-epoxy-1,10-phenanthroline; F<sub>2</sub>MeOppy, 2-(2',4'-difluorophenyl)pyridine; Fbpy, 5-(9,9-diethyl-9*H*-fluoren-2-ylethynyl)-2,2'-bipyridine; FbpyF, 5,5'-bis(9,9-diethyl-9*H*-fluoren-2-ylethynyl)-2,2'-bipyridine; hfac, hexafluoroacetylacetonate; hpbpy, 4-(4-hydroxyphenyl)-6'-phenyl-2,2'-bipyridine; MTHF, 2-methyltetrahydrofuran; *m*CP, *N,N'*-dicarbazolyl-3,5-benzene; mor, morpholine; ox, 8-quinolato; PBD, polybutadiene; PdOEP, palladium octaethylporphyrin; PdTPP, palladium tetraphenylporphyrin; phen, 1,10-phenanthroline; phpyH, 2-phenylpyridine; picH, 2-picolinic acid; pmbp, 4,4'-diphenyl-6,6'-dimethyl-2,2'-bipyrimidine; PMIP, tris(1-phenyl-3-methyl-4-isobutyl-5-pyrazolone); PMMA, polymethylmethacrylate; PNI, 4-piperidinyl-1,8-naphthalimide; PNI-phen, *N*-(1,10-phenanthroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide; POP, bis(2-diphenylphosphino)phenylether; PPO, triphenylphosphine oxide; PtOEP, platinum octaethylporphyrin; PtTPP, platinum tetraphenylporphyrin; PVK, polyvinylcarbazole; Py, pyridine; pyzch, 2-pyrazinecarboxylic acid; q, 8-hydroxyquinolate; sal, *N*-methylsalicylimine-*N,O*; tdtH<sub>2</sub>, 3,4-toluenedithiol; thpyH, 2-(2'-thienyl)pyridine; tmdH, 2,2,6,6-tetramethyl-3,5-heptanedione; tpbpy, 4'-(4-tolyl)-6'-phenyl-2,2'-bipyridine; tta, thenoyl-trifluoroacetate; ttpy, 4'-(4-tolyl)-2,2':6'2''-terpyridine

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## Abstract

The aim of this review is to evaluate the potential of known main-group, transition metal and lanthanide complexes exhibiting room-temperature phosphorescence, either for direct application as dopants in the emissive layer of OLED devices, or as an aid to deduce which structural trends might lead to new materials for this purpose. A systematic analysis of emission characteristics such as wavelength, quantum yields and lifetimes is given for known classes of complexes and their suitability as OLED phosphors evaluated. Blue electroluminescent devices remain to date the most challenging area of this technology, and polynuclear copper(I), mono-, di- and polynuclear gold(I) and osmium(II) complexes are identified as being of particular promise in this regard. Heterobimetallic complexes are also identified as being of interest because of the possibility for emission tuning, by suitable choice of metals and ligands, which these complexes may offer.

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**Keywords:** Coordination complex; Organic light-emitting diode; OLED; Phosphorescence; Triplet emitter

## 1. Introduction

Organic light-emitting diodes (OLEDs) are emerging as the leading technology for the new generation of full colour flat panel displays [1]. Based on the principle of electroluminescence, a phenomenon first observed in organic semiconductors by Pope et al. in 1963 [2], the commercial potential was not realized until 1987 when Tang and VanSlyke of Kodak reported efficient low voltage electroluminescence in an organic thin-film device [3]. This principle was later extended by Friend and coworkers to devices incorporating polymers as the emitting layer [4]. Recent advances in materials and manufacturing techniques have led to the lucrative commercialisation of this technology and OLEDs are already used in small displays in mobile phones, car stereos and digital cameras [1].

OLED technology offers many advantages over traditional liquid crystal displays (LCDs). OLED displays are self-luminescent, eliminating the requirement for backlighting and allowing them to be thinner, lighter, and more efficient than LCDs. Light is emitted only from the required pixels rather than the entire panel, reducing the overall power consumption to 20–80% of that of LCDs [1]. OLEDs are extremely robust and may be deposited on most substrates, rigid or flexible, introducing the possibility of many new applications. Finally, OLED displays are aesthetically superior to LCDs, providing truer colours, higher contrast and wider viewing angles.

The rapidly growing market for OLED technology is driving both academic and industrial research towards the development of new materials and advanced manufacturing technology. In particular, the demand for novel luminescent materials capable of both withstanding the manufacturing process and exhibiting the desired photophysical properties has generated significant activity in the last decade.

### 1.1. The OLED structure

Fig. 1 illustrates a typical multilayered OLED device. The basic structure consists of a stack of thin organic layers sandwiched between an anode such as indium tin oxide (ITO) and a metallic cathode of Mg–Ag or Li–Al. The organic layers typically comprise a hole transport layer, an electron transport layer and, in state-of-the-art devices, an exciton blocking layer such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), which confines excitons within the organic emissive layer improving the electroluminescence quantum efficiency [5–8]. The organic emitter is either deposited directly between the conducting layers or more commonly doped into the electron transport layer, typically tris(8-hydroxyquinolate)aluminum (Alq<sub>3</sub>).

Application of an external voltage causes the injection of holes from the anode and electrons from the cathode. The holes migrate through the hole transport layer and the electrons migrate through the electron transport layer. As electrons and holes move from site to site they occasionally land in the same place, forming a neutral bound state, or exciton. Relaxation from the excited to the ground state may occur, resulting in the emission of light. Where the organic emitter is doped in a host

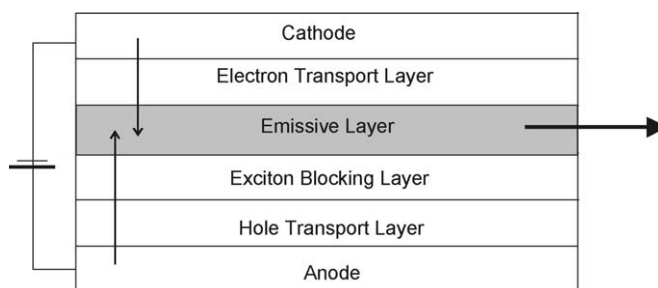


Fig. 1. Typical OLED cell structure.

polymer layer, exciton formation occurs in the polymer layer and excitation energy must be efficiently transferred to the excited states of the dopant molecules, which then relax radiatively to the ground state.

### 1.2. The emitter layer: singlet versus triplet emitters

Early OLED devices utilised small fluorescent organic compounds as the dopant molecules [3]. However, in more recent times, emphasis has been placed on the identification of novel phosphorescent materials for this application, since the luminous efficiency of OLEDs may potentially be improved by up to a factor of four when phosphorescent emitters are used.

Fluorescence is limited to radiative relaxations of organic molecules that conserve electron spin and typically involve transitions between singlet excited and ground states. In contrast, phosphorescence results from a spin-forbidden transition, where electron spin is not conserved, usually between a triplet excited and singlet ground state. Under electrical excitation excitons are formed in both singlet and triplet states; thus, harvesting luminescence from only singlet excitons significantly limits the luminescence efficiency in purely fluorescent devices [9].

If the spin-statistics for an exciton generated by a non-geminate pair combination (as in electroluminescence) are considered, there are four possible ways to combine the half-integer spins of the two charge carriers (electrons and holes) [9,10]. Of these, three give a resultant spin of one i.e. a triplet state and only one gives the zero spin singlet state. If the recombination of the electrons and holes is statistically controlled, then 25% of them lead to the generation of pure singlet states and 75% go to pure triplet states.

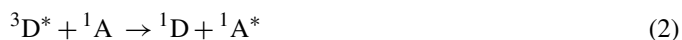
This rule may be relaxed if the recombination is not statistically controlled or if the excited state generated is not a pure singlet or triplet state [11]. This latter situation is quite common for organometallic compounds containing heavy atoms, where efficient spin–orbit coupling leads to mixing of singlet and triplet states. Strong back-bonding with a metal centre exhibiting large spin–orbit coupling facilitates intersystem crossing, leading to enhanced triplet formation. As both singlet and triplet states are utilised this may lead to a theoretical maximum internal quantum efficiency of 100% [12–14]. Based on these spin-statistics, the modern approach to OLED technology has focussed on employing a triplet-based phosphorescent guest complex in an organic or polymer host layer (e.g. [12,15–19]).

### 1.3. Intermolecular energy transfer from host to guest molecules

Upon electrical excitation excitons are formed in the host layer. To induce electroluminescence in the guest phosphor molecules, excitons must transfer their energy to the excited states of the dopant molecules. There are three mechanisms for energy transfer from the host to the dopant molecule: Förster, Dexter and charge-trapping [20,21].

Förster transfer is a long-range ( $\sim 40$ – $100$  Å) coulombic interaction, involving dipole–dipole coupling of the donor (D) and acceptor (A) states [22]. Due to the need for an allowed

transition in the acceptor, this mechanism only transfers energy to the singlet state of the acceptor molecule via:



Generally, for efficient energy transfer the donor exciton must also be a singlet. However, for donor materials where a triplet-to-ground state transition is weakly allowed the long lifetime of the triplet donor exciton can compensate for the slower rate of energy transfer, to give relatively slow, but still efficient, energy transfer [20,22].

Dexter energy transfer occurs over much shorter ranges ( $\sim 10$  Å), where excitons diffuse from donor to acceptor sites via intermolecular electron exchange [23]. Dexter transfer requires only that spin is conserved. This permits the Dexter process for both singlet–singlet and triplet–triplet transfer.



The rate of Dexter transfer decreases rapidly with increasing donor–acceptor distance and a third mechanism known as charge trapping may successfully compete for triplet–triplet transfer. In charge-trapping the guest molecule traps the charge and generates an exciton by recombination with an opposite charge on a neighbouring molecule [9].

The relative competition between the individual mechanisms of energy transfer in organic light-emitting diodes depends on the lifetime of the exciton, its mobility within the film and the thickness of the emissive film layer. For singlet–singlet modes, although all three mechanisms operate to some extent, Förster energy transfer generally dominates. All three energy transfer mechanisms are also available for triplet excitons, but for this case Dexter and charge-trapping mechanisms are the major modes for triplet exciton energy transfer (Fig. 2).

### 1.4. Requirements of triplet emitters for OLEDs

In the search for novel phosphorescent materials for OLEDs, emission wavelength ( $\lambda_{em}$ ), lifetimes ( $\tau$ ) and quantum yields ( $\Phi_p$ ) must all be considered. For full-colour displays, efficient OLEDs emitting the three primary colours, blue ( $\sim 450$ – $470$  nm), green ( $\sim 500$ – $550$  nm) and red ( $\sim 650$ – $700$  nm), are required. Red and green emitters for OLEDs have been readily identified, however blue emitters remain more challenging due to the large energy gap required between the excited triplet and ground states to obtain this emission wavelength. Long emission lifetimes severely decrease the OLED saturation threshold. If a molecule remains in the triplet state for an extended period, this becomes the limiting factor in the conversion of electrical to photon energy by inhibiting the rapid repopulation of excited states. Consequently the guest phosphor should ideally exhibit a phosphorescence lifetime in the region of 5–50  $\mu$ s at 298 K. Since OLED efficiency is governed by the phosphorescence quantum yield of the dopant molecule, ideally  $\Phi_p$  should approach unity at 298 K. In prac-

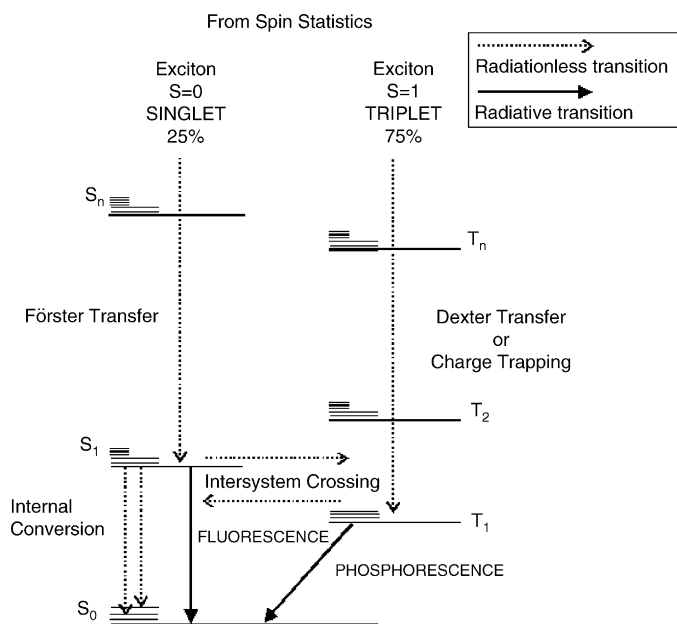


Fig. 2. Population of S<sub>1</sub> and T<sub>1</sub> emitter states by energy transfer from singlet and triplet excitons.

tice this is difficult to achieve, but to obtain any advantage over fluorescence emitters  $\Phi_p$  should be at least 0.25 at 298 K. In addition, suitable triplet emitters should ideally be stable, exhibit reversible redox behaviour and for ease of device fabrication, undergo vacuum sublimation.

### 1.5. Scope of review

This review is not intended to describe the major developments in the design of electroluminescent materials and devices for OLED technology. Several good publications have already adequately reviewed this field in recent years [24,25]. Rather, the purpose of this review is to evaluate the potential of known classes of main-group, transition-metal and lanthanide coordination complexes exhibiting room-temperature phosphorescence, either for direct application as dopants in the emissive layer of OLED devices, or as an aid to deduce which structural trends might lead to new materials for this purpose. Whilst the review is intended to be comprehensive, it is inevitably impossible to include every reported phosphorescent complex, and therefore, attention is drawn to structural classes exhibiting considerable potential in this field, rather than individual species. Written from the chemists' perspective, a systematic analysis of emission characteristics such as wavelength, quantum yields and lifetimes for known classes of phosphorescent complexes is given, and their suitability as OLED phosphors evaluated. Where available, electrochemical data are also included.

### 1.6. Units and standards

We are primarily concerned with characterising compounds with respect to their emission colour. For this reason data are discussed and tabulated in terms of the wavelength of maximum emission intensity,  $\lambda_{em}$ , or in some cases a series of emission

maxima. For those more accustomed to working in electron volts (eV), the emission energy at  $\lambda_{em}$ , is given by

$$\text{Emission energy} = 1240/\lambda_{em} \text{ (eV)} \quad (5)$$

The energy at  $\lambda_{em}$ , of that for the highest energy maximum when a series of maxima is given, can be used as a good approximation to the corresponding state energy.

Where available, electrochemical data are also tabulated. For reversible redox processes the half-peak potential ( $E_{1/2}$ ) is reported for reduction ( $E_{1/2}^{RED}$ ) and/or oxidation ( $E_{1/2}^{OX}$ ), where  $E_{1/2}$  is given by  $E_{1/2} = 1/2(E_{pa} + E_{pc})$ , where  $E_{pa}$  and  $E_{pc}$  are the anodic and cathodic peak potentials respectively. For irreversible couples, the appropriate  $E_{pa}$  or  $E_{pc}$  values are given. All electrochemical data are given as reported in the original literature against the experimental reference electrode used. For comparison, the electrode potentials of some standard reference electrodes versus the normal hydrogen electrode (NHE) at 25 °C are as follows: standard calomel electrode (SCE) = +0.244 V [26], silver/silver chloride (Ag/AgCl) = +0.197 V [27]. In some cases values are reported against the ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) redox couple as an internal standard ( $E_{1/2}$  = +0.42 V versus SCE) [28,29] and in non-polar solvents (e.g. CH<sub>2</sub>Cl<sub>2</sub>) the silver/silver nitrate (Ag/AgNO<sub>3</sub>) electrode is often used as a reference ( $E_{1/2}$  = +0.31 V versus SCE; in MeCN) [30]. Unless otherwise stated all quantum yields are for degassed or N<sub>2</sub> purged solution.

## 2. Structural classes exhibiting room-temperature phosphorescence

### 2.1. Transition metal complexes

In general, emission will occur from the lowest excited electronic state [31]. With judicious ligand selection it is therefore possible to design a series of complexes where the identity of the emitting state is predetermined [31]. This is particularly important when designing new luminescent materials with a specific application in mind.

There are four types of electronic states or transitions expected for transition metal complexes.

- (i) dd states (metal-centred (MC) transition): Upon ligand coordination the metal d orbitals are split. Excited dd states arise from promotion of an electron within d orbitals which are essentially confined to the metal centre.
- (ii) dπ\* states (metal-to-ligand-charge-transfer (MLCT)): These involve excitation of a metal centred electron to a π\* anti-bonding orbital located on the ligand system.
- (iii) π,π\* or n,π\* states (intraligand (IL) transition): Promotion of an electron from a π-bonding or non-bonding orbital to a higher energy anti-bonding orbital gives rise to these states.
- (iv) πd states (ligand-to-metal-charge-transfer (LMCT)): These states arise from the transfer of electronic charge from the ligand π system to a metal centred orbital.

The relative ordering of these four states may be altered by exchanging the metal centre, using different ligands, modifying



Table 1

Photophysical characteristics of selected chromium(III) complexes in aerated aqueous solutions at room temperature

Complex	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau_{\text{P}}$ ( $\mu\text{s}$ )	Reference
$[\text{Cr}(\text{en})_3]^{3+}$	670	$6.2 \times 10^{-5}$	1.85	[43,44]
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	667	$5.5 \times 10^{-5}$	2.2	[43,44]
$[\text{Cr}(\text{NH}_3)_5\text{SCN}]^{2+}$	688	$2.9 \times 10^{-5}$	0.26	[43,44]
$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$	668	$6.0 \times 10^{-7}$	–	[43]
<i>trans</i> - $[\text{Cr}(\text{en})_2(\text{NH}_3)\text{SCN}]^{2+}$	696	$2.4 \times 10^{-4}$	–	[43]
<i>trans</i> - $[\text{Cr}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$	684	$5.3 \times 10^{-7}$	–	[43]
<i>cis</i> - $[\text{Cr}(\text{en})_2(\text{NH}_3)_2]^{3+}$	669	$5.2 \times 10^{-5}$	–	[43]

the ligands or by changing the geometry of the complex [31]. This gives rise to the extensively varied photophysical properties exhibited by transition metal complexes and has led to the design of many new complexes with predetermined luminescent characteristics [31–33].

### 2.1.1. First row transition metal complexes

Due to weak spin–orbit coupling room-temperature phosphorescence is not a common feature of first row transition metal complexes. Low temperature emission in solid glasses has been reported for isolated manganese(I) [34] and manganese(II) complexes [35] and weak phosphorescence has been observed for several Ni(0) complexes in solution [36–38]. However the main examples of room-temperature phosphorescence are chromium(III) and copper(I) complexes.

**2.1.1.1. Chromium(III).** There are several comprehensive reviews detailing the photophysics of chromium(III) complexes [39–41]. Irradiation in the  $d \rightarrow d$ , charge transfer or intra-ligand bands results in population of the excited  $^4T_2$  state in chromium(III) complexes. Subsequent intersystem crossing to the excited  $^2E$  state is efficient ( $10^{10}$ – $10^{11} \text{ s}^{-1}$ ), with yields close to unity frequently obtained [42]. Although both fluorescence ( $^4T_2 \rightarrow ^4A_2$ ) and phosphorescence ( $^2E \rightarrow ^4A_2$ ) have been reported, phosphorescence is more frequently observed. Emission wavelengths are predominantly restricted to the red spectral region, due to the small excited-ground state energy gaps in first row transition metal complexes. Room-temperature quantum yields are typically small ( $10^{-3}$  to  $10^{-8}$ ) but may be enhanced by the incorporation of rigid ligands which limit non-radiative decay processes (Table 1) [40,43,44].

**2.1.1.2. Copper(I).** The  $d^{10}$  configuration of the copper(I) metal centre prevents the stabilisation of its excited states via the ligand field and consequently charge transfer and intra-ligand transitions dominate the photophysics. Emission from copper(I) complexes tends to be weak and short-lived and significant room-temperature phosphorescence is generally confined to multinuclear or cluster complexes of copper, rather than the monomeric species. Short metal–metal internuclear distances and consequently significant interaction between the metal centres are believed to enhance the luminescent properties of polynuclear  $d^{10}$  metal complexes [45].

Phosphorescence emission wavelengths for copper(I) complexes span the visible spectrum. Emission from monomeric ionic Cu(I) complexes is principally located in the red due to the small energy gap between excited and ground states (Table 2) [46,47]. In multinuclear complexes where metal–metal internuclear distances are exceptionally short and/or a formal bond exists between the two centres, emission may result from ligand-to-metal-to-metal charge transfer (LMMCT) states, introducing the possibility of emission wavelengths spanning the visible region [45].

The photophysics of polynuclear copper(I) acetylide complexes has been widely studied [48–50]. Mono-, bi- and polynuclear Cu(I) acetylide complexes have been shown to exhibit long-lived intense phosphorescence both in the solid state and solution (Table 2). Two excellent reviews by Yam's group examine the rich photophysical properties of these complexes in depth [32,48]. The *triangulo* trinuclear Cu(I) acetylides (e.g. **11**) have attracted considerable attention. Judicious selection of the acetylide group may be used to tune the emission wavelength across the visible spectrum, from the blue to the red on substitution with increasingly electron-rich ligands [51]. In these complexes the emitting state is considered to involve a mixture of the triplet LMCT[acetylide  $\rightarrow \text{Cu}_3$ ] state and a metal-centred  $3d^9 4s^1$  state, particularly where Cu–Cu distances are short [48,51].

