

Recent Advances on Phosphorescent Cycloplatinated Compounds Containing Tetradentate Nitrogen Ligands for OLED Applications

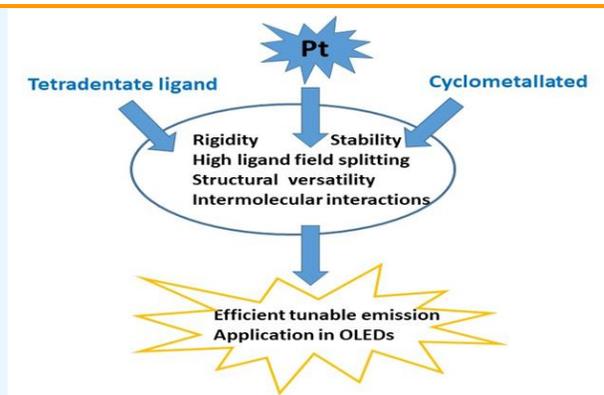
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Abstract: Tetradentate Pt(II) emitters have attracted great interest since they can be used as dopants for organic light emitting diodes (OLEDs). These compounds benefit from the square-planar geometry of Pt(II) and the rigidity of the tetradentate ligand. Cyclometallated ligands are particularly appealing since they are thermally stable and display a high ligand field splitting which favours efficient emission. The photophysical properties of these complexes can be tuned by structural modifications, introduction of substituents or control of the intermolecular interactions. Several of the studied compounds have been successfully tested for electroluminescent devices. An overview of the advances reported in this field for the last five years is presented in this work.



Keywords: Platinum, Cyclometallated, Tetradentate ligands, Luminescence, Electroluminescent devices

This paper is dedicated to the memory of Professor Mehdi Rashidi in appreciation of his great contributions to Pt(II) chemistry.

1. INTRODUCTION

In recent years, the luminescence properties of Pt complexes have been extensively studied with the aim of using such compounds as phosphorescent emitters in organic light emitting diodes (OLEDs) or in other applications such as bioimaging agents, optical sensors, or photocatalysts.¹⁻³ As for other heavy metals, the high spin-orbit coupling constant of Pt promotes rapid intersystem crossing (ISC) from both lowest excited singlet state (S_1) to triplet state (T_1) and T_1 to ground state (S_0) thus allowing efficient emission from the triplet state.^{4,5} For these compounds, the presence of strong-field C-donor ligands such as cyanide or acetylides avoid non radiative decay associated with d-d excited states and favour efficient emission at room temperature. In this sense, cyclometallated Pt compounds are more efficient than other types of coordination compounds since they contain a chelate ligand which, in addition to coordinate through donor atoms such as nitrogen, is bound to the metal through at least one carbon atom. In addition to a high ligand field splitting, the metal-carbon bond contributes to increase the stability of the compound, and the rigid nature of the

cyclometallated ligand hinders molecular distortions thus restricting non-radiative processes.

The emission takes place from the lowest triplet excited state (T_1) which originates from mixed ligand centred (LC) and metal-to-ligand charge transfer (MLCT) states and it can be modulated by modifying the frontier orbitals of the cyclometallated ligand or the involvement of the MLCT character.^{1,3,6} A higher MLCT character leads to high quantum efficiency but broad emission spectra. In contrast, when ligand centred emission is dominant the efficiency is lower but the spectra are narrow resulting in high colour purity.⁷

Complexes of Pt(II) are four-coordinated with a square planar geometry which facilitates the formation of excimers or aggregates *via* $\pi \cdots \pi$ or Pt \cdots Pt interactions with emission features different than those of the isolated monomers.¹

Either bidentate, tridentate or tetradentate cyclometallating ligands can be accommodated around Pt(II) leading to different classes of cycloplatinated compounds which, in turn, can be classified according to the type and arrangement of the donor atoms, the structure of the ligand

or the neutral or ionic nature of the compound. It is assumed that rigidity favours luminescence over non-radiative decay so that an increase in the hapticity of the cyclometallated ligand should improve the luminescence efficiency. Indeed, although a high number of cyclometallated Pt(II) complexes containing bidentate [C,N] or terdentate [C,N,N] or [N,C,N] are strongly luminescent,^{3,8,9} increasing interest is devoted to tetradentate ligands which constitute a very promising class of compounds because they can suppress the vibration and rotation around the metal.¹⁰⁻¹²

The aim of this article is to present an overview of the most relevant achievements published in the last five years in the field concerning the luminescence properties and applications of cyclometallated Pt(II) compounds containing tetradentate nitrogen ligands.

2. ORGANIC LIGHT EMITTING DIODES AND THE ROLE OF PT(II) COMPOUNDS IN THESE DEVICES

OLEDs are electroluminescent devices, in which thin film layers of organic molecules or polymers, placed between a cathode and an anode, emit light in response to an electric current. When applying an electric potential, electron carriers and hole carriers are formed at the cathode and anode, respectively. Combination of charge carriers of opposite sign lead to one ground state molecule and an exciton in singlet or triplet states. Since emission from triplet states (phosphorescence) is spin-forbidden in purely organic molecules, emission takes place only from singlet states, thus limiting the efficiency of the device.

The high spin-orbit coupling constant of heavy transition metals promotes rapid intersystem crossing (ISC) from singlet to triplet states, thus allowing emission from the triplet state. For this reason phosphorescent transition metal complexes incorporated into the emissive organic layer as dopants allow emission from both singlet and triplet states and the internal electroluminescent quantum efficiency (IQE), defined as the ratio of number of photons emitted to the number of electrons injected, may increase up to 100%, instead of a maximum value of 25% expected from the statistical 1:3 ratio of singlet and triplet excitons. Nevertheless, somewhat lower values are obtained for the external quantum efficiency (EQE) defined as the number of photons observed externally to the device to the number of electrons injected.^{1,10,12}

Other parameters commonly used to measure the efficiency of the device are the luminous intensity under unit current or current efficiency (CE) and the luminous flux emitted by unit power or power efficiency (PE), and both CE and PE should be high for devices with excellent performance.¹³