The copper centre exerts a negligible heavy atom effect in these complexes and, with the exclusion of some exceptional complexes, phosphorescence quantum yields in room-temperature solution are typically low ( $\sim 10^{-4}$ ). However, in the solid state quantum yields in the range of 0.1–0.4 have been observed [49,52]. Furthermore, emission lifetimes for Cu(I) clusters range between 0.1 and 100  $\mu\text{s}$ , falling within acceptable limits for OLED applications.

To date just one OLED device incorporating a copper(I) complex as a triplet emitter has been reported [52]. Ma et al. designed a green OLED device based on the tetranuclear complex  $[\text{Cu}_4(\text{C}\equiv\text{CPh})_4\text{L}_2]$  (where L is 1,8-bis(diphenylphosphino)-3,6-dioxaoctane) in a polyvinylcarbazole (PVK) host matrix. Electroluminescence (EL) was detected at 516 nm with an external emission quantum efficiency,  $\eta_{\text{ext}}$ , of  $\sim 0.1\%$ . The introduction of an electron-transporting layer was shown to enhance the emission efficiency by 10-fold at the same injecting current density, illustrating that shrewd cell design is as crucial as the selection of the guest phosphor (Fig. 3).

### 2.1.2. Second and third row transition metal complexes

Room-temperature phosphorescence in both solution and the solid state is far more frequent for complexes of second and third row transition metals. Strong spin–orbit coupling induced by the heavy atom leads to efficient intersystem crossing from the singlet excited state to the triplet manifold. Furthermore, mixing singlet and triplet states via spin–orbit coupling eliminates the spin-forbidden nature of the  $T_1 \rightarrow S_0$  radiative transition, resulting in high phosphorescence quantum yields.

A large number of second and third row transition metal ions possessing  $d^6$ ,  $d^8$  or  $d^{10}$  electron configuration are known to be luminescent. Complexes of isoelectronic metal ions with  $d^6$ ,  $d^8$

Table 2  
Photophysical and electrochemical properties of some phosphorescent copper(I) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	Reference
<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	700	0.0018	0.19	–	[53]
<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	570	0.15	14.3	–	[53]
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	560	0.16	16.1	–	[53]
<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	630	0.010	1.33	–	[53]
<b>2</b>	CH <sub>2</sub> Cl <sub>2</sub>	663	$1.0 \times 10^{-4}$	0.016	–	[47]
<b>3</b>	CH <sub>2</sub> Cl <sub>2</sub>	670	$0.4 \times 10^{-4}$	0.013	–	[47]
<b>4a</b>	Solid	431, 452	<0.1	–	+0.68 <sup>a,b</sup>	[49]
	Acetone	630	–	–	–	
<b>4b</b>	Solid	440, 468	<0.1	–	+0.70 <sup>a,b</sup>	[49]
	Acetone	626	<0.1	–	–	
<b>4c</b>	Solid	439, 464	<0.1	–	+0.79 <sup>a,b</sup>	[49]
	Acetone	607	<0.1	–	–	
<b>4d</b>	Solid	438, 463	<0.1	–	+0.80 <sup>a,b</sup>	[49]
	Acetone	601	<0.1	–	–	
<b>5</b>	Solid	401	$2.0 \times 10^{-3}$	1.0	–	[54]
<b>6</b>	Solid	415	$3.0 \times 10^{-3}$	2.0	–	[54]
<b>7</b>	Solid	470	$8.0 \times 10^{-2}$	28	–	[54]
<b>8</b>	Solid	462	$4.9 \times 10^{-3}$	4.8	–	[54]
<b>9</b>	Solid	422	$6.8 \times 10^{-3}$	3.7	–	[54]
<b>10</b>	Solid	445, 630	–	20.7	–	[55]
	CH <sub>2</sub> Cl <sub>2</sub>	675	–	4.0	–	
<b>11</b>	Solid	583	–	222	–	[56]
	CH <sub>2</sub> Cl <sub>2</sub>	596	–	40	–	
[Cu(dmphen) <sub>2</sub> ] <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	670	$2.1 \times 10^{-4}$	0.09	–	[57]
[Cu(tmbpy) <sub>2</sub> ] <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	680	$0.5 \times 10^{-4}$	0.02	–	[57]
[Cu(py) <sub>4</sub> ] <sup>+</sup>	Benzene	698	0.04	0.09	–	[58]
[Cu(mor) <sub>4</sub> ] <sup>+</sup>	Benzene	654	0.004	0.03	–	[58]

<sup>a</sup> Quasi-reversible couple.

<sup>b</sup> vs. SCE.

and d<sup>10</sup> electron configurations will be considered respectively, with emphasis placed on the use of ligand tuning to obtain the desired photophysical properties.

#### 2.1.2.1. *d<sup>6</sup> configuration.*

**2.1.2.1.1. Rhenium(I) (*5d<sup>6</sup>*).** Many tricarbonylrhenium(I)  $\alpha, \alpha'$ -diimine complexes of the type  $[\text{Re}(\text{N}^{\text{N}})(\text{CO})_3(\text{L})]^{n+}$  ( $\text{N}^{\text{N}}$ =diimine ligand, L=monodentate ligand and  $n=0$  or 1) are known to exhibit room-temperature phosphorescence [59–73]. Emission wavelengths lie predominantly in the orange–yellow spectral region and lifetimes are in the  $10^2$  to  $10^{-1}$   $\mu\text{s}$  region (Table 3). The origin of emission is typically assigned to the <sup>3</sup>MLCT state [70]. Carbonyl ligands undergo significant  $\pi$  back-bonding with the metal-centre and consequently the energy gap between the metal d orbitals and the  $\pi^*$  ligand orbitals involved in the MLCT transition is small, resulting in low-energy emission.

For these compounds quantum yields are typically small ( $\sim 10^{-3}$ ) when compared with complexes of the later transition metals. However, Demas and DeGraff reported a series of  $[\text{Re}(\text{N}^{\text{N}})(\text{CO})_3(\text{L})]^{n+}$  compounds (**12a–l**) with exceptionally high quantum yields ( $\Phi_{\text{P}}=0.39\text{--}0.77$ ) and long lifetimes in room-temperature solution [59]. In these complexes the ligand localized excited states are situated lower in energy than the

<sup>3</sup>MLCT state and emission originates from the <sup>3</sup> $\pi\text{--}\pi^*$  diimine excited state. Emission quantum yields are enhanced compared to the free ligand due to the heavy-atom effect exerted by the Re(I) centre. This series of complexes is particularly interesting as emission wavelengths are centred between 450 and 500 nm, characteristic of the diimine ligand emission. Along with a novel Re(I) complex containing the cyclophane ligand, phanephos (**13**) [60] these are the only Re(I) complexes encountered emitting in the near-blue spectral region.

The photophysics of tricarbonylrhenium(I)  $\alpha, \alpha'$ -diimine complexes containing an acetylide moiety (e.g. **15a–f**) has also been investigated [48,62,69]. These complexes show intense orange–red phosphorescence in solution and the solid state at room-temperature attributed to a <sup>3</sup>MLCT[ $d\pi(\text{Re}) \rightarrow \pi^*(t\text{-Bu}_2\text{bpy})$ ] transition (Table 3). A blue shift in the emission wavelength is generally obtained on substitution with electron-deficient acetylides [48]. The dinuclear rhenium(I)  $\alpha, \alpha'$ -diimine analogue of **14e** has also been studied, where the acetylide ligand bridges the two Re(I) centre [62]. The emission wavelength is red-shifted by 30 nm to ca. 640 nm when compared to the mononuclear complex (Table 3) [62].

Bisdicarbonylrhenium(I)  $\alpha, \alpha'$ -diimine complexes  $[\text{Re}(\text{N}^{\text{N}})(\text{CO})_2(\text{L})(\text{L}')] ]$  are less frequently encountered due to the lack of a

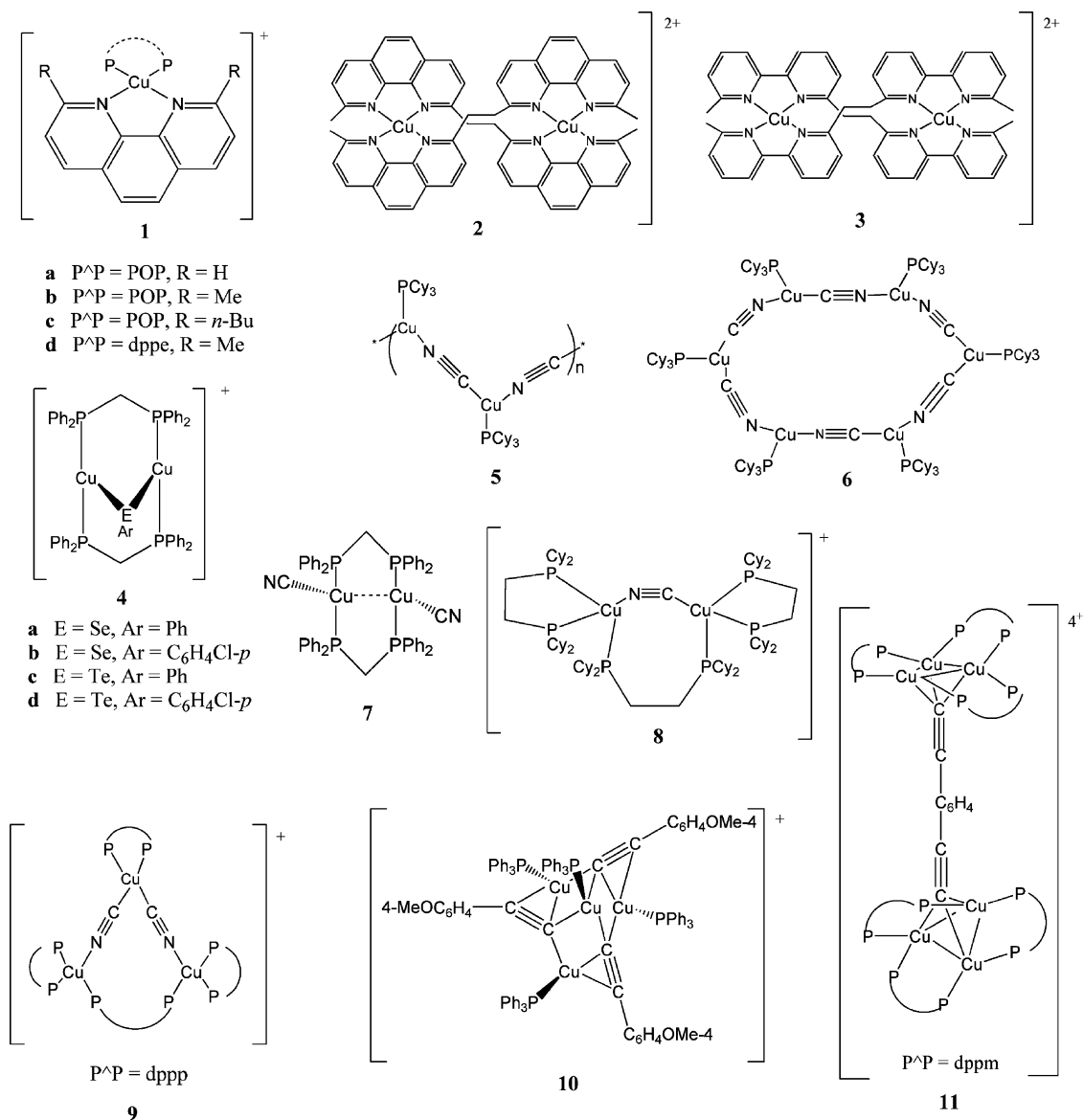


Fig. 3. Structures 1–11.

general synthetic pathway [61,68]. However, from the few examples reported they exhibit several interesting features favorable for OLED technology including room-temperature phosphorescence and thermal and photochemical stability [61,68]. A series of *cis*-, *trans*-[Re(X<sub>2</sub>bpy)(CO)<sub>2</sub>(PR<sub>3</sub>)(Y)]<sup>n+</sup> complexes (**14a–e**) (X<sub>2</sub>bpy = 4,4'-X<sub>2</sub>-2,2'-bipyridine; X = Me, H, CF<sub>3</sub>, R = OEt, Ph, Y = Cl, pyridine, PR<sub>3</sub>) was reported by Ishitani et al. to exhibit relatively long-lived red phosphorescence with reasonable quantum yields [61] (Fig. 4).

The relatively short excited state lifetimes and the excellent thermal, chemical and photochemical stability displayed by Re(I) complexes make them particularly interesting for OLED technology [8,72]. Several OLEDs utilizing Re(I) complexes as the triplet emitter have been reported. Wang et al. prepared a yellow OLED based on [Re(*t*-Bubpy)(CO)<sub>3</sub>Cl] (*t*-Bubpy = 4,4'-bi(*tert*-butyl)-2,2'-bipyridine) with an efficiency of up to 1.6 lm W<sup>-1</sup> [72]. Li et al. have also reported two

highly efficient devices based on [Re(phen)(CO)<sub>3</sub>Cl] and [Re(dmphen)(CO)<sub>3</sub>Cl] doped in a dicarbazole host material [8]. The maximum efficiency and brightness achieved respectively for these devices were 6.67 cd A<sup>-1</sup> and 2769 cd m<sup>-2</sup> for [Re(phen)(CO)<sub>3</sub>Cl] and 7.15 cd A<sup>-1</sup> and 3686 cd m<sup>-2</sup> for [Re(dmphen)(CO)<sub>3</sub>Cl]. Whilst these are promising discoveries, rhenium is an expensive element and any rhenium-based OLED must offer something exceptional for it to be commercially viable.

**2.1.2.1.2. Ruthenium(II) (4d<sup>6</sup>) and osmium(II) (5d<sup>6</sup>).** Luminescent ruthenium(II) complexes containing simple polypyridine ligands such as 2,2'-bipyridine or 1,10-phenanthroline have been the subject of extensive research over the last 50 years [74–98]. The photophysical and electrochemical properties of Ru(II) polypyridyl complexes have been discussed in a comprehensive review by Juris et al. [74] Phosphorescence emission is frequently detected in

Table 3  
Photophysical and electrochemical properties of selected Re(I) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{p}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{RED}}$ (V)	Reference
<b>12a</b>	CH <sub>2</sub> Cl <sub>2</sub>	468 <sup>a</sup>	0.47	120.7	–	–	[59]
<b>12b</b>	CH <sub>2</sub> Cl <sub>2</sub>	468 <sup>a</sup>	0.41	120.3	–	–	[59]
<b>12c</b>	CH <sub>2</sub> Cl <sub>2</sub>	468 <sup>a</sup>	0.40	139.9	–	–	[59]
<b>12d</b>	CH <sub>2</sub> Cl <sub>2</sub>	468 <sup>a</sup>	0.39	135.1	–	–	[59]
<b>12e</b>	CH <sub>2</sub> Cl <sub>2</sub>	466 <sup>a</sup>	0.48	70.5	–	–	[59]
<b>12f</b>	CH <sub>2</sub> Cl <sub>2</sub>	466 <sup>a</sup>	0.56	63.3	–	–	[59]
<b>12g</b>	CH <sub>2</sub> Cl <sub>2</sub>	466 <sup>a</sup>	0.53	68.9	–	–	[59]
<b>12h</b>	CH <sub>2</sub> Cl <sub>2</sub>	462 <sup>a</sup>	0.68	23.8	–	–	[59]
<b>12i</b>	CH <sub>2</sub> Cl <sub>2</sub>	466 <sup>a</sup>	0.69	28.7	–	–	[59]
<b>12j</b>	CH <sub>2</sub> Cl <sub>2</sub>	458 <sup>a</sup>	0.77	10.6	–	–	[59]
<b>12k</b>	CH <sub>2</sub> Cl <sub>2</sub>	474 <sup>a</sup>	0.75	19.2	–	–	[59]
<b>12l</b>	CH <sub>2</sub> Cl <sub>2</sub>	496 <sup>a</sup>	0.60	44.4	–	–	[59]
<b>13</b>	MeCN	480	–	–	–	–	[60]
<b>14a</b>	DMF	620	0.031	0.35	+1.09 <sup>b,c,d,e</sup>	–1.71 <sup>f,c,d</sup> , –2.26 <sup>b,c,d,g</sup>	[61]
<b>14b</b>	MeCN	618	0.017	0.25	+1.10 <sup>f,c,d</sup>	–1.71 <sup>f,c,d</sup> , –2.32 <sup>b,c,d,g</sup>	[61]
<b>14c</b>	DMF	619	0.037	0.64	+1.10 <sup>b,c,d,e</sup>	–1.71 <sup>f,c,d</sup> , –2.26 <sup>b,c,d,g</sup>	[61]
<b>14d</b>	DMF	612	0.040	0.56	+1.05 <sup>b,c,d,e</sup>	–1.80 <sup>f,c,d</sup> , –2.33 <sup>b,c,d,g</sup>	[61]
<b>14e</b>	MeCN	609	0.026	0.34	+1.06 <sup>b,c,d,e</sup>	–1.80 <sup>f,c,d</sup> , –2.37 <sup>b,c,d,g</sup>	[61]
<b>15a</b>	THF	700	–	0.13	–	–	[48,62]
<b>15b</b>	THF	670	–	0.25	–	–	[48,62]
<b>15c</b>	THF	688	–	0.20	–	–	[48,62]
<b>15d</b>	THF	680	–	<0.1	–	–	[48]
<b>15e</b>	CH <sub>2</sub> Cl <sub>2</sub>	610	–	<0.1	–	–	[48]
<b>15f</b>	CH <sub>2</sub> Cl <sub>2</sub>	670	–	<0.1	–	–	[48]
[Re(bpy)(CO) <sub>3</sub> Cl]	CH <sub>2</sub> Cl <sub>2</sub>	642	0.0031	0.039	–	–	[63]
[Re(Fbpy)(CO) <sub>3</sub> Cl]	CH <sub>2</sub> Cl <sub>2</sub>	637	0.0021	–	+1.24, +1.67 <sup>b,c,h</sup>	–1.43 <sup>f,c,h</sup> , –1.79 <sup>b,c,h</sup>	[63]
[Re(FbpyF)(CO) <sub>3</sub> Cl]	CH <sub>2</sub> Cl <sub>2</sub>	651	0.0008	–	+1.26, +1.61 <sup>b,c,h</sup>	–1.29 <sup>f,c,h</sup> , –1.80 <sup>b,c,h</sup>	[63]
[Re(binap)(CO) <sub>3</sub> Cl]	EtOH	570	0.007	–	–	–	[64]
[Re(CO) <sub>4</sub> (ox)]	MeCN	653	–	–	–	–	[65]
[Re(phen)(CO) <sub>3</sub> Cl]	MeCN	573	0.0177	0.183	–	–	[66]
[Re(ephen)(CO) <sub>3</sub> Cl]	MeCN	585	0.0013	0.0015	–	–	[66]
[Re(CO) <sub>4</sub> (bt)]	MeCN	521,562,606 <sup>i</sup>	0.3	15	+0.84 <sup>f,j,d</sup>	–2.08 <sup>b,j,d</sup>	[67]

<sup>a</sup> At 77 K.

<sup>b</sup> Irreversible couple.

<sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>d</sup> Reversible/quasi-reversible couple.

<sup>e</sup>  $E_{\text{pc}}$ .

<sup>f</sup> Estimated from emission spectrum.

<sup>g</sup> vs. Ag/AgNO<sub>3</sub>.

<sup>h</sup>  $E_{\text{pa}}$ .

<sup>i</sup> vs. Fc/Fc<sup>+</sup>.

<sup>j</sup> In MeCN.

room-temperature fluid solution from these complexes and is attributed to low-lying <sup>3</sup>MLCT excited states. Phosphorescence quantum yields range between 10<sup>–1</sup> and 10<sup>–3</sup> and lifetimes are in the region of 1  $\mu\text{s}$  in room-temperature solution (Table 4). Ligand tuning has proved largely ineffective and emission wavelengths are generally restricted to the orange-red spectral region.

Extensive work has been carried out on dinuclear ruthenium(II) and osmium(II) homo- and heterometallic complexes by de Cola and coworkers [90–98]. In these complexes the two metal centres are connected either by an organic wire type bridge [90–96] or by a photoactive switching unit [97,98]. This latter class of materials is particularly interesting as they behave as photoactive molecular switches. The photophysical properties of some specific Ru–Ru, Os–Os and Ru–Os systems will be discussed in more depth in Section 2.5.

In recent years the electrochemistry of the ruthenium(II)  $\alpha,\alpha'$ -diimines has been investigated and several light-emitting electrochemical cells (LECs) based on tris(bipyridyl)ruthenium(II) and its derivatives have been prepared [87,99–102]. Handy et al. reported a device consisting of a solid state film of [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> sandwiched between two electrodes with an external quantum efficiency of 1% [99]. The external quantum efficiency was later improved to 3% by diluting the lumophore in a polymer such as polymethylmethacrylate (PMMA) [101]. This remains to date the maximum external quantum efficiency obtained for a Ru(II) based LEC (Fig. 5).

Osmium(II) polypyridine complexes have also been intensively studied [75,103–108]. Osmium(II) complexes exhibit much shorter emission lifetimes ( $\sim 10^{-2}$   $\mu\text{s}$ ) than their ruthenium(II) analogues due to strong backbonding to the ligands from the osmium centre [91,109]. However, it has been demon-



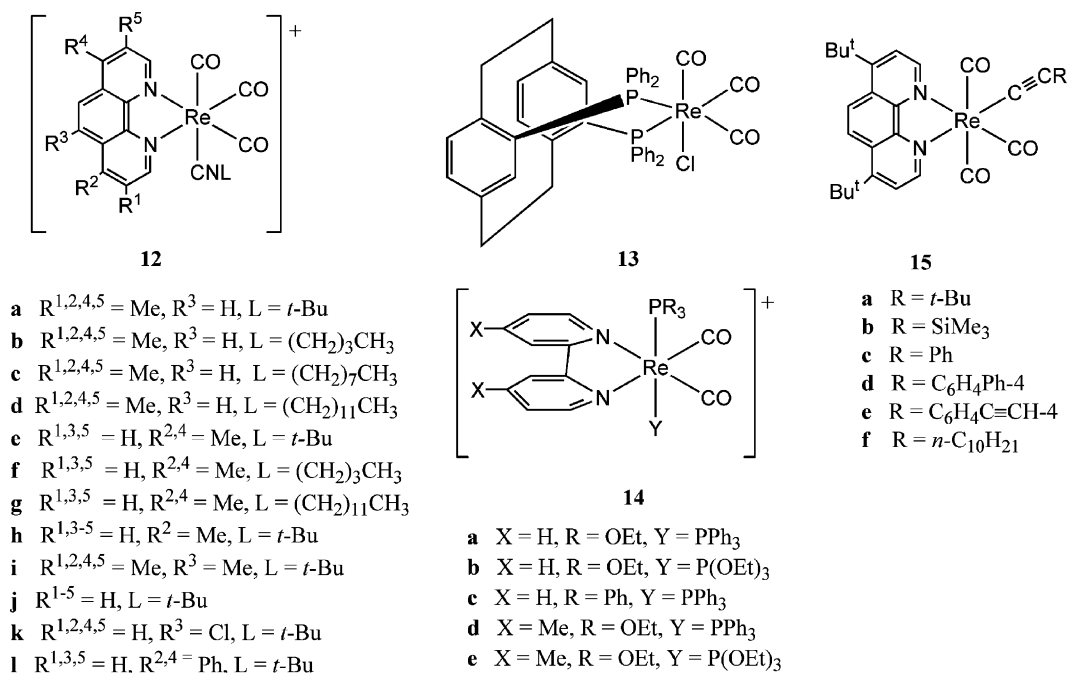


Fig. 4. Structures 12–15.

strated that the incorporation of strong  $\pi$ -acid ligands such as phosphine or arsine, in combination with polypyridyl ligands can extend the excited triplet state triplet lifetime to tens of microseconds [103,104,106,108]. In these complexes the  $^3\text{MLCT}$  excited state is low-lying and coincides with the  $\pi\pi^*$  IL states; equilibrium between these two states results in an extended excited state lifetime (Table 5).

Simple osmium(II) tris- $\alpha,\alpha'$ -diimine complexes such as  $[\text{Os}(\text{bpy})_3]^{2+}$  or  $[\text{Os}(\text{phen})_3]^{2+}$  emit in the far red/near-IR region [75,103]. However, with judicious ligand selection, it has been possible to blue-shift the emission bands from the infrared as far as the green spectral region with a mixed ligand system [104]. Phelan et al. reported a series of  $[\text{OsCl}(\text{N}^*\text{N})(\text{L}^*\text{L})]^+$  complexes ( $\text{N}^*\text{N} = 1,10$ -phenanthroline derivative and  $\text{L}^*\text{L} =$  phosphine type ligand) (21a–c) where the osmium emission was tuned from yellow, to yellow–green, and then green, on increasing the  $\sigma$ -donor character of the ligand [104]. These complexes exhibit exceptionally high room-temperature quantum yields (0.63–0.75) compared to red and orange emitting osmium complexes, which is in accordance with the energy gap law [104,110]. Several osmium(II) complexes containing the 2-pyridyl pyrazolate ligand and emitting in the blue region have been recently reported (24a–e) [105,106]. Quantum yields as high as 0.42 (24a) were obtained and this is attributed to a combination of the heavy atom effect, the relative orientation of the 2-pyridyl pyrazolate ligand and the presence of a  $\pi$ -accepting CO ligand [106]. The ligand orientation is believed to be especially important since the “loose-bolt” effect of metal–ligand bonding interactions may result in rapid radiationless deactivation of excited states.

Several red OLED devices based on osmium(II) phosphors have already been reported [16,104,111–113] and it has been shown that Os(II) complexes trap both electrons and holes

on the complex site, enhancing the device efficiency [112]. Recently Carlson et al. prepared a series of OLEDs consisting of  $[\text{Os}(\text{N}^*\text{N})_2(\text{L}^*\text{L})]^{2+}$  derivatives ( $\text{N}^*\text{N} =$  a bipyridine or phenanthroline and  $\text{L}^*\text{L} =$  phosphine or arsine) doped in a PVK /PBD blend [104]. The highest external quantum efficiency of 0.78% was obtained for a double layer device based on (21g) and it was found that generally complexes using the arsine ligand exhibited higher quantum yields than those using the phosphine ligand [104].

**2.1.2.1.3. Rhodium (III) ( $4d^6$ ) and iridium(III) ( $5d^6$ ).** Although room-temperature phosphorescence from iridium(III) complexes is well-known, rhodium(III) phosphorescence is generally limited to low temperature glasses [114,115] with a few exceptions such as cyclometallated rhodium(III) diimine complexes (26a–e, 27a–c) [116,117]. This is a consequence of higher spin–orbit coupling in iridium, which leads to more efficient mixing of the singlet and triplet states. Emission wavelengths are substantially blue-shifted in comparison to the isoelectronic group 8 metal ions, Ru(II) and Os(II), with typical emission observed between 500 and 600 nm for Ir(III) complexes in both solution and solid state at room-temperature (Table 6).

Most studies have centred around iridium (III) complexes containing cyclometallated ligands such as 2-phenylpyridine and its derivatives (Table 7) [17,18,118–131]. The use of cyclometallated ligands enables the formation of neutral Ir(III) complexes which is advantageous for OLED technology. The origin of phosphorescence is typically attributed to a  $^3\text{MLCT}$  excited state [131], although when electron-withdrawing ligands are employed, which decrease the energy of the  $^3\pi\pi^*$  states, emission may be considered to be a mixture of both MLCT and IL character [118]. Ir(III) complexes typically exhibit high phosphorescence quantum yields ( $\Phi_p = 0.1$ –0.9) and excited state lifetimes in the microsecond region [18,120].

Table 4

Photophysical and electrochemical properties of selected phosphorescent ruthenium(II) complexes at room temperature

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{RED}}$ (V)	Reference
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>		626	0.062	0.9			[75]
	MeCN	606	0.075	0.87	+1.33 <sup>a,b,c</sup>	−1.33 <sup>a,b,c</sup>	[76]
[Ru(phen) <sub>3</sub> ] <sup>2+</sup>	EtOH	587	0.023	0.34	+1.35 <sup>a,b,c</sup>	−1.36 <sup>a,b,c</sup>	[76]
<b>16a</b>	MeCN	614	0.0023	0.940	—	—	[77]
<b>16b</b>	MeCN	711	0.0012	0.258	—	—	[77]
<b>16c</b>	MeCN	660	0.045	0.615	—	—	[77]
<b>16d</b>	MeCN	711	0.0011	0.271	—	—	[77]
<b>16e</b>	MeCN	711	0.0004	0.425	—	—	[77]
<b>16f</b>	MeCN	637	0.0022	0.534	—	—	[77]
<b>16g</b>	MeCN	660	0.0026	0.671	—	—	[77]
<b>16h</b>	H <sub>2</sub> O	630	0.00036	0.41	—	—	[78]
<b>16i</b>	H <sub>2</sub> O	620	0.025	0.470	—	—	[79]
<b>16j</b>	H <sub>2</sub> O	686	0.006	0.299	—	—	[80]
<b>16k</b>	MeCN	620	—	0.9	—	—	[81]
<b>17a</b>	MeCN	616	0.063	0.84	—	—	[82]
<b>17b</b>	MeCN	671	0.011	56.5	—	—	[82]
<b>17c</b>	MeCN	640	0.092	1.51	—	—	[82]
<b>17d</b>	MeCN	611	0.044	0.50	—	—	[82]
<b>17e</b>	MeCN	672	0.009	65.1	—	—	[82]
<b>17f</b>	MeCN	634	0.122	1.38	—	—	[82]
<b>17g</b>	MeCN	636	0.088	1.26	—	—	[82]
<b>17h</b>	MeCN	690	0.013	4.96	—	—	[82]
<b>17i</b>	MeCN	675	0.037	0.72	—	—	[82]
<b>17j</b>	MeCN	623	0.062	1.076	+1.48 <sup>a,d,e</sup>	−1.35, −1.73 <sup>a,d,e</sup>	[63]
<b>17k</b>	MeCN	650	0.058	1.187	+1.53 <sup>a,d,e</sup>	−1.19, −1.68 <sup>a,d,e</sup>	[63]
<b>18a</b>	MeCN	615	0.06	0.76	+1.32 <sup>a,b</sup>	−1.30, −1.49 <sup>a,b</sup>	[83]
<b>18b</b>	MeCN	610	0.09	0.698	+1.33 <sup>a,b</sup>	−1.26, −1.48, −1.72 <sup>a,b</sup>	[83]
<b>18c</b>	MeCN	605	0.038	33.78	—	—	[84]
<b>18d</b>	MeCN	595	0.013	60.80	—	—	[84]
<b>19a</b>	EtOH	595	0.053	0.90	—	—	[76]
<b>19b</b>	EtOH	599	0.053	0.90	+1.29 <sup>a,b,c</sup>	−1.37, −1.55 <sup>a,b,c</sup>	[76]
<b>19c</b>	EtOH	605	0.064	1.025	+1.40 <sup>a,b,c</sup>	−1.32, −1.50, −1.87 <sup>a,b,c</sup>	[76]
<b>20a</b>	EtOH	594	0.055	1.005	+1.33 <sup>a,b,c</sup>	−1.36, −1.53, −1.63 <sup>a,b,c</sup>	[76]
<b>20b</b>	EtOH	596	0.050	0.88	+1.25 <sup>a,b,c</sup>	−1.40, −1.54 <sup>a,b,c</sup>	[76]
<b>20c</b>	EtOH	596	0.057	0.85	+1.29 <sup>a,b,c</sup>	−1.42, −1.54 <sup>a,b,c</sup>	[76]

<sup>a</sup> Reversible couple.<sup>b</sup> vs. SCE.<sup>c</sup> In MeCN.<sup>d</sup> vs. Ag/AgNO<sub>3</sub>.<sup>e</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

The occurrence of phosphorescence from both <sup>3</sup>MLCT and <sup>3</sup>IL excited states means that Ir(III) complexes respond well to ligand tuning. Recently Hwang et al. reported a series of Ir(III) complexes bearing two substituted quinoxalines (**29a–d**) exhibiting red emission [118]. With judicious ligand selection the energy gap between the ground  $\pi\pi^*$  state and the excited MLCT state was reduced, either by substituting a nitrogen atom with a less electronegative carbon atom (**29c**), or by extending the  $\pi$ -electron delocalization of the aromatic chromophore [118]. Furthermore, by employing a rigid ligand framework, radiationless decay was minimized and quantum yields between 0.4 and 0.85 were obtained [118].

Blue-emitting iridium(III) based complexes have been reported [17,18,119,125,130,132,133]. Coppo et al. reported a series of blue-emitting phenylpyridine Ir(III) complexes with triazolyl pyridine derivatives as the ancillary ligands [125]. Laskar et al. recently extended this work on phenylpyridine complexes by introducing strong electron donating substituents such as

OMe at the *para*-position of the pyridyl ligand (**34a–c**) [119]. The incorporation of electron-rich ligands raises the energy of the lowest excited state, thus increasing the HOMO–LUMO energy gap and resulting in a blue-shift in the emission wavelength when compared to the parent complex [119]. Nazeeruddin et al. also reported a series of blue-emitting mixed ligand Ir(III) complexes containing electron-rich ancillary ligands such as CN, NCS, NCO with exceptionally high room-temperature quantum yields ( $\Phi_{\text{P}} = 0.9$ ) [18].

Due to their desirable photophysical properties Ir(III)-based triplet emitters have attracted substantial interest for OLED technology [5–7,15,18,118,119,134–140], with the major developments originating from the collaboration between Thompson (University of Southern California) and Forrest (Princeton University). Several highly efficient green devices using [Ir(ppy)<sub>3</sub>] or [Ir(ppy)<sub>2</sub>(acac)] as the emitting materials with external quantum efficiencies reaching 19% have been reported [6,7,134]. Devices emitting in other regions of the visible spectrum have

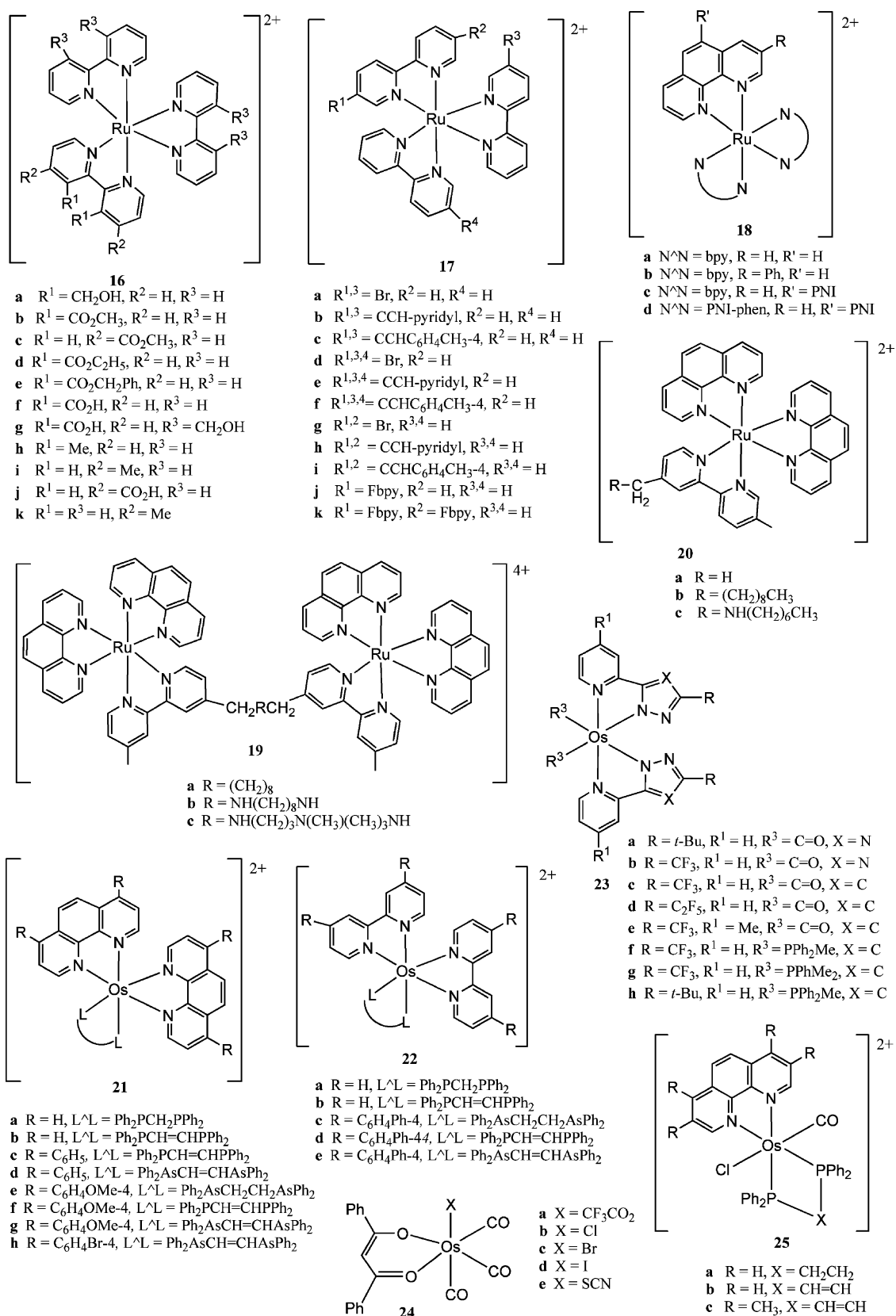


Fig. 5. Structures 16–25.

Table 5  
Photophysical and electrochemical properties of selected phosphorescent osmium(II) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{p}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{RED}}$ (V)	Reference
$[\text{Os}(\text{bpy})_3]^{2+}$	MeCN	740	0.005	0.049	–	–	[75]
$[\text{Os}(\text{phen})_3]^{2+}$	MeCN	690	–	0.08	+0.82 <sup>a,b,c</sup>	–1.21 <sup>a,b,c</sup>	[103]
<b>21a</b>	MeCN	610	–	1.13	+1.32 <sup>a,b,c</sup>	–1.24 <sup>a,b,c</sup>	[103]
<b>21b</b>	MeCN	596	–	1.84	+1.41 <sup>a,b,c</sup>	–1.22 <sup>a,b,c</sup>	[103]
<b>21c</b>	EtOH	613	0.33	1.81	–	–	[104]
<b>21d</b>	EtOH	623	0.38	1.53	–	–	[104]
<b>21e</b>	EtOH	635	0.27	1.20	–	–	[104]
<b>21f</b>	EtOH	611	0.36	1.97	–	–	[104]
<b>21g</b>	EtOH	629	0.45	1.55	–	–	[104]
<b>21h</b>	EtOH	635	0.39	1.40	–	–	[104]
<b>22a</b>	MeCN	622	–	0.3	+1.27 <sup>a,b,c</sup>	–1.26 <sup>a,b,c</sup>	[104]
<b>22b</b>	MeCN	609	–	0.5	+1.40 <sup>a,b,c</sup>	–1.26 <sup>a,b,c</sup>	[103]
<b>22c</b>	EtOH	650	0.19	0.41	–	–	[104]
<b>22d</b>	EtOH	623	0.23	0.52	–	–	[104]
<b>22e</b>	EtOH	640	0.25	0.46	–	–	[104]
<b>23a</b>	MeCN	455, 480, 507	0.42	39.9	–	–	[105]
<b>23b</b>	MeCN	420, 446, 468	0.233	2.88	–	–	[105]
<b>23c</b>	MeCN	430, 457, 480	0.14	18.5	–	–	[106]
<b>23d</b>	MeCN	430, 455, 480	0.0869	13.4	–	–	[106]
<b>23e</b>	MeCN	428, 455, 480	0.0406	6.3	–	–	[106]
<b>23f</b>	$\text{CH}_2\text{Cl}_2$	620	0.5	0.86	+0.23 <sup>a,d,e</sup>	–	[107]
<b>23g</b>	$\text{CH}_2\text{Cl}_2$	631	0.19	0.73	+0.16 <sup>a,d,e</sup>	–	[107]
<b>23h</b>	$\text{CH}_2\text{Cl}_2$	648	0.25	0.63	+0.18 <sup>a,d,e</sup>	–	[107]
<b>24a</b>	$\text{CH}_2\text{Cl}_2$	538	0.13	64	+1.75 <sup>f,g,c,h</sup>	–1.53 <sup>f,g,c,h</sup>	[108]
<b>24b</b>	$\text{CH}_2\text{Cl}_2$	557	0.13	46	+1.68 <sup>f,g,c,h</sup>	–1.60 <sup>f,g,c,h</sup>	[108]
<b>24c</b>	$\text{CH}_2\text{Cl}_2$	563	0.08	29	+1.64 <sup>f,g,c,h</sup>	–1.58 <sup>f,g,c,h</sup>	[108]
<b>24d</b>	$\text{CH}_2\text{Cl}_2$	574	0.007	0.72	+1.60 <sup>f,g,c,h</sup>	–1.59 <sup>f,g,c,h</sup>	[108]
<b>24e</b>	$\text{CH}_2\text{Cl}_2$	539	0.13	53	+1.74 <sup>f,g,c,h</sup>	–1.55 <sup>f,g,c,h</sup>	[108]
<b>25a</b>	EtOH	522	0.75	38.0	–	–	[104]
<b>25b</b>	EtOH	553	0.70	7.5	–	–	[104]
<b>25c</b>	EtOH	561	0.63	6.5	–	–	[104]

<sup>a</sup> Reversible couple.

<sup>b</sup> In MeCN.

<sup>c</sup> vs. Ag/AgCl.

<sup>d</sup> In  $\text{CH}_2\text{Cl}_2$ .

<sup>e</sup> Irreversible couple.

<sup>f</sup> vs. quasi-Ag electrode.

<sup>g</sup> vs. SCE.

<sup>h</sup>  $E_{\text{pa}}$ .

also been prepared. A yellow OLED based on  $[\text{Ir}(\text{bt})_2(\text{acac})]$  and a red device based on  $[\text{Ir}(\text{btp})_2(\text{acac})]$  were reported by the Thompson group with maximum external quantum efficiencies of 9.5 and 11.6%, respectively [134,135].

A red device based on complex (**29a**) doped in a PVK-PBD polymer blend was also reported [118]. The maximum external quantum efficiency was 3.15% with a brightness of  $1751 \text{ cd m}^{-2}$  at a current density of  $67.4 \text{ mA cm}^{-2}$  [118]. There have been limited reports of blue Ir(III)-based OLEDs. The Thompson group reported a blue device emitting at 470 nm with an external quantum efficiency of 5.7%, where emission from the higher energy blue triplet state of the  $[\text{Ir}(\text{N}^{\wedge}\text{N})_2(\text{pic})]$  phosphor ( $\text{N}^{\wedge}\text{N}$  = bis(4,6-difluorophenyl)-pyridinato-*N,C2'*) was forced by endothermic energy transfer from the CBP host [15]. Laskar et al. prepared a device using  $[\text{Ir}(\text{F}_2\text{MeOppy})_2(\text{acac})]$  (**34b**) doped in a CBP host yielding blue emission with a maximum at 472 nm and an external quantum efficiency of  $0.66 \text{ cd m}^{-2}$  at  $20 \text{ mA cm}^{-2}$  [119]. The efficiency was improved to  $1.63 \text{ cd m}^{-2}$  on doping in a *m*CP host [119]. Recently Tokito et al. reported a blue OLED incor-

porating  $[\text{Ir}(3,5\text{-F}_2\text{-ppy})_2(\text{pic})]$  in the emissive layer exhibiting a maximum external quantum efficiency of 10.4% [141]. A white device incorporating two emissive layers, a blue–green one incorporating  $[\text{Ir}(\text{CF}_3\text{ppy})_2(\text{pic})]$  and a red one based on  $[\text{Ir}(\text{btp})_2(\text{pic})]$ , with a maximum external quantum efficiency of 12% was also reported by the same group [141] (Fig. 6).

**2.1.2.2.  $d^8$  configuration: palladium(II) ( $4d^8$ ) and platinum(II) ( $5d^8$ ).** Although fewer  $d^8$  metal complexes are known to be emissive in fluid solution at room-temperature compared to the  $d^6$  metal ions already discussed, the phosphorescence of mono- and dinuclear platinum(II) complexes has been well-documented [144–158]. The heavy Pt(II) metal ion results in strong spin–orbit coupling in these complexes, which promotes efficient mixing of singlet and triplet states, thus enhancing phosphorescence emission and shortening emission lifetimes. The heavy atom effect exerted by a Pd(II) metal centre is much weaker and consequently phosphorescent palladium(II) complexes are rare when compared with analogous Pt(II)

Table 6  
Photophysical and electrochemical properties of selected phosphorescent rhodium(III) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{RED}}$ (V)	Reference
<b>26a</b>	MeCN	506, 545, 586	0.030	6.63	+1.64 <sup>a,b,c,d</sup>	−1.45 <sup>e,b,c</sup> , −1.60, −1.75, −2.31, −2.56 <sup>a,b,c,f</sup>	[116]
<b>26b</b>	MeCN	506, 545, 586	0.021	6.28	+1.68 <sup>a,b,c,d</sup>	−1.50 <sup>e,b,c</sup> , −1.65, −1.78, −2.30, −2.54 <sup>a,b,c,f</sup>	[116]
<b>26c</b>	MeCN	506, 545, 586	0.030	7.92	+1.71 <sup>a,b,c,d</sup>	−1.43 <sup>e,b,c</sup> , −1.63, −1.91, −2.38, −2.70 <sup>a,b,c,f</sup>	[116]
<b>26d</b>	MeCN	506, 545, 586	0.032	7.67	+1.64 <sup>a,b,c,d</sup>	−1.52 <sup>e,b,c</sup> , −1.67, −1.87, −2.38, −2.73 <sup>a,b,c,f</sup>	[116]
<b>26e</b>	MeCN	506, 545, 586	0.028	8.68	+1.70 <sup>a,b,c,d</sup>	−1.40 <sup>e,b,c</sup> , −1.59, −1.99, −2.22, −2.41 <sup>a,b,c,f</sup>	[116]
<b>27a</b>	MeCN <sup>g</sup>	460	–	<0.015	–	–	[117]
<b>27b</b>	MeOH <sup>h</sup>	454	–	<0.05	+1.1 <sup>a,i,d</sup>	−1.41 <sup>j,i,k</sup>	[117]
<b>27c</b>	MeOH	526, 565	–	1.0	+1.1 <sup>a,i,k,d</sup>	−1.42 <sup>j,i,k</sup>	[117]

<sup>a</sup> Irreversible couple.

<sup>b</sup> vs. SCE.

<sup>c</sup> In MeCN.

<sup>d</sup>  $E_{\text{pa}}$ .

<sup>e</sup> Quasi-reversible couple.

<sup>f</sup>  $E_{\text{pc}}$ .

<sup>g</sup> 263 K.

<sup>h</sup> 222 K – no emission detected at higher temperatures.

<sup>i</sup> vs. NHE.

<sup>j</sup> Reversible couple.

<sup>k</sup> In DMF.

lumophores. Most Pd(II) systems display weak triplet emission only at low temperatures [159,160], with room-temperature emission generally restricted to fluorescence [155,161–163], although a phosphorescent Pd(II)  $\alpha,\alpha'$ -diimine complex (**37**) emitting at 650 nm ( $\tau = 1 \mu\text{s}$ ) in room-temperature solution has recently been reported [159]. In contrast to metalloporphyrins of the earlier transition metals, platinum(II) and palladium(II) porphyrins display intense red phosphorescence due to the enhanced heavy-atom effect [164]. Exceptionally high quantum yields are obtained for platinum(II) porphyrins; 0.9 for PtTPP in a low-temperature glass [165] and 0.45 for PtOEP in room-temperature solution [166]. Quantum yields for palladium(II) porphyrins are significantly lower; 0.08 and 0.43 for PdTPP and PdOEP respectively at 77 K [167]. Phosphorescence lifetimes range from 10 to 100  $\mu\text{s}$  for platinum and palladium porphyrins, which are on the margins of suitability for OLED applications [165–167].

Not until the late 1980s did the first reports of room-temperature phosphorescence in fluid solution from square planar platinum(II) complexes appear [117,146,168,169]. Emission from simple mononuclear Pt(II) bipyridine or terpyridine complexes is rarely detected due to the presence of low lying metal-centred excited states, which provide facile radiationless deactivation pathways via molecular distortion [150]. Thus, in order to obtain significant luminescence at room temperature it is necessary to utilize ligands with low-lying excited state orbitals and/or a large electron donating ability. The strong ligand field associated with such ligands raises the energy of the metal d–d states, withdrawing their deactivating effect. Cyclometalated ligands such as 2-phenylpyridine and its analogues exert this effect due to the strong ligand field associated with the cyclometalated carbon (**38**, **43**, **48**) [144,149,170]. Room-temperature phosphorescence is observed from many cyclometalated Pt(II) complexes, either from excited  $\pi$ – $\pi^*$  or MLCT states. The origin of the emission is largely dependent on the substituents on the cyclometalated ligands and also the

coordination mode of the ligand, that is, whether the ligand coordinates via  $\text{N}^*\text{N}^*\text{C}$ ,  $\text{C}^*\text{N}^*\text{C}$  or  $\text{N}^*\text{C}^*\text{N}$  modes [171–173] (Fig. 7). Emission from mononuclear platinum(II) complexes generally occurs in the red spectral region (Table 8). Lu et al. have recently reported the successful use of ligand tuning to modify the emission wavelength in a series of  $[\text{Pt}(\text{C}^*\text{N}^*\text{N})(\text{C}\equiv\text{C})\text{nR}]$  complexes where ( $\text{C}^*\text{N}^*\text{N}$ ) is a cyclometalated aryl-2,2'-bipyridine (**43a–i**) [149]. Substitution at the para-position of the ( $\text{C}^*\text{N}^*\text{N}$ ) ligand resulted in a blue shift in emission energy for electron-donating groups and in a red-shift for electron-withdrawing groups, consistent with emission from a  $^3\text{MLCT}$  state [149]. Williams et al. reported an interesting series of Pt(II) complexes with cyclometalated  $\text{N}^*\text{C}^*\text{N}$ -coordinating bipyridylbenzene ligands (**38a–c**) [144]. These complexes show intense green luminescence ( $\lambda_{\text{em}} = 480$ –580 nm) in solution, attributed to emission primarily from a  $3\pi$ – $\pi^*$  excited state. Exceptionally high phosphorescence quantum yields ( $\Phi_{\text{P}} = 0.58$ –0.68) were obtained, which are much higher than those previously reported for cyclometalated–Pt(II) complexes.

The development of a number of luminescent complexes containing the dinuclear Pt(II) core has been reported since the discovery of the green phosphorescent complex  $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$  [174–176].  $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$  exhibits intense room-temperature phosphorescence at 514 nm ( $\tau \sim 9 \mu\text{s}$ ), attributed to emission from the MLCT state [175]. Dinuclear platinum(II) acetylide complexes have also received considerable attention and extensive work has been carried out on these complexes by Yam and coworkers (Table 9) [48,177–180]. They reported a series of dinuclear Pt(II) acetylides with an A-frame structure,  $[\text{Pt}_2(\mu\text{-dppm})(\mu\text{-C}\equiv\text{C-R})(\text{C}\equiv\text{C-R})]^+$ , which exhibit long-lived room-temperature luminescence in both solution and the solid state (**52a–f**) [178,179]. As the R group of the ligand becomes increasingly electron-withdrawing a red-shift in the emission energy is observed. Emission in these complexes has been



Table 7  
Photophysical and electrochemical properties of selected phosphorescent iridium(III) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{RED}}$ (V)	Reference
<b>28a</b>	MeCN	458	0.025	1.0	–	–0.76, –0.91 <sup>a,b,c,d</sup>	[17]
<b>28b</b>	MeCN	506	0.022	1.6	–	–0.77, –0.92 <sup>e,c,d</sup>	[17]
<b>28c</b>	MeCN	506	0.029	2.4	–	–0.81, –0.91 <sup>a,b,c,d</sup>	[17]
<b>28d</b>	MeCN	506	0.026	2.3	–	–0.81, –0.89, –1.04 <sup>a,b,c,d</sup>	[17]
<b>29a</b>	CH <sub>2</sub> Cl <sub>2</sub>	642	0.40	1.9	+0.76 <sup>e,f,g</sup>	–1.73, –2.06 <sup>e,f,g</sup>	[118]
<b>29b</b>	CH <sub>2</sub> Cl <sub>2</sub>	630	0.83	2.8	+0.96 <sup>e,f,g</sup>	–1.65, –2.00 <sup>e,f,g</sup>	[118]
<b>29c</b>	CH <sub>2</sub> Cl <sub>2</sub>	622	0.85	3.3	+1.03 <sup>e,f,g</sup>	–1.61, –1.95 <sup>e,f,g</sup>	[118]
<b>29d</b>	CH <sub>2</sub> Cl <sub>2</sub>	649	0.62	1.9	+0.77 <sup>e,f,g</sup>	–1.71, –2.04 <sup>e,f,g</sup>	[118]
<b>30a</b>	CH <sub>2</sub> Cl <sub>2</sub> solid	470, 502	0.94	–	+0.91 <sup>h,f,g</sup>	–1.7 <sup>a,b,f,g</sup>	[18]
		500	0.75	3.14			
<b>30b</b>	CH <sub>2</sub> Cl <sub>2</sub> solid	506, 520	0.97	–	+0.45 <sup>h,f,g</sup>	–1.95 <sup>a,b,f,g</sup>	[18]
		506	0.78	1.43			
<b>30c</b>	CH <sub>2</sub> Cl <sub>2</sub> solid	538, 560	0.99	–	+0.18 <sup>h,f,g</sup>	–2.07 <sup>a,b,f,g</sup>	[18]
		556	0.86	0.85			
<b>30d</b>	CH <sub>2</sub> Cl <sub>2</sub>	471	–	0.59	+0.508 <sup>e,f,g</sup>	–	[119]
<b>30e</b>	CH <sub>2</sub> Cl <sub>2</sub>	509	–	0.84	+0.661 <sup>e,f,g</sup>	–	[119]
<b>31a</b>	MTHF	514	0.4	1.3	–	–	[13,142]
<b>31b</b>	CH <sub>2</sub> Cl <sub>2</sub>	471	–	0.74	+0.551 <sup>e,f,g</sup>	–	[119]
<b>31c</b>	CH <sub>2</sub> Cl <sub>2</sub>	477	–	0.68	+0.345 <sup>e,f,g</sup>	–	[119]
<b>32a</b>	MeOH	606	–	0.337	+0.86 <sup>e,g,i</sup>	–1.77, –2.42, –2.77 <sup>e,g,i</sup>	[121]
<b>32b</b>	MeCN	620	0.032	0.180	+1.19 <sup>a,j,c,i</sup>	–1.35, –1.68 <sup>e,h,i</sup>	[122]
<b>32c</b>	MeCN	645	0.023	0.135	+1.18 <sup>a,j,c,i</sup>	–1.24 <sup>e,h,i</sup>	[122]
<b>32d</b>	MeCN	630	0.031	0.16	+1.19 <sup>a,j,c,i</sup>	–1.20, –1.35 <sup>e,c,i</sup>	[122]
<b>32e</b>	MeCN	660	0.017	0.125	+1.19 <sup>a,j,c,i</sup>	–1.35, –1.53 <sup>e,c,i</sup>	[122]
<b>32f</b>	MeCN	625	0.017	0.070	+1.34 <sup>a,j,c,i</sup>	–1.25 <sup>e,c,i</sup>	[122]
<b>32g</b>	MeCN <sup>a</sup>	560	0.246	0.870	+1.23 <sup>e,c,i</sup>	–1.75, –2.08 <sup>a,b,c,i</sup>	[129]
<b>33a</b>	CH <sub>2</sub> Cl <sub>2</sub>	593	0.273	–	–	–	[123]
<b>33b</b>	CH <sub>2</sub> Cl <sub>2</sub>	600	0.221	–	–	–	[123]
<b>33c</b>	CH <sub>2</sub> Cl <sub>2</sub>	630	0.147	–	–	–	[123]
<b>33d</b>	CH <sub>2</sub> Cl <sub>2</sub>	645	0.097	–	–	–	[123]
<b>33e</b>	CH <sub>2</sub> Cl <sub>2</sub>	649	0.058	–	–	–	[123]
<b>33f</b>	CH <sub>2</sub> Cl <sub>2</sub>	664	0.060	–	–	–	[123]
<b>34a</b>	–	545	0.54	–	+0.70 <sup>e,f</sup>	–2.28 <sup>e,f</sup>	[124]
<b>34b</b>	–	548	0.46	–	+0.51 <sup>e,f</sup>	–2.40 <sup>e,f</sup>	[124]
<b>34c</b>	–	560	0.41	–	+0.53 <sup>e,f</sup>	–2.35 <sup>e,f</sup>	[124]
<b>34d</b>	–	562	0.46	–	+0.72 <sup>e,f</sup>	–2.16 <sup>e,f</sup>	[124]
<b>34e</b>	–	566	0.44	–	+0.57 <sup>e,f</sup>	–2.30 <sup>e,f</sup>	[124]
<b>34f</b>	–	576	0.32	–	+0.79 <sup>e,f</sup>	–2.28 <sup>e,f</sup>	[124]
<b>35a</b>	CH <sub>2</sub> Cl <sub>2</sub>	461, 491	0.27	1.4	0.99 <sup>h,f,k</sup>	–2.47 <sup>h,f,k</sup>	[125]
<b>35b</b>	CH <sub>2</sub> Cl <sub>2</sub>	484, 518	0.38	2.4	0.84 <sup>h,f,k</sup>	–2.52 <sup>h,f,k</sup>	[125]
<b>35c</b>	CH <sub>2</sub> Cl <sub>2</sub>	511, 544	0.39	3.9	1.10 <sup>h,f,k</sup>	–2.44 <sup>h,f,k</sup>	[125]
<b>35d</b>	CH <sub>2</sub> Cl <sub>2</sub>	466, 499	0.30	0.30	1.16 <sup>h,f,k</sup>	–2.35 <sup>h,f,k</sup>	[125]
<b>35e</b>	CH <sub>2</sub> Cl <sub>2</sub>	489, 517	0.45	0.45	0.64 <sup>h,f,k</sup>	–2.53 <sup>h,f,k</sup>	[125]
<b>36a</b>	2-MeTHF	516	0.34	1.6	+0.87 <sup>a,b</sup>	–	[142]
<b>36b</b>	2-MeTHF	512	0.31	3.1	+0.82 <sup>a,b</sup>	–	[142]
<b>36c</b>	2-MeTHF	548	0.27	4.5	+0.86 <sup>a,b</sup>	–	[142]
<b>36d</b>	2-MeTHF	557	0.36	1.8	+1.00 <sup>a,b</sup>	–	[142]
<b>36e</b>	2-MeTHF	541	0.37	2.3	–	–	[142]
<b>36f</b>	2-MeTHF	562	0.22	1.4	–	–	[142]
<b>36g</b>	2-MeTHF	606	0.22	1.8	+0.93 <sup>a,b</sup>	–	[142]
<b>36h</b>	2-MeTHF	597	0.10	2.0	–	–	[142]
<b>37</b>	2-MeTHF	665	0.04	2.0	–	–	[143]

<sup>a</sup> Irreversible couple.

<sup>b</sup>  $E_{\text{pc}}$ .

<sup>c</sup> vs. SCE.

<sup>d</sup> In DMF.

<sup>e</sup> Reversible couple.

<sup>f</sup> vs.  $\text{Fc}/\text{Fc}^+$ .

<sup>g</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>h</sup> Quasi-reversible couple.

<sup>i</sup>  $E_{\text{pa}}$ .

<sup>j</sup> In MeCN.

<sup>k</sup> In BuCN.

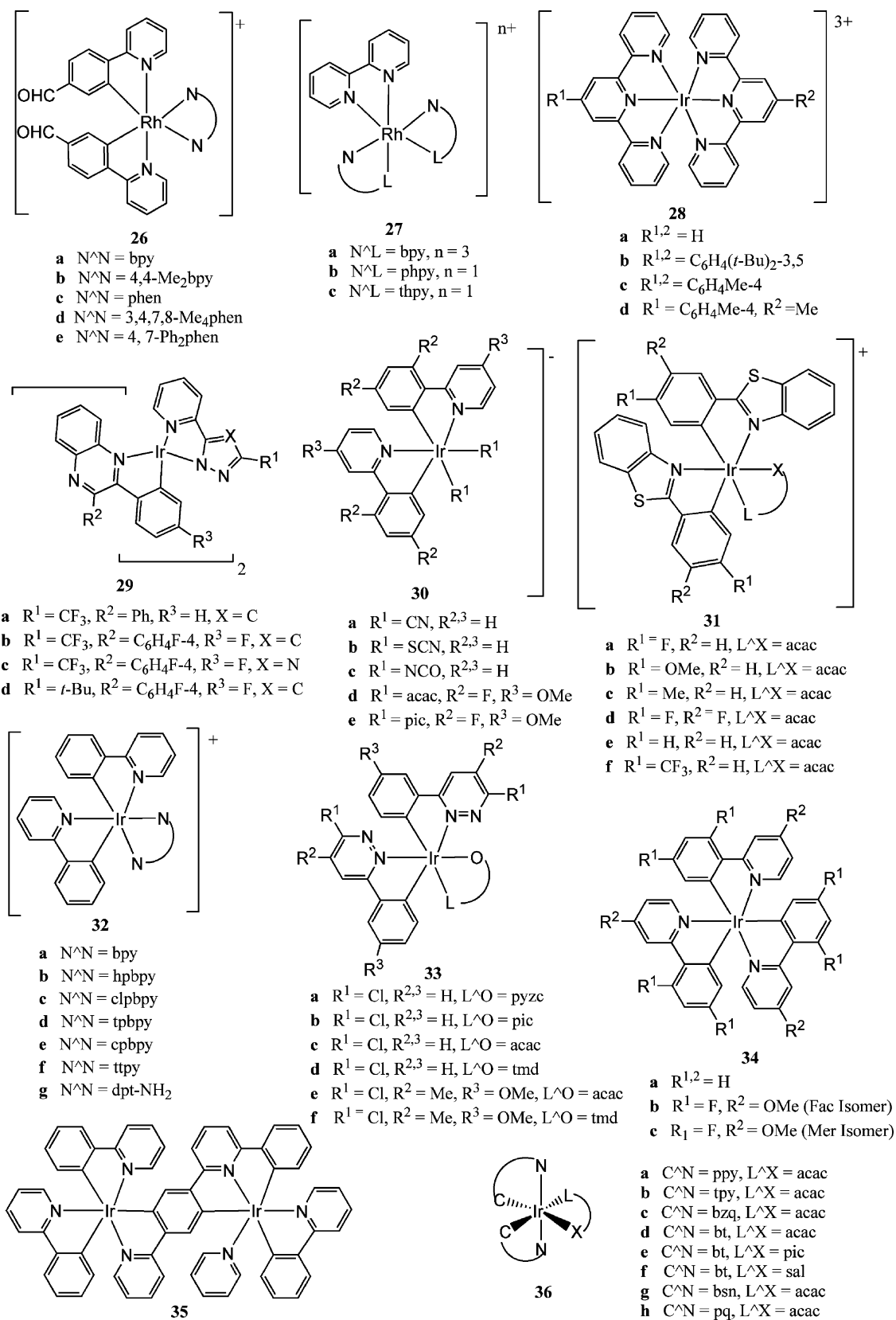


Fig. 6. Structures 26–36.

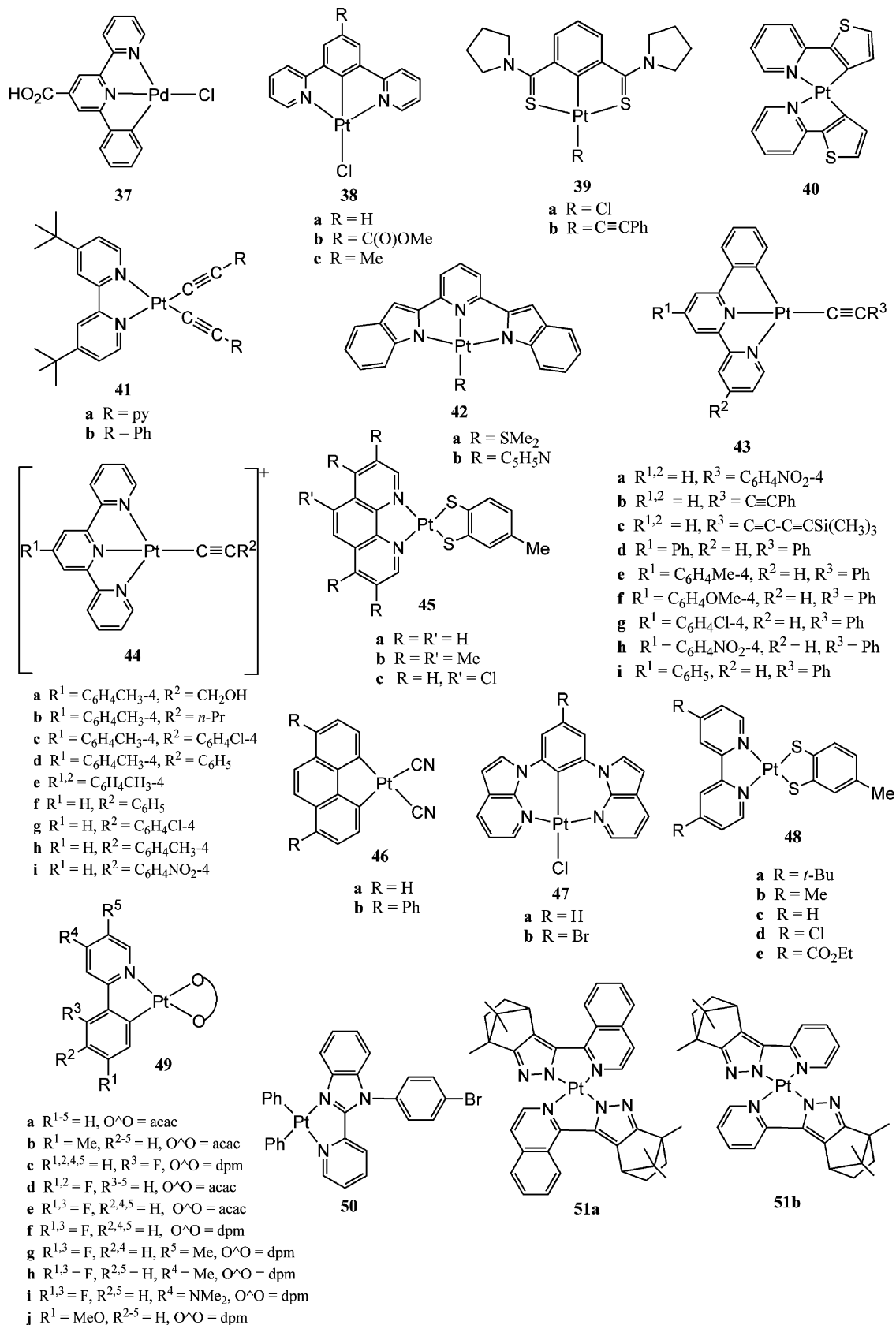


Fig. 7. Structures 37–51.

Table 8  
Photophysical and electrochemical properties of mononuclear platinum(II) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	$E_{\text{pa}}^{\text{OX}}$ (V)	$E_{\text{pc}}^{\text{RED}}$ (V)	Reference
38a	CH <sub>2</sub> Cl <sub>2</sub>	491, 524, 562	0.60	7.2	+0.350 <sup>a,b,c,d</sup>	−2.140 <sup>e,c,d</sup>	[144]
38b	CH <sub>2</sub> Cl <sub>2</sub>	481, 513, 550	0.58	8.0	+0.390 <sup>a,b,c,d</sup>	−2.040 <sup>e,c,d</sup>	[144]
38c	CH <sub>2</sub> Cl <sub>2</sub>	505, 539, 578	0.68	7.8	+0.290 <sup>a,b,c,d</sup>	−2.150 <sup>e,c,d</sup>	[144]
39a	Solid	630	0.11	11.0	—	—	[145]
39b	Solid	640	0.24	8.3	—	—	[145]
40	CH <sub>2</sub> Cl <sub>2</sub>	580	0.3	3.0	—	—	[181]
41a	CH <sub>2</sub> Cl <sub>2</sub>	~670	0.011	48.5	—	—	[147]
41b	CH <sub>2</sub> Cl <sub>2</sub>	~560	—	1.25	—	—	[147]
42a	Poly(carbonate)	585	—	22.1	—	—	[148]
42b	Poly(carbonate)	585	—	19	—	—	[148]
43a	CH <sub>2</sub> Cl <sub>2</sub>	560	0.08	0.9	+0.12 <sup>a,b,c,f</sup>	−1.61 <sup>e,c,f</sup>	[149]
43b	CH <sub>2</sub> Cl <sub>2</sub>	571	0.08	1.0	—	—	[149]
43c	CH <sub>2</sub> Cl <sub>2</sub>	557	0.07	0.8	+0.22 <sup>a,b,c,f</sup>	−1.76 <sup>e,c,f</sup>	[149]
43d	CH <sub>2</sub> Cl <sub>2</sub>	597	0.07	0.8	—	—	[149]
43e	CH <sub>2</sub> Cl <sub>2</sub>	597	0.09	0.8	—	—	[149]
43f	CH <sub>2</sub> Cl <sub>2</sub>	594	0.09	1.0	—	—	[149]
43g	CH <sub>2</sub> Cl <sub>2</sub>	603	0.08	0.7	—	—	[149]
43h	CH <sub>2</sub> Cl <sub>2</sub>	592	1.0	0.5	—	—	[149]
43i	CH <sub>2</sub> Cl <sub>2</sub>	593	0.08	1.6	—	—	[149]
44a	CH <sub>2</sub> Cl <sub>2</sub>	552	0.30	14.6	—	—	[150]
44b	CH <sub>2</sub> Cl <sub>2</sub>	580	0.25	10.3	—	—	[150]
44c	CH <sub>2</sub> Cl <sub>2</sub>	611	0.071	4.7	—	—	[150]
44d	CH <sub>2</sub> Cl <sub>2</sub>	619	0.052	4.6	—	—	[150]
44e	CH <sub>2</sub> Cl <sub>2</sub>	639	0.0076	0.8	—	—	[150]
44f	CH <sub>2</sub> Cl <sub>2</sub>	618	0.036	1.9	—	—	[150]
	MeCN	630	0.0124	0.5	—	—	[151]
44g	MeCN	620	0.0073	0.5	—	—	[151]
44h	MeCN	665	0.0015	0.1	—	—	[151]
44i	MeCN	560	0.0011	<0.1	—	—	[151]
45a	CH <sub>2</sub> Cl <sub>2</sub>	674	0.00067	0.517	+0.376 <sup>g,h</sup> , +0.52 <sup>g,h</sup>	−1.319 <sup>e,h</sup>	[152]
45b	CH <sub>2</sub> Cl <sub>2</sub>	639	0.0057	0.315	+0.347 <sup>a,b,h</sup> , +0.45 <sup>g,h</sup>	−1.495 <sup>e,h</sup>	[152]
45c	CH <sub>2</sub> Cl <sub>2</sub>	685	0.00026	1.02	+0.359 <sup>g,h</sup> , +0.56 <sup>g,h</sup>	−1.257 <sup>e,h</sup>	[152]
46a	CH <sub>2</sub> Cl <sub>2</sub>	525	0.097	223	—	—	[153]
46b	PEG	520	—	0.1	—	—	[154]
47a	Solid	536	—	—	—	—	[155]
47b	Solid	548	—	16	—	—	[155]
48a	CH <sub>2</sub> Cl <sub>2</sub>	642	0.00108	0.504	+0.389 <sup>a,b,h</sup> , +0.54 <sup>c,h</sup>	−1.398 <sup>e,h</sup>	[152]
48b	CH <sub>2</sub> Cl <sub>2</sub>	663	0.00074	0.381	+0.390 <sup>a,b,h</sup> , +0.50 <sup>g,h</sup>	−1.371 <sup>e,h</sup>	[152]
48c	CH <sub>2</sub> Cl <sub>2</sub>	667	0.00031	0.291	+0.376 <sup>g,h</sup> , +0.52 <sup>g,h</sup>	−1.339 <sup>d,h</sup>	[152]
48d	CH <sub>2</sub> Cl <sub>2</sub>	738	0.000043	0.157	+0.380 <sup>a,b,h</sup> , +0.64 <sup>g,h</sup>	−1.043 <sup>e,h</sup>	[152]
48e	CH <sub>2</sub> Cl <sub>2</sub>	785	0.000004	0.068	+0.412 <sup>a,b,h</sup> , +0.62 <sup>g,h</sup>	−0.962 <sup>e,h</sup>	[152]
48f	2-MeTHF	486	0.15	2.6	—	−2.39 <sup>e,c,f</sup>	[156]
48g	2-MeTHF	485	0.22	4.5	—	−2.34 <sup>e,c,f</sup>	[156]
48h	2-MeTHF	476	0.06	<1.0	—	−2.37 <sup>e,c,f</sup>	[156]
48i	2-MeTHF	484	0.22	3.0	—	−2.27 <sup>e,c,f</sup>	[156]
48j	2-MeTHF	466	0.02	<1.0	—	−2.29 <sup>e,c,f</sup>	[156]
49a	2-MeTHF	466	0.02	<1.0	—	−2.31 <sup>e,c,f</sup>	[156]
49b	2-MeTHF	472	0.05	<1.0	—	−2.32 <sup>e,c,f</sup>	[156]
49c	2-MeTHF	456	—	<1.0	—	−2.51 <sup>e,c,f</sup>	[156]
49d	2-MeTHF	447	—	<1.0	—	−2.60 <sup>e,c,f</sup>	[156]
49e	2-MeTHF	490	0.20	7.4	—	−2.50 <sup>g,c,f</sup>	[156]
50	Solid	592	—	7.5	+0.98 <sup>a,b,c,d</sup>	−1.46 <sup>e,c,d</sup>	[157]
51a	CH <sub>2</sub> Cl <sub>2</sub>	635	0.81	5.34	—	—	[158]
51b	CH <sub>2</sub> Cl <sub>2</sub>	553	0.64	3.63	—	—	[158]

<sup>a</sup> Irreversible couple.

<sup>b</sup>  $E_{\text{pa}}$ .

<sup>c</sup> vs. Fc/Fc<sup>+</sup>.

<sup>d</sup> In MeCN.

<sup>e</sup> Reversible couple.

<sup>f</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>g</sup> Quasi-reversible couple.

<sup>h</sup> vs. NHE.

Table 9

Photophysical and electrochemical properties of selected phosphorescent polynuclear platinum(II) complexes

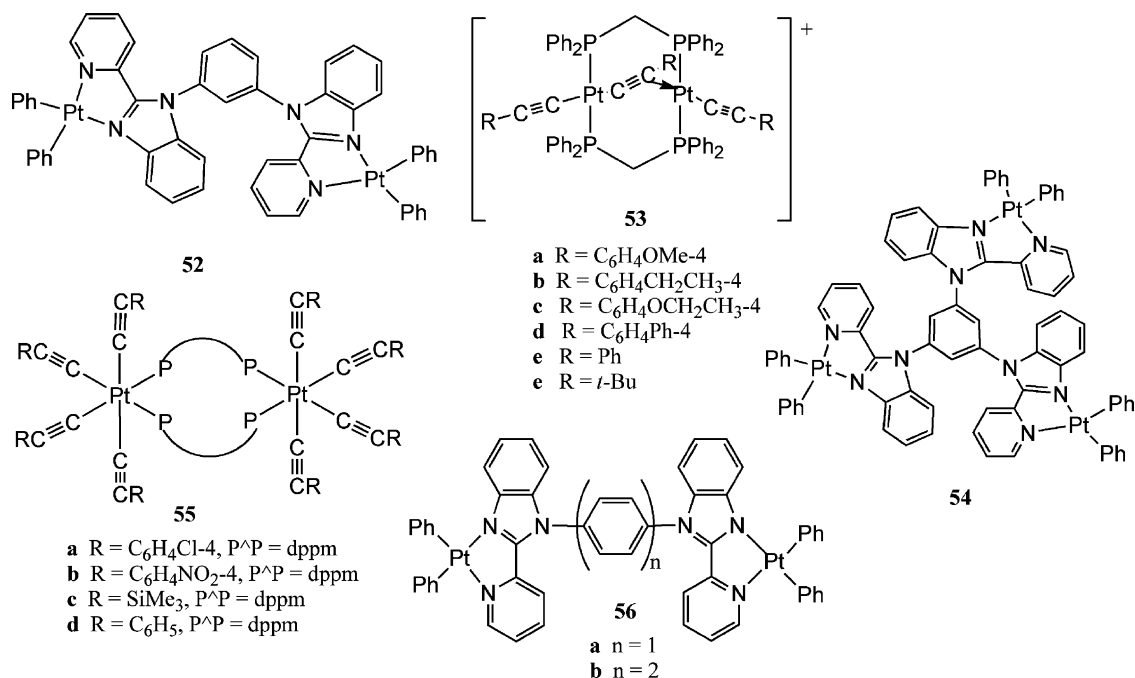
Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\tau$ ( $\mu\text{s}$ )	$E_{\text{pa}}^{\text{OX}}$ (V)	$E_{\text{pc}}^{\text{RED}}$ (V)	Reference
<b>52</b>	Solid	611	8.1	+1.18 <sup>a,b,c,d</sup>	−1.34 <sup>e,c,d</sup>	[157]
<b>53a</b>	Solid	610	10.0	–	–	[179]
	MeCN	630	0.1	–	–	
<b>53b</b>	Solid	590	11.0	–	–	[179]
	MeCN	620	0.15	–	–	
<b>53c</b>	Solid	595	9.0	–	–	[179]
	MeCN	630	0.15	–	–	
<b>53d</b>	Solid	635	5.0	–	–	[179]
	MeCN	640	0.9	–	–	
<b>53e</b>	Solid	618	2.2	–	–	[179]
	MeCN	614	0.11	–	–	
<b>52f</b>	Solid	554	11	–	–	[179]
	MeCN	500	<0.1	–	–	
<b>54</b>	Solid	621	8.2	+1.15 <sup>a,b,c,d</sup>	−1.30 <sup>e,c,d</sup>	[157]
<b>55a</b>	CH <sub>2</sub> Cl <sub>2</sub>	628	1.3	–	–	[182]
<b>55b</b>	CH <sub>2</sub> Cl <sub>2</sub>	664	1.3	–	–	[182]
<b>55c</b>	CH <sub>2</sub> Cl <sub>2</sub>	622	<0.1	–	–	[182]
<b>55d</b>	CH <sub>2</sub> Cl <sub>2</sub>	620	<0.1	–	–	[182]
<b>56a</b>	Solid	582	7.9	+1.16, +1.30 <sup>a,b,c,d</sup>	−1.33 <sup>e,c,d</sup>	[157]
<b>56b</b>	Solid	587	8.0	+1.11 <sup>a,b,c,d</sup>	−1.36 <sup>e,c,d</sup>	[157]

<sup>a</sup> Irreversible couple.<sup>b</sup>  $E_{\text{pa}}$ .<sup>c</sup> vs. Fc/Fc<sup>+</sup>.<sup>d</sup> In DMF.<sup>e</sup> Reversible couple.

attributed to a MMLCT state, since emission from the dimer [Pt(dppm)<sub>2</sub>(C≡CR)<sub>2</sub>]<sub>2</sub> is red-shifted compared to that of the corresponding monomer [48] (Fig. 8).

Despite the favorable phosphorescence characteristics identified for several platinum(II) complexes, only recently has investigation into their suitability for OLED technology been carried

out [19,148,149,183–188]. Thompson and Forrest first reported an OLED based on platinum octaethylporphyrin (PtOEP) doped in Alq<sub>3</sub> which exhibited saturated red emission with an external quantum efficiency of 4% [12]. Lu et al. prepared a series of OLEDs based on the cyclometalated mononuclear Pt(II) complexes (**43a–i**), generating yellow to red-emitting devices with

Fig. 8. Structures **52–56**.



a maximum external quantum efficiency of 1.6% [149]. Several white OLED devices have been reported using the triplet excimer emission of square-planar Pt(II) complexes [183,184], which are known to form excimers in concentrated solution and in the solid state [144,172,183,184]. Thompson and Forrest reported a series of white OLEDs based on emission from Pt(II) complexes containing cyclometalated 2-(4,6-difluorophenyl)pyridine ligands (**49**) [156,183,184]. The monomeric form of these complexes exhibits strong blue phosphorescence, whilst at high concentrations the formation of excimers results in orange emission at about 580 nm [156,183,184]. With careful control of the levels of doping in the polymer layer it is possible to generate emission from both the monomer and the excimer, resulting in white electroluminescence with a maximum external quantum efficiency of 6.4% when doped in *m*CP [184].

Recently, a highly luminescent red device incorporating a square planar platinum(II) complex containing isoquinolinyl indazole coordinating ligands (**51a**) has been reported [158]. Here, the molecular geometry of the coordinating ligands is analogous to platinum porphyrin complexes and the introduction of a camphor-like structure to the ligand prevents the stacking effect which leads to excimer formation. The combination of these two features results in a complex which is highly luminescent in both solution and thin films, yielding a device with a maximum external quantum efficiency of 14.9% ( $24.57 \text{ cd A}^{-1}$ ) at  $100 \text{ mA cm}^{-2}$  [158].

**2.1.2.3.  $d^{10}$  configuration: silver(I) ( $4d^{10}$ ) and gold(I) ( $5d^{10}$ ).** Despite the large number of silver(I) complexes reported in the literature, their photophysics remains comparatively unexplored. This is generally attributed to the photosensitivity exhibited by many silver complexes. Room-temperature phosphorescence has been reported for just a few Ag(I) compounds (Table 10) [54,56,189]. Due to the similar bonding geometry of copper(I) and silver(I), these complexes tend to be the sil-

Table 10

Photophysical characteristics of selected silver(I) complexes at room temperature

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	Origin	Reference
<b>57</b>	Solid	395	0.0037	31	$^3\text{MC}$	[54]
<b>58</b>	Solid	356	0.0080	5.4	$^3\text{MC}$	[54]
<b>59</b>	Solid	360	0.0065	0.6	$^3\text{MC}$	[54]
<b>60a</b>	$\text{CH}_2\text{Cl}_2$	418, 434, 455, 480	0.025	0.31	$^3\text{IL}$	[189]
<b>60b</b>	$\text{CH}_2\text{Cl}_2$	399, 435, 487, 540	0.00513	0.22	$^3\text{IL}$	[189]
<b>60c</b>	$\text{CH}_2\text{Cl}_2$	464, 491, 514, 543, 579	0.033	0.29	$^3\text{IL}$	[189]
<b>61</b>	$\text{CH}_2\text{Cl}_2$ Solid	515 513	– –	426 351	$^3\text{LMCT}$	[56]

ver analogues of previously reported phosphorescent copper(I) complexes. For instance, a hexanuclear silver(I) complex (**61**) was reported to phosphoresce in both the solid state and solution at room temperature, with emission maximum at 515 nm [56]. This is substantially blue-shifted when compared to the equivalent hexanuclear copper(I) complex (**11**) ( $\lambda_{\text{em}} = 596 \text{ nm}$  in RT solution). Furthermore, emission from the silver(I) analogue is much longer-lived ( $\tau = 426$  and  $40 \mu\text{s}$  for the Ag(I) and Cu(I) complexes, respectively) [56]. Although emission wavelengths are generally found in the blue–green region for the few reported phosphorescent Ag(I) complexes, the low emission quantum yields and photostability suggest that silver(I) complexes will probably have a limited role to play in developing OLED technology (Fig. 9).

The photophysics of luminescent mono-, di- and polynuclear Au(I) complexes has been extensively studied [45,48,190–203]. The most common coordination geometry observed for gold(I) is two-coordinate (linear) or three-coordinate (trigonal planar)

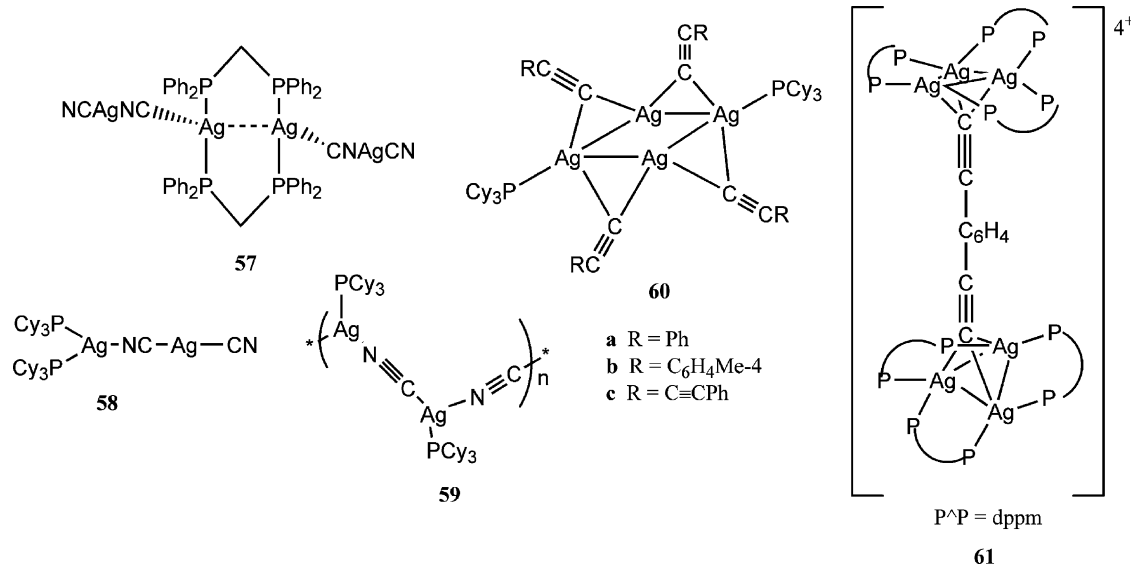
Fig. 9. Structures **57**–**61**.

Table 11

Photophysical characteristics of some mononuclear gold(I) and gold(III) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	Origin	Reference
<b>62a</b>	Solid	420	–	30	$^3\text{IL}$	[204]
<b>62b</b>	Solid	438	–	27	$^3\text{IL}$	[204]
<b>62c</b>	Solid	440	–	44	$^3\text{IL}$	[204]
<b>62d</b>	Solid	421	–	32	$^3\text{IL}$	[204]
<b>62e</b>	Solid	425	–	22	$^3\text{IL}$	[204]
<b>62f</b>	Solid	435	–	61	$^3\text{IL}$	[204]
<b>62g</b>	Solid	397	–	56	$^3\text{IL}$	[204]
<b>62h</b>	Solid	397	–	43	$^3\text{IL}$	[204]
<b>62i</b>	Solid	421	–	41	$^3\text{IL}$	[204]
<b>62j</b>	Solid	425	–	31	$^3\text{IL}$	[204]
<b>63a</b>	$\text{CH}_2\text{Cl}_2$	693	–	0.7	$^3\text{IL}$	[191]
<b>63b</b>	$\text{CH}_2\text{Cl}_2$	666	–	1.5	$^3\text{IL}$	[191]
<b>64a</b>	Solid	685	–	15	$^3\text{LMCT}$	[192]
<b>64b</b>	Solid	702	–	15	$^3\text{LMCT}$	[192]
<b>64c</b>	Solid	698	–	16	$^3\text{LMCT}$	[192]
<b>65</b>	MeCN	570	0.001	–	$^3\text{IL}$	[193]
<b>66a</b>	$\text{CH}_2\text{Cl}_2$	420	–	<0.1	–	[194]
<b>66b</b>	$\text{CH}_2\text{Cl}_2$	422	–	0.7	–	[194]
<b>66c</b>	$\text{CH}_2\text{Cl}_2$	418	–	<0.1	–	[194]
<b>66d</b>	$\text{CH}_2\text{Cl}_2$	418	–	<0.1	–	[194]

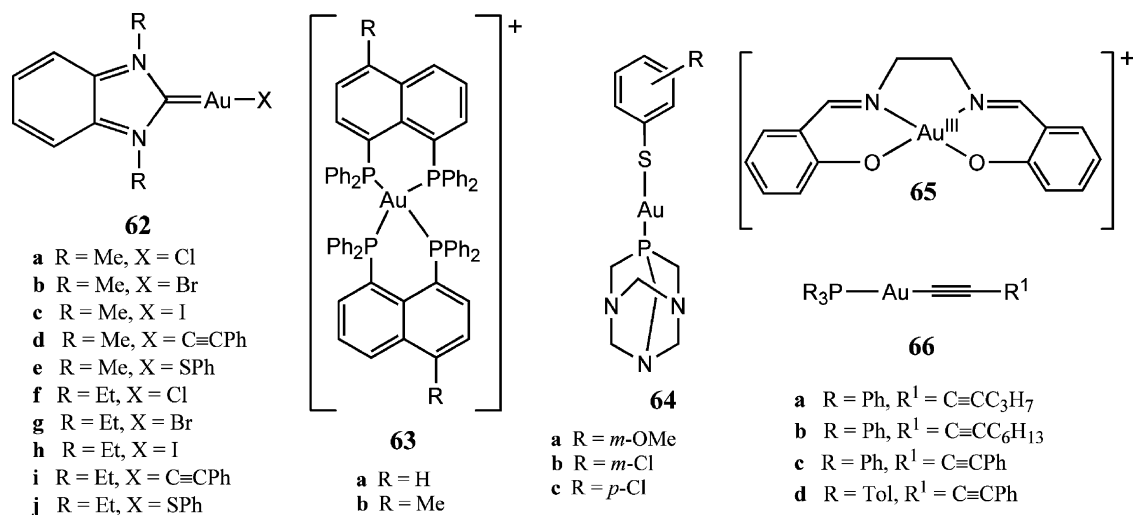
resulting in quite different molecular structures compared to related copper(I) or silver(I) complexes [48].

Many mononuclear gold(I) complexes containing carbene, phosphine, thiolate and acetylide ligands exhibiting room-temperature phosphorescence have been reported [49,192,194,204]. Emission wavelengths across the visible spectrum have been reported for these complexes, depending upon the ligand employed (Table 11). The  $d^{10}$  configuration prevents stabilisation of excited states via the ligand field; thus LMCT and intra-ligand transitions dominate the photophysics of these compounds. Consequently, with judicious ligand selection, it is possible to tune the emission to the desired wavelength, resulting in blue phosphorescence from Au(I)-carbene complexes ( $^3\text{IL}$  state) [204] and red emission from Au(I) thiolate complexes

( $^3\text{LMCT}$  state) [192]. It is interesting to note that unlike the isoelectronic platinum(II) systems, gold(III) complexes are generally not luminescent at room-temperature. However, recently a Au(III) complex containing the salen ligand (**65**) has been reported to exhibit weak IL phosphorescence in addition to fluorescence at room temperature [193] (Fig. 10).

Luminescence in  $d^{10}$  complexes is frequently associated with the presence of weak intermolecular bonding between neighbouring metal centres. This is remarkably evident in gold(I) metal complexes, where short Au–Au contacts are often observed as a result of relativistic effects. This phenomenon has been termed *aurophilicity* by Schmidbaur [205]. The metal(I)–metal(I) internuclear distance has been shown to significantly affect the energy gap of the frontier orbitals [206]. Metal–metal interactions cause destabilisation of the filled  $d_{z^2}$  orbital, resulting in the mixing of empty  $p_z$  orbitals on the metal centres, thus stabilising the LUMO state. Consequently the energy gap between the HOMO–LUMO states is lowered, resulting in a red-shift in the emission wavelength. The extent of interaction between metal centres is also influenced by temperature; at higher temperatures thermal expansion results in an increase in distance between metal centres and is accompanied by a blue shift in the emission wavelength [198]. In exceptional complexes, such as alkynyl gold(I) compounds, the presence of low-lying ligand  $\pi^*$  orbitals means that Au–Au interactions no longer govern the lowest excited state properties [207]. However, in the majority of cases, emission originates from an excited  $^3\text{LMCT}$  state, where *aurophilic* interactions are very important.

Aurophilic interaction has been shown to affect the luminescent properties in gold(I) complexes in a number of ways. Emission wavelengths depend considerably on the extent of aggregation caused by *aurophilic* bonding [202] and several Au(I) complexes exhibit concentration dependent emission in solution [206]. *Aurophilic* interactions do not necessarily require formal bonds between the two metal centres and short gold–gold contacts between neighbouring molecules will exert the same influence. Thus many gold(I) complexes exhibit room-temperature phosphorescence in the solid state but display no detectable

Fig. 10. Structures **62**–**66**.

emission in fluid solution [192]. The extent of Au–Au interaction is also influenced by ligand softness, with a reduction in the ligand softness shown to increase the Au–Au internuclear distance [192].

The photophysics of luminescent di-, tri- and polynuclear gold(I) complexes has been extensively studied. A thorough review by the Yam group discusses how the luminescence properties of dinuclear gold(I) complexes containing phosphine and thiolate ligands (**69a–i**) may be controlled by molecular design [196]. In these complexes both the [thiolate → Au(I)]

and [phosphine → Au(I)]  $^3\text{LMCT}$  excited states are located at similar energies. With careful selection of the substituents on these ligands it is possible to shift the origin of emission from the phosphine to the thiolate excited  $^3\text{LMCT}$  state. The Yam group also reported an extensive series of luminescent mono-, di- and trinuclear gold(I) phosphine alkynyl complexes emitting across the entire visible spectrum [194]. Emission from the mononuclear Au(I) series (**66a–d**) is attributed to emission from metal-perturbed  $^3\text{IL } \pi \rightarrow \pi^*$  ( $\text{C}\equiv\text{C}$ ) transitions with some metal-to-alkynyl MLCT character [194]. The corresponding dinuclear

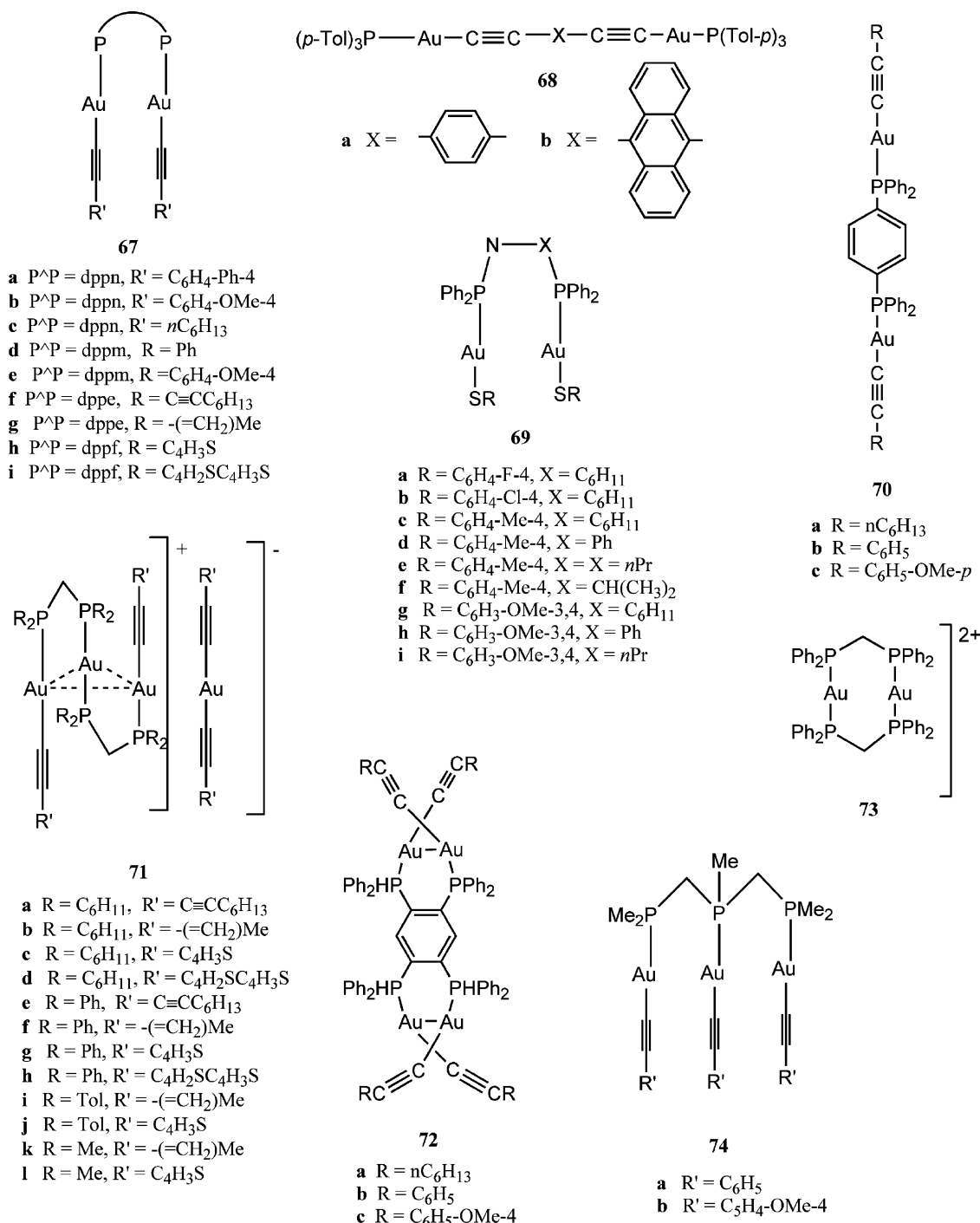


Fig. 11. Structures **67–74**.

complexes (**67f–i**) exhibit similar emission characteristics to their mononuclear counterparts in room-temperature solution, suggesting that the two Au units do not interact and function as two independent chromophores. However, in the solid state emission is substantially red shifted for complex (**67g**) compared to the other dinuclear complexes, indicative of the presence of short Au–Au contacts giving rise to low-energy solid state emission [194]. For the trinuclear Au(I) complexes, both a high energy (ca. 400–480 nm) and a low energy (500–622 nm) emission band were observed. The high-energy band is assigned to emission from the anion as emission bands of similar energy are observed for  $[\text{Au}(\text{C}\equiv\text{CR})_2]^-$  [208]. The low-energy bands are attributed to emission from metal-perturbed  $^3\text{IL } \pi \rightarrow \pi^*$  ( $\text{C}\equiv\text{C}$ ) transitions with some metal-to-alkynyl MLCT character. These bands are red-shifted compared to the corresponding mono- and dinuclear species due to the presence of metal–metal interactions in the trinuclear species [194] (Fig. 11).

The emission energies of gold(I) complexes may be tuned across a broad spectral range by changing the auxiliary ligands, the coordination geometry and the extent of Au(I)–Au(I) interaction. The flexibility in emission wavelength, coupled with lifetimes in the microsecond regime, has led to some interest in gold(I) complexes for OLED phosphors. Ma and coworkers have reported two devices incorporating Au(I) phosphors [52,209]. The first device was based on  $[\text{Au}_2(\text{dppm})_2]^{2+}$  (**72**) and exhibited green electroluminescence with an emission maximum at 520 nm [52]. The second device incorporated the neutral complex  $[\text{Au}_2(\text{dppm})_2\text{Cl}_2]$ , which also showed an emission maximum at 520 nm with an estimated electroluminescence yield of 0.1% [209]. Electroluminescent thin-film devices incorporating the four-coordinate tetrahedral gold(I) complexes (**63a**) and (**63b**) have also been prepared, with maximum electroluminescence efficiencies of 82 and 73  $\text{cd m}^{-2}$  (at 13 V) observed respectively [191].

## 2.2. Group 12: zinc(II), cadmium(II) and mercury(II)

The group 12 metal(II) ions contain a  $d^{10}$  closed shell electron configuration. Due to the high ionization potentials of closed shell metal ions (40 eV for Zn(II) and 38 eV for Cd(II)), any states involving excitation of the d electron should have a high energy. Thus d–d transitions are predominantly absent in group 12 complexes. Consequently the lowest energy excited states for these complexes are principally composed of ligand-centred and/or ligand–ligand charge transfer states [210,211].

Many Zn(II) complexes are known to exhibit intense fluorescence at room-temperature [212–220] and there has been substantial research into the potential of zinc(II) complexes for fluorescence-based OLED devices [217–219]. Phosphorescence is generally observed only in low-temperature glasses [212,213]. Recently however two blue phosphorescent zinc complexes of 4,4'-diphenyl-6,6'-dimethyl-2,2'-bipyrimidine (pmbp) have been reported [221].  $[\text{Zn}(\text{pmbp})_2]^{2+}$  (**75**) and  $[\text{Zn}(\text{pmbp})\text{Cl}_2]$  (**76**) both emit in the solid state at room temperature, with emission maxima at 441 and 452 nm, respectively. The emission is assigned to a  $^3\text{IL } \pi \rightarrow \pi^*$  state due to the long decay lifetimes observed for these complexes (6.8 and 8.7  $\mu\text{s}$  for **75** and **76**,

Table 12

Photophysical data for some polynuclear gold(I) complexes

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{P}}$	$\tau$ ( $\mu\text{s}$ )	Reference
<b>67a</b>	Solid	655	–	6.2	[207]
<b>67b</b>	Solid	571	–	1.32	[207]
<b>67c</b>	Solid	644	–	2.0	[207]
<b>67d</b>	Solid	490	–	0.42	[207]
<b>67e</b>	Solid	521	–	0.95	[207]
<b>67f</b>	$\text{CH}_2\text{Cl}_2$	420	–	<0.1	[194]
<b>67g</b>	$\text{CH}_2\text{Cl}_2$	422	–	<0.7	[194]
<b>67h</b>	$\text{CH}_2\text{Cl}_2$	418	–	<0.1	[194]
<b>67i</b>	$\text{CH}_2\text{Cl}_2$	418	–	<0.1	[194]
<b>68a</b>	$\text{CH}_2\text{Cl}_2$	489, 521	–	<0.1	[207]
<b>68b</b>	$\text{CH}_2\text{Cl}_2$	479, 500, 529	–	0.4	[207]
<b>69a</b>	$\text{CH}_2\text{Cl}_2$	503	–	<0.1	[196]
<b>69b</b>	$\text{CH}_2\text{Cl}_2$	499	–	<0.1	[196]
<b>69c</b>	$\text{CH}_2\text{Cl}_2$	503	–	<0.1	[196]
<b>69d</b>	$\text{CH}_2\text{Cl}_2$	518	–	<0.1	[196]
<b>69e</b>	$\text{CH}_2\text{Cl}_2$	557	–	<0.1	[196]
<b>69f</b>	$\text{CH}_2\text{Cl}_2$	540	–	<0.1	[196]
<b>69g</b>	$\text{CH}_2\text{Cl}_2$	552	–	<0.1	[196]
<b>69h</b>	$\text{CH}_2\text{Cl}_2$	586	–	<0.1	[196]
<b>69i</b>	$\text{CH}_2\text{Cl}_2$	602	–	<0.1	[196]
<b>70a</b>	Solid	510	–	153.8	[69]
<b>70b</b>	Solid	507	–	532	[69]
<b>70c</b>	Solid	486, 563	–	5.06	[69]
<b>71a</b>	$\text{CH}_2\text{Cl}_2$	399, 478, 533, 552	–	3.4	[194]
<b>71b</b>	$\text{CH}_2\text{Cl}_2$	425, 582	–	1.2	[194]
<b>71c</b>	$\text{CH}_2\text{Cl}_2$	418, 499, 519	–	3.0	[194]
<b>71d</b>	$\text{CH}_2\text{Cl}_2$	429	–	0.3	[194]
<b>71e</b>	$\text{CH}_2\text{Cl}_2$	645	–	3.9	[194]
<b>71f</b>	$\text{CH}_2\text{Cl}_2$	425, 574	–	1.6	[194]
<b>71g</b>	$\text{CH}_2\text{Cl}_2$	410, 499, 519	–	7.5	[194]
<b>71h</b>	$\text{CH}_2\text{Cl}_2$	429	–	0.2	[194]
<b>71i</b>	$\text{CH}_2\text{Cl}_2$	427, 589	–	5.0	[194]
<b>71j</b>	$\text{CH}_2\text{Cl}_2$	440, 500	–	4.3	[194]
<b>71k</b>	$\text{CH}_2\text{Cl}_2$	425, 618	–	5.4	[194]
<b>71l</b>	$\text{CH}_2\text{Cl}_2$	416, 503, 520	–	5.8	[194]
<b>72a</b>	Solid	405, 602	–	1.28	[69]
<b>72b</b>	Solid	599, 611	–	0.57	[69]
<b>72c</b>	Solid	415, 628	–	1.85	[69]
<b>73</b>	MeCN	570	0.21	–	[197]
<b>74a</b>	Solid	538	–	1.29	[207]
<b>74b</b>	Solid	539	–	1.16	[207]

respectively). The heavy atom effect associated with the Zn(II) centre is believed to enhance the ligand centred emission.

Room-temperature phosphorescence in both the solid state and solution has been observed in a series of dinuclear cadmium(II) diimine complexes with bridging chalcogenolate ligands (Table 12) [222]. The emission from these complexes is assigned to a LLCT triplet state and consequently the emission energy is dependent on both the identity of the chalcogenolate and the diimine ligands. Increasing the electron-donating ability of the phenyl group on the chalcogenolate ligand results in a blue shift in the emission wavelength (**77c** < **77b** < **77a** < **77d**), whilst substitution of a phenylthiolate group for the equivalent phenylselenolate group results in a red-shift [222]. Cyclic voltammetric data for this series of compounds is given in Table 13. Similar cyclic voltagrams are obtained for all complexes, with one irreversible oxidation wave assigned to the

Table 13

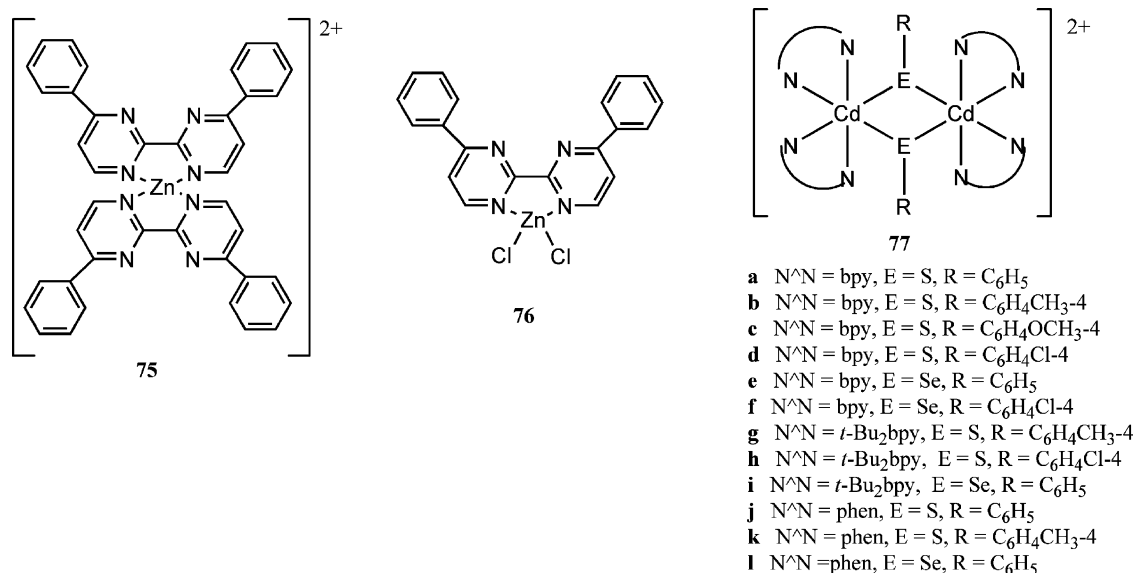
Photophysical and electrochemical data for phosphorescent  $[\text{Cd}_2(\text{N}^{\wedge}\text{N})(\mu\text{-X})_2]$  complexes<sup>222</sup>

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V) vs. SCE <sup>a</sup>	$E_{\text{pc}}^{\text{RED}}$ (V) vs. SCE <sup>b</sup>
<b>77a</b>	Solid	550	–		
	MeCN	421, 582		+1.62	–1.16, –1.28
<b>77b</b>	Solid	558	0.12		
	MeCN	420, 608		+1.57	–1.19, –1.30
<b>77c</b>	Solid	570	–		
	MeCN	442, 612		+1.42	–1.20, –1.32
<b>77d</b>	Solid	536	1.26		
	MeCN	418, 590		+1.74	–1.15, –1.26
<b>77e</b>	Solid	562	0.16		
	MeCN	420, 598		+1.43	–1.21, –1.36
<b>77f</b>	Solid	545	–		
	MeCN	424, 594		+1.61	–1.19, –1.35
<b>77g</b>	Solid	530	–		
	MeCN	416, 580		+1.62	–1.25, –1.34
<b>77h</b>	Solid	523	–		
	MeCN	428, 565		+1.71	–1.24, –1.32
<b>77i</b>	Solid	540	–		
	MeCN	415, 580		+1.50	–1.23, –1.29
<b>77j</b>	Solid	565	–		
	MeCN	420, 582		+1.63	–1.21, –1.29
<b>77k</b>	Solid	575	–		
	MeCN	434, 585		+1.56	–1.23, –1.30

<sup>a</sup> Irreversible ( $E_{\text{pa}}$ ).<sup>b</sup> Irreversible ( $E_{\text{pc}}$ ).

oxidation of the chalcogenolate ligand and two irreversible reduction waves assigned to the reduction of the  $\alpha, \alpha'$ -diimine ligands [222]. The electrochemical behaviour is consistent with the assignment of a  $^3\text{LLCT}$  transition origin but the irreversible redox characteristics are unfavourable for OLED applications (Fig. 12).

Several mercury(II) complexes form luminescent adducts with organic lumophores [223,224]. The interaction of  $[(o\text{-C}_6\text{F}_4\text{Hg})_3]$  with pyrene, naphthalene and biphenyl leads to the formation of 1:1 adducts [225]. Phosphorescence from these organic compounds is generally restricted to low-temperature glasses, but the heavy atom effect exerted by Hg(II) results in

Fig. 12. Structures **75**–**77**.



enhanced spin–orbit coupling and consequently the occurrence of long-lived red, green and blue room-temperature phosphorescence for the pyrene, naphthalene and biphenyl adducts, respectively.

### 2.3. Main group complexes

Extensive research has been carried out on fluorescent main-group compounds, especially group 13 chelates based on 8-hydroxyquinoline, 7-azaindolyl and azomethine derivatives, for OLED technology [190,226–230]. The discovery of tris(8-hydroxyquinolato) aluminum ( $\text{Alq}_3$ ), which is used as an electron-transport emitting layer, was instrumental in the development of stable OLED devices.  $\text{Alq}_3$  emits with a maximum at 532 nm with a PL quantum efficiency of around 32% in thin films at room temperature and is used as the host material for most modern red and green devices [226,227,229]. Whilst research into alternative fluorescent chelates of gallium, indium, beryllium and boron has been carried out, aluminum chelates have been found to exhibit the best combination of device efficiency and stability [226,229].

Reports of phosphorescent main-group complexes remain scarce and are predominantly restricted to groups 14 and 15 compounds. Germanium(II), tin(II) and lead(II) chlorides are known to exhibit green phosphorescence in room-temperature solution [231,232]. The emitting states are identified as being a metal-centred  $\text{sp}$  type, originating from the  $^3\text{P}$  state of the free  $\text{s}^2$  ions. The maximum quantum yield obtained for  $[\text{PbCl}_4]^{2-}$  was 0.054 in deaerated solution [232,233]. Recently, intra-ligand phosphorescence from a series of lead(II)  $\beta$ -diketonates  $[\text{Pb}(\text{O}\ddot{\text{O}})_2]$  ( $\text{O}\ddot{\text{O}} = \text{acac}, \text{hfac}, \text{tta}, \text{dbm}, \text{dpm}$ ) in both the solid state and room-temperature solution was reported [234,235]. Weak emission was observed between 400 and 500 nm, attributed to increased spin–orbit coupling as a consequence of the heavy atom effect induced by lead. The equivalent  $[\text{Tl}(\text{hfac})]$  and  $[\text{Bi}(\text{hfac})_3]$  complexes also exhibit phosphorescence under ambient conditions with emission maxima at 477 and 472 nm, respectively [234].

Antimony and bismuth chlorides exhibit weak room-temperature phosphorescence ( $\Phi_{\text{P}} \sim 10^{-2}$ ) in solution, with emission maxima at 520 and 475 nm for the respective hexachloride anions [233]. However, they are not suitable for OLED devices due to their ionic character and low volatility. Phosphorescence from group 15 complexes with *p*-(*N*-7-azaindolyl)phenyl ligands has been reported in the solid state at room-temperature (Table 14) (78a–c) [236]. Emission is assigned to a ligand-centred transition with some contribution from the metal lone electron pair. There is an increasing heavy atom effect on descending the group, with no visible fluorescence for antimony and bismuth complexes (Fig. 13 and Table 14).

### 2.4. Lanthanide complexes

Metal centred emission from lanthanide(III) complexes does not originate from a transition between two states of different multiplicity and as such is not phosphorescence in the conven-

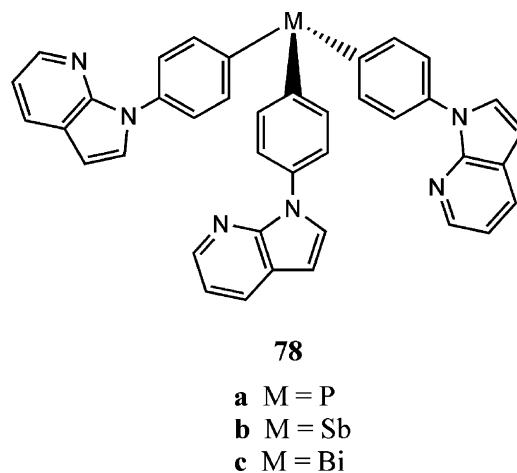


Fig. 13. Structure 78.

tional sense. The emission is assigned to transitions between states of a given  $f^n$  configuration, which are strictly parity forbidden resulting in emission lifetimes in the millisecond regime. Furthermore, unlike d-transition metal ion complexes, in which the electronic excited states are strongly coupled to the environment via the ligand field, in lanthanide complexes the coupling between f-excited electronic states and the environment is small due to shielding from the overlying  $5\text{s}^2$  and  $5\text{p}^6$  shells. Consequently f–f transitions from one J state of an  $f^n$  configuration to another J state of this configuration are extremely sharp [237].

The forbidden nature of f–f transitions is apparent in the small molar extinction coefficients observed for  $\text{Ln}(\text{III})$  ions ( $\epsilon < 3 \text{ mol dm}^{-3} \text{ cm}^{-1}$ ) for europium and terbium [238–240]. This may be overcome by utilising the “antenna effect”, a concept first proposed by Lehn, where a distinct absorption, energy-transfer and emission sequence operates [241]. Energy is first absorbed by an organic chromophoric ligand in the  $\text{Ln}(\text{III})$  coordination sphere and is subsequently transferred to the excited triplet of the chromophore via intersystem crossing. The energy is then intramolecularly transferred to a resonance level of the lanthanide ion which finally emits luminescence.

The  $4f^n$  configuration of a given  $\text{Ln}(\text{III})$  ion gives rise to several terms whose energies are determined by a combination of interelectronic repulsion and spin–orbit coupling [237,242]. Due to negligible ligand field perturbations, the states formed tend to be constant for a given ion and consequently luminescence is observed in a characteristic region for a given ion [237]. Terbium(III) [243–247] and europium(III) [242–244,246,248–251] are green and red emitters respectively and are the most extensively studied lanthanide ions in solution since luminescence

Table 14  
Photophysics of group 15 *p*-(*N*-7-azaindolyl)phenyl compounds

Complex	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\tau$ (ms)	Reference
<b>77a</b>	Solid	465	0.69, 0.195	[236]
<b>77b</b>	Solid	461	0.597, 0.167	[236]
<b>77c</b>	Solid	472	0.368, 0.098	[236]

is much less intense for other members of the series unless in the solid state [252]. There are some examples of other Ln(III) complexes which emit in other regions of the visible spectrum in the solid state: orange ( $\text{Sm}^{3+}$ ) [240,247,249,253], yellow ( $\text{Dy}^{3+}$ ) [247,249,253] and blue ( $\text{Tm}^{3+}$ ) [247,249,254]. However, the luminescence intensity is generally weak in the solid state for these ions and in solution it is virtually undetectable.

The design of efficient luminescent lanthanide coordination compounds has become of interest in recent years [242,255–258]. The electronic configuration of  $\text{Ln}^{3+}$  ions means that they are unable to exhibit strong coordination ability and conventional ligands are frequently displaced by competing water molecules in aqueous solution. Novel ligands possessing multiple convergent pendant arms with N–O and P–O groups which are able to strongly bind the  $\text{Ln}^{3+}$  ion have emerged resulting in a new generation of stable luminescent lanthanide complexes. These include cryptands [256,259], calixarenes [256,259], 1,3-diketones [260], macrocyclic ligands [256,261], carboxylic acid derivatives [262] and heterobiaryl ligands [263].

The observed luminescence intensity from these complexes is controlled by two main factors: (i) the extent of non-radiative deactivation of the excited state and (ii) the ability of the excited triplet state of the ligand to transfer energy to the emitting state of the Ln(III) ion. These factors are affected by the nature of the ion, the ligand structure, the ion–ligand bond and the solvent [264]. Non-radiative deactivation is dependent mainly on the energy gap between the ground and excited states and the ion environment [265]. Lanthanide luminescence may be quenched in aqueous solution due to efficient energy transfer between the resonance level of the ion and O–H oscillators in the coordination sphere [246,266]. Complete occupation of all nine available coordination sites on the trivalent lanthanide ion can eliminate this effect, restoring the emission intensity. Ligands with N–H and N–N oscillators, with similar vibronic frequencies to O–H, are also effective non-radiative deactivators of excited states in  $\text{Eu}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  chelates [240]. In the case of  $\text{Eu}^{\text{III}}$  complexes the quenching by the azide ligand,  $\text{N}_3^-$ , is even more efficient than O–H or N–H [267].

To ensure efficient energy transfer, the ligand should possess one or more chromophores with high extinction coefficients and deactivating ligand transitions such as luminescence should be minimal [254,268]. Rigidity of molecular structure also enhances luminescence intensity by minimising radiationless deactivation [254]. Several extensive studies have been performed on the correlation of the lowest ligand triplet state energy with photophysical properties such as the luminescence quantum yield [255,256,258]. The energy of the emitting level should be just below that of the triplet state of the ligand, so that the probability of transition from the triplet to the emitting level is high [268].

Remarkably high luminescence quantum yields ( $\Phi_{\text{p}} \sim 0.3$ – $0.6$ ) have been achieved for  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  chelates with a wide range of ligands [255,256]. This has led to a surge of interest in  $\text{Eu}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$  and other Ln(III) chelates for OLED technology.

#### 2.4.1. Europium

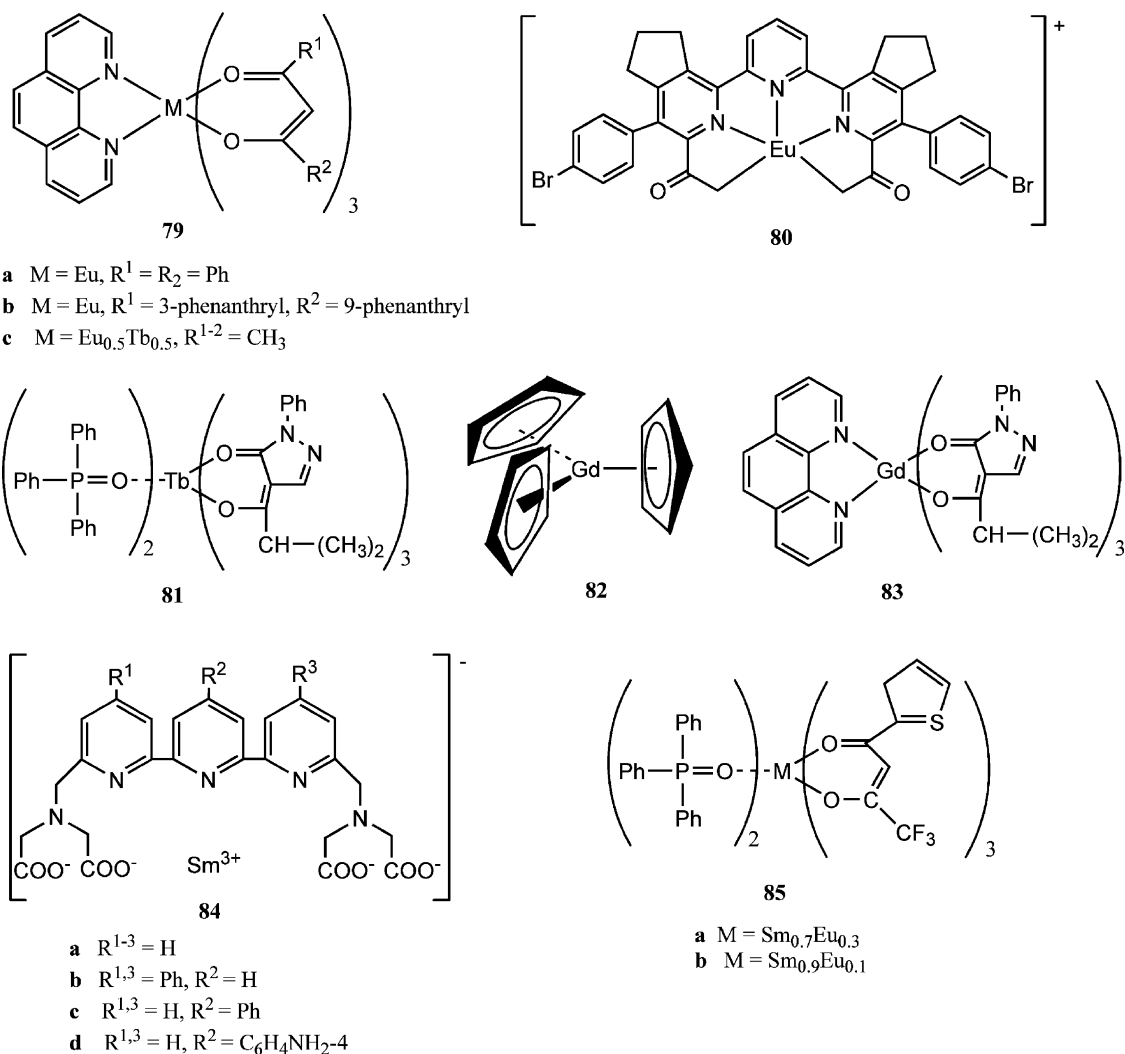
$\text{Eu}^{\text{III}}$  ions are able to accept energy with all of their  $^5\text{D}$  levels, depending on the triplet state energy of the donor. Although luminescence may arise from the  $^5\text{D}_1$  level, the main emission originates from electronic transitions from the lowest excited state,  $^5\text{D}_0$ , to the ground state manifold,  $^7\text{F}_J$  ( $J=6$ – $0$ ) level, with the most intense emission line corresponding to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition, observed at 614 nm, in the red spectral region [243]. Frey et al. showed that the magnitude of the energy gap between the triplet ligand state and the lower-energy europium(III) excited  $^5\text{D}_0$  state influences the luminescence quantum yield [250]. In a series of europium(III)  $\beta$ -diketonate ternary complexes, relative emission intensities were shown to increase by  $\sim 200$ -fold on introduction of a 1,10-phenanthroline ligand, which contains lower-lying triplet states than the  $\beta$ -diketonate ligand, into the complex. A highly luminescent europium(III) complex of a terpyridine derivative (**80**) has recently been reported [269]. The characteristic  $\text{Eu}^{\text{III}}$  line emission in the red spectral region is observed, with a quantum yield of 0.33 in  $\text{D}_2\text{O}$  and an emission lifetime of 1900  $\mu\text{s}$  [269].

Several red devices incorporating europium(III) complexes as the emitter have been reported [270–273]. In 1994 Kido et al. prepared a device incorporating  $[\text{Eu}(\text{dpp})_3(\text{phen})]$  (**79a**) doped in a 1,3,4-oxadiazole matrix, which exhibited red electroluminescence at an efficiency of  $460 \text{ cd m}^{-2}$  at 16 V [271]. More recently Jiang et al. reported a device based on red electroluminescence from  $[\text{Eu}(\text{phen})(\text{L})_3]$  ( $\text{L} = 1,3\text{-di}(9\text{-phenanthryl})\text{-propane-1,3-dione}$ ) (**79b**) with an external quantum efficiency of 0.032% at a current density of  $90 \text{ mA cm}^{-2}$  [270]. An efficient red double layer device incorporating both  $[\text{Eu}(\text{phen})(\text{acac})_3]$  and the mixed lanthanide complex  $[\text{Tb}_{0.5}\text{Eu}_{0.5}(\text{phen})(\text{acac})_3]$  (**79c**) has also been reported [273]. The red EL observed from this double layer structure was approximately ten times stronger than that observed for a single layer device containing only  $[\text{Eu}(\text{phen})(\text{acac})_3]$  in the emitting layer. The increase in electroluminescence for the double layer device was attributed to efficient  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  energy transfer (Fig. 14).

#### 2.4.2. Terbium

In  $\text{Tb}^{\text{III}}$  complexes energy is primarily transferred from the ligand triplet to the  $^5\text{D}_4$  level from which luminescent transitions to the ground state manifold  $^7\text{F}_J$  ( $J=6$ – $0$ ) are observed in the green spectral region [243]. The most intense transition for terbium(III) is the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition, corresponding to a green emission band at 545 nm. Lifetimes for  $\text{Tb}^{\text{III}}$  emission are in the region of a few hundred microseconds and emission quantum yields of  $\sim 0.4$  have been obtained for terbium(III) cryptates at 300 K [242].

Green emission has been obtained from a number of terbium(III)-based devices (Table 15) [274–276]. To date the most efficient device has incorporated the complex  $[\text{Tb}(\text{PPO})_2(\text{PMIP})_3]$  (**81**) in the emitting layer, which gave a maximum luminance of  $920 \text{ cd m}^{-2}$  at 18 V [275]. It is interesting to note that  $[\text{Tb}(\text{PPO})_2(\text{PTT})_3]$  also possesses a much higher photoluminescence efficiency than the commonly used green emitter  $\text{Alq}_3$ .

Fig. 14. Structures **79–85**.

### 2.4.3. Thulium

The emission of thulium(III) in solution is weak, but in the solid state the  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transition is sufficiently intense to allow the observation of blue luminescence at 480 nm in some thulium(III) complexes [254,277]. Li et al. [277] reported the fabrication of an OLED device with  $[\text{Tm}(\text{acac})_3(\text{phen})]$  as the emitting layer, analogous to the terbium and europium based devices prepared by the same group [277]. The relatively weak electroluminescence and poor device efficiency ( $\sim 0.0074 \text{ lm W}^{-1}$  at 16 V) was attributed to the large energy

difference between the excited triplet state of the ligand and the  $^1\text{G}_4$  level of the Tm(III) centre.

### 2.4.4. Gadolinium

Due to the stability of the half-filled  $4f^7$  shell configuration in gadolinium(III), the metal-centred f–f states are located at exceptionally high energies. Consequently the lowest energy f–f transition appears at 313 nm, outside of the visible spectral region [278]. Intraligand states frequently occur at lower energies in gadolinium(III) complexes. This introduces the pos-

Table 15  
Device characteristics of several terbium(III) green OLEDs

Complex	Host	Luminance ( $\text{cd m}^{-2}$ )	Drive-voltage (V)	$\eta_{\text{ext}}^a$ (%)	Reference
<b>81</b>	–	920	18	–	[275]
$[\text{Tb}(\text{acac})_3(\text{phen})]$	PVK	210	16	–	[274]
$[\text{Tb}(\text{Tfacac})_3(\text{phen})]$	PVK	58	25	0.25	[245]
$[\text{Tb}(\text{Tfacac})_3]$	PVK	36	25	0.16	[245]
$[\text{Tb}(\text{acac})_3(\text{phen})]$	PVK	25	25	0.11	[245]
$[\text{Tb}(\text{acac})_3]$	PVK	17	25	0.08	[245]

<sup>a</sup>  $\eta_{\text{ext}}$ : OLED external quantum efficiency.

sibility of observing ligand-based phosphorescence, which is intensified by the heavy atom effect exerted by the metal centre. This effect has been reported for [Gd(Cp)<sub>3</sub>] (**82**), which exhibits green luminescence (525 nm) in ether solution at room-temperature with a significant quantum yield ( $\Phi_P=0.2$ ) [278]. This concept has been applied to an organic electroluminescent device based on the gadolinium ternary complex, [Gd(PMIP)<sub>3</sub>(phen)] (**83**) [279]. Green electroluminescence at 535 nm was observed and attributed to an intraligand triplet state transition, with a maximum luminance of 230 cd m<sup>-2</sup> at a drive voltage of 17 V. This indicates that heavy lanthanide atom sensitised ligand phosphorescence may provide a viable alternative for the utilisation of lanthanide complexes in OLED devices. This approach would allow the emitting ligand to be specifi-

cally selected, depending on the emission requirements, which would broaden the variety of emission wavelengths currently available.

#### 2.4.5. Samarium

The most intense transition for samarium(III) is <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>7/2</sub>, corresponding to an emission line at ~600 nm in the red spectral region. Sm(III) emission is generally much weaker than observed for the equivalent Eu(III) complexes and consequently research into orange-red emitters has tended to focus on europium compounds [280]. However, recently a series of novel Sm(III) chelates (**84a–d**) with high luminescence quantum yields ( $\Phi_P=0.15$ – $0.32$ ) and fairly short lifetimes ( $\tau=16.2$ – $19\ \mu\text{s}$ ) have been reported [281].

Table 16  
Photophysical and electrochemical properties of some heterometallic complexes

Complex	Metal	Medium (298 K)	$\lambda_{\text{em}}$ (nm)	$\Phi_P$	$\tau$ ( $\mu\text{s}$ )	$E_{1/2}^{\text{OX}}$ (V)	$E_{1/2}^{\text{Red}}$ (V)	Reference
<b>86a</b>	Re–Cu	CH <sub>2</sub> Cl <sub>2</sub>	590	–	0.18	–	–	[284]
<b>86b</b>	Re–Ag	CH <sub>2</sub> Cl <sub>2</sub>	600	–	0.16	–	–	[284]
<b>87a</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	550	–	0.80	+1.78 <sup>a,b,c</sup>	–1.23 <sup>d,c</sup> , –1.4 <sup>a,e,c</sup>	[285]
<b>87b</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	550	–	0.67	+1.79 <sup>a,c,e</sup>	–1.23 <sup>d,c</sup> , –1.47 <sup>a,e,c</sup>	[285]
<b>87c</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	539	–	0.73	+1.67 <sup>a,c,e</sup>	–1.36 <sup>d,c</sup> , 1.58 <sup>a,e,c</sup>	[285]
<b>87d</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	539	–	1.36	+1.66 <sup>a,c,e</sup>	–1.36 <sup>d,c</sup> , –1.60 <sup>a,e,c</sup>	[285]
<b>88</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	637	0.0032	–	–	–	[286]
<b>89</b>	Re–Au	CH <sub>2</sub> Cl <sub>2</sub>	644	0.0018	–	–	–	[286]
<b>90a</b>	Ru–Rh	MeOH/EtOH	636	–	0.13	+1.03 <sup>b,e</sup>	–1.65, –2.03 <sup>d,c</sup>	[293]
						+1.39 <sup>e,f</sup>	–2.26, –2.49 <sup>a,e,c</sup>	
<b>90b</b>	Ru–Ir	MeOH/EtOH	635	–	0.13	+1.05 <sup>b,e</sup>	–1.66, –1.98 <sup>d,c</sup>	[293]
						+1.35 <sup>a,c,e</sup>	–2.27 <sup>a,e,c</sup>	
<b>91a</b>	Pt–Ag	CH <sub>2</sub> Cl <sub>2</sub>	622	–	<0.1	–	–	[182]
<b>91b</b>	Pt–Cu	CH <sub>2</sub> Cl <sub>2</sub>	625	–	<0.22	–	–	[151]
<b>92</b>	Pt–Cu	Solid	616	–	1.97	–	–	[288]
<b>93a</b>	Pt–Cu	Solid	618	–	0.078	–	–	[288]
<b>93b</b>	Pt–Cu	Solid	600	–	0.21	–	–	[288]
<b>93c</b>	Pt–Cu	Solid	601	–	0.1	–	–	[288]
<b>93d</b>	Pt–Cu	Solid	626	–	0.26	–	–	[288]
<b>94a</b>	Pt–Au	Solid	642	–	1.44	–	–	[288]
<b>94b</b>	Pt–Au	Solid	609	–	1.17	–	–	[288]
<b>95</b>	Pt–Au	Solid	563	–	0.66	–	–	[288]
<b>96a</b>	Au–Cu	CH <sub>2</sub> Cl <sub>2</sub>	639	–	0.22	–	–	[289]
<b>96b</b>	Au–Cu	CH <sub>2</sub> Cl <sub>2</sub>	660	–	0.39	–	–	[289]
<b>97</b>	Pt–Ti	Solid	444	–	0.25	–	–	[290]
<b>98</b>	Au–Ti	Solid	575	–	0.98	–	–	[291]
<b>99a</b>	Au–Cu	CH <sub>2</sub> Cl <sub>2</sub>	585	–	<0.1	–	–	[289]
<b>99b</b>	Au–Ag	CH <sub>2</sub> Cl <sub>2</sub>	553	–	<0.1	–	–	[289]
<b>100</b>	Ir–Eu	CD <sub>3</sub> OD	460, 491, 615	0.07	0.48 (Ir), 1900 (Eu)	–	–	[269]
<b>101a</b>	Ru–Ru	MeCN	625	1.7	0.079	+1.27 <sup>d,c,g</sup>	–1.31, –1.52, –1.84 <sup>d,c,g</sup>	[95]
<b>101b</b>	Os–Os	MeCN	751	0.06	0.004	+0.86 <sup>d,c,g</sup>	–1.20, –1.42, –1.78 <sup>d,c,g</sup>	[95]
<b>101c</b>	Ru–Ru	MeCN	625	1.7	0.070	+1.26 <sup>d,c,g</sup>	–1.31, –1.51, –1.84 <sup>d,c,g</sup>	[95]
<b>101d</b>	Os–Os	MeCN	746	0.06	0.004	+0.83 <sup>d,c,g</sup>	–1.23, –1.45, –1.87 <sup>d,c,g</sup>	[95]
<b>101e</b>	Ru–Os	MeCN	–(Ru) 752 (Os)	4 × 10 <sup>-6</sup> 0.043	– –	– –	– –	[96]
<b>101f</b>	Ru–Os	MeCN	621 (Ru) 751 (Os)	2 × 10 <sup>-3</sup> 0.043	– –	– –	– –	[96]

<sup>a</sup> Irreversible couple.

<sup>b</sup>  $E_{\text{pa}}$ .

<sup>c</sup> vs. SCE; in MeCN.

<sup>d</sup> Reversible couple.

<sup>e</sup>  $E_{\text{pc}}$ .

<sup>f</sup> Bi-electronic wave.

<sup>g</sup> In BuCN.

Electroluminescence has been reported from several devices incorporating mixed Sm(III) and Eu(III) complexes (**85a–b**) [282,283]. The emission is comprised of both the typical Sm(III) transitions at 563, 598 and 644 nm and the Eu(III) transitions at 579 and 612 nm. In addition, a broad band attributed to ligand phosphorescence is also observed. The relative contribution of metal centred and ligand centred emission may be controlled by altering the bias voltage applied to the OLED, thus allowing the

electroluminescence colour to be electrically tuned [282,283]. At low voltages emission from the Eu(III) centre dominates and red electroluminescence is observed. As the voltage increases to 16 V emission from Eu(III), Sm(III) and the ligand is observed. On application of 22 V emission from Eu(III) is absent and Sm(III) emission is maximized. Overall this corresponds to a shift from the red to the orange spectral region as the voltage is increased.

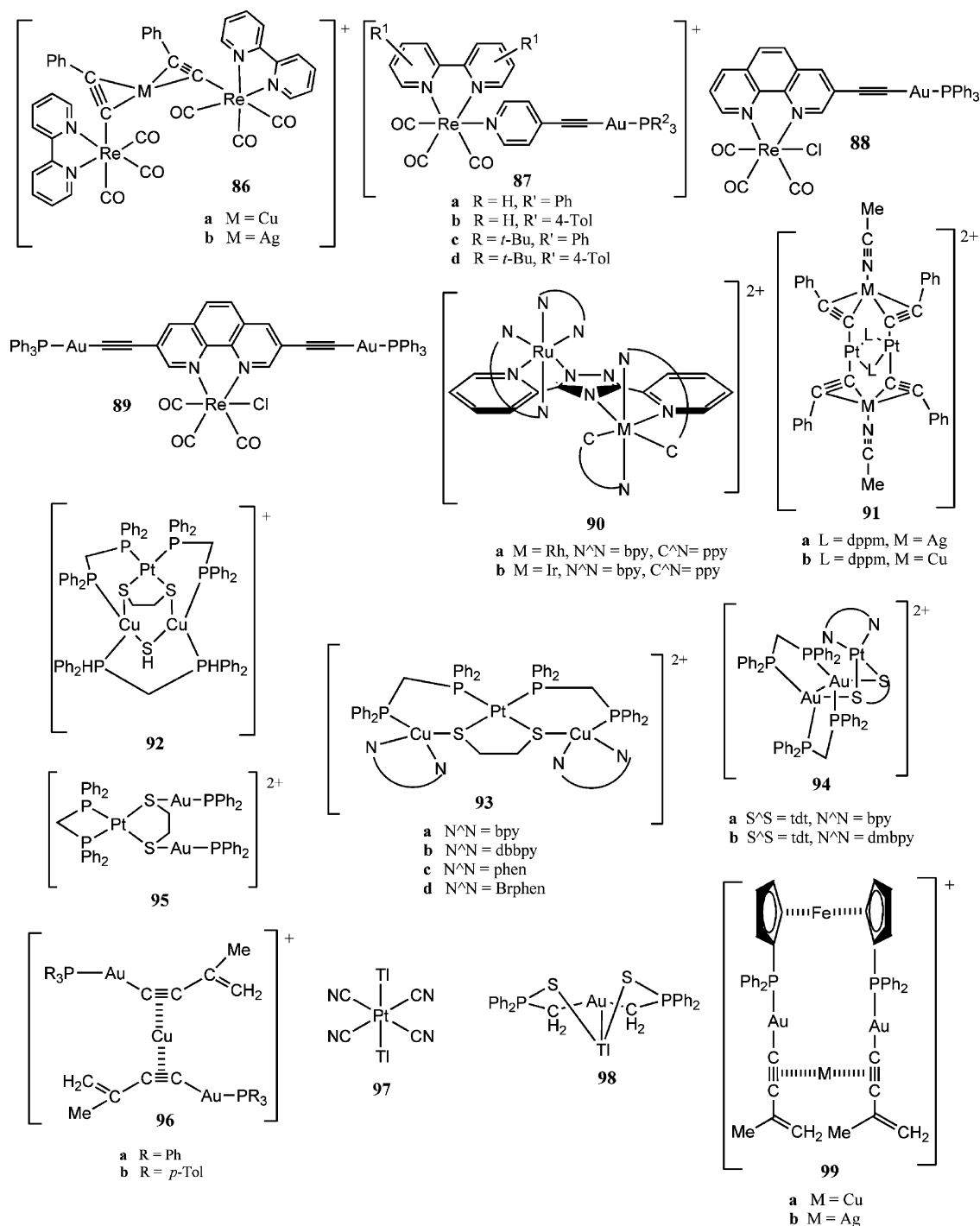


Fig. 15. Structures **86–99**.



## 2.5. Heterobimetallic complexes

A variety of luminescent heterometallic complexes incorporating the heavier groups 8–11 transition metals have been developed (Table 16). The lowest luminescent level in these complexes is attributed to a  $^3\text{MLCT}$  state, which contains contributions from both metal centres. Emission wavelengths are therefore typically situated between the characteristic emission energies observed for the analogous monometallic complexes.

Several mixed-metal alkynyl complexes containing rhenium(I) and a  $d^{10}$  metal centre (copper(I), silver(I) or gold(I)) have been reported [284–286]. Characteristic emission from the  $\text{M(I)-alkynyl}$  centre ( $\text{M}=\text{Cu}, \text{Ag}, \text{Au}$ ) is absent in these complexes, which is attributed to efficient energy transfer to the lower-lying  $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$   $^3\text{MLCT}$  excited state [285]. This is accompanied by an increase in the luminescence quantum yield in the  $\text{Re(I)-M(I)}$  complexes compared to the  $\text{Re(I)}$  precursors. Emission energies for these mixed-metal  $\text{Re(I)-M(I)}$  complexes lie in the green–orange spectral region, which is characteristic  $\text{Re(I)}$  emission.

Mixed  $\text{Pt(II)-M(I)}$  alkynyl complexes ( $\text{M(I)}=\text{Cu}, \text{Ag}, \text{Au}$ ) have also been reported (91–95) [182,287,288]. The origin of emission in these complexes is largely dependent on the ligands present and has been attributed to  $^3\text{MMLCT}$ ,  $^3\text{MLCT}$  and  $^3\text{LMCT}$  states. Emission wavelengths lie in the orange–red spectral region, with lifetimes in the microsecond regime. Luminescent heterometallic  $\text{Au(I)-M(I)}$  alkynyl complexes ( $\text{M(I)}=\text{Ag(I)}, \text{Cu(I)}$ ) have also been prepared (96, 99) [289]. Emission from the  $\text{Au(I)-alkynyl}$  excited states is again absent in these complexes, due to efficient energy transfer to the lower-lying  $\text{Cu(I)/Ag(I)-alkynyl}$  excited states [289]. These states are tentatively assigned to  $\text{LMCT}$  parentage mixed with metal-centred  $\text{nd}^9(n+1)\text{s}^1$  state, with some additional  $[\pi \rightarrow \pi^*(\text{C}\equiv\text{C})]$  IL character [56]. Heterobimetallic complexes of platinum(II) and gold(I) with thallium(I) have also been reported (97–98) [290–292]. The  $\text{Pt(II)-Tl(I)}$  complex is particularly interesting as it emits at 444 nm in the solid state [290]. Direct  $\text{Tl-Pt-Tl}$  bonding is believed to dominate the luminescence behaviour of

this complex, with emission assigned to a triplet mixed metal centred excited state (Fig. 15).

An assembly (100) comprising the blue luminescent iridium(III) unit and a red luminescent europium(III) unit (80) has recently been reported [269]. In this system the function of the iridium unit is to sensitise the europium(III) complex via the antenna effect. Selective excitation of the iridium moiety results in the emission of almost white light due to the combination of residual blue–green emission from the iridium component and the sensitised red emission of the europium(III) complex.

Homo- and heterobimetallic complexes of ruthenium(II) and osmium(II) have been extensively studied by de Cola and co-workers, with the intent of designing photoactive molecular switches [90–98]. In these complexes the two metal centres are connected by an organic wire type bridge [90–96]. An example system is the  $[\text{M}(\text{bpy})_3\text{-BL-M}(\text{bpy})_3]^{4+}$  series ( $\text{M}=\text{Ru}, \text{Os}$ ,  $\text{BL}=\text{polyphenylene}$ ) (101) [95,96]. Characteristic emission in the orange–red and infra-red regions is observed for the  $\text{Ru}$  and  $\text{Os}$  series respectively. The extended delocalisation results in comparatively long excited state lifetimes but increasing the length of the polyphenylene spacer group has little influence on the general photophysical properties of either the  $\text{Ru}$  or  $\text{Os}$  series (Table 16). In the mixed  $\text{Ru-Os}$  complex (101) energy transfer from the  $\text{Ru(II)}$  to the  $\text{Os(II)}$  metal centre occurs via the bridging ligand, which is confirmed by a decrease in the  $\text{Ru(II)}$  excited state lifetime compared to the analogous  $\text{Ru-Ru}$  complex (Table 16) [96]. The introduction of a photoactive switching unit such as a dithienylethene derivative has been shown to be effective in controlling communication between the two metal centres [97,98] (Fig. 16).

Due to the synthetic difficulties associated with the preparation of heterometallic complexes, the examples of complexes of this type exhibiting room-temperature phosphorescence are limited. However the relatively short emission lifetimes, accompanied by the increased emission tuning possibilities created by introducing a second type of metal centre mean that mixed-metal complexes may be a huge source of untapped potential for OLED technology.

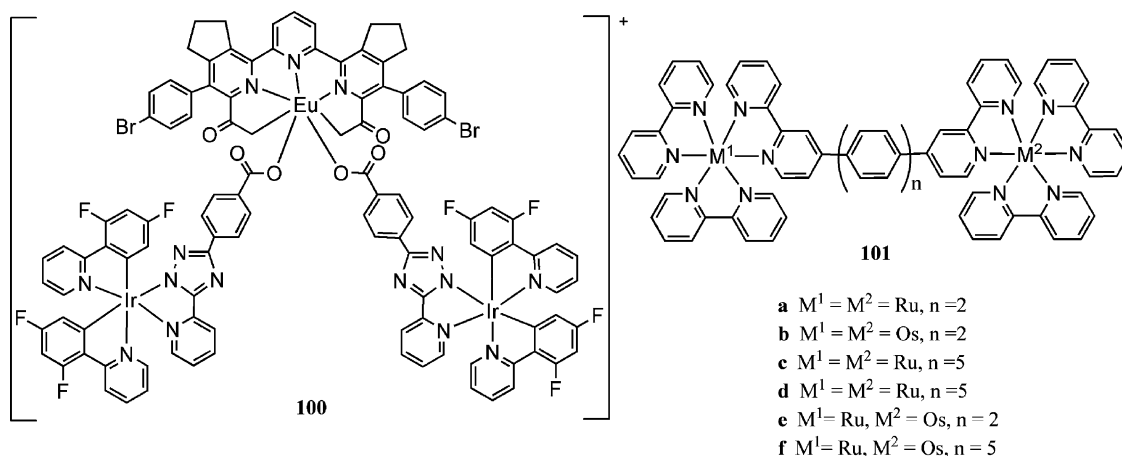


Fig. 16. Structures 100 and 101.

### 3. Conclusions

The photophysical emission characteristics of known luminescent complexes have been systematically reviewed and discussed in relation to the potential of these complexes as phosphorescent emitters for organic light emitting diodes. In terms of possible future developments, and in particular for blue emitters, we identify the following groups of compounds as being of particular interest: (1) polynuclear copper(I) complexes, (2) mono-, di- and polynuclear gold(I) complexes and (3) osmium(III) complexes. Compounds of these types exhibiting intense blue room-temperature phosphorescence have all been reported, but as yet there have been limited examples of application of this potential to OLED devices. This is an area worthy of considerable investigation. In addition, although the synthesis of luminescent heterobimetallic transition and main group metal complexes has received growing interest in recent years, little attention has been given to the application of these luminescent complexes in technological applications such as OLED devices. Depending on the choice of metals and ligands, emission wavelengths span the visible spectrum and lifetimes are in the 0.1–10  $\mu$ s region. This suggests that heterometallic complexes may offer the possibility for molecular design, to give phosphors with emission properties which may be tuned specifically for optimum performance in OLED technology.

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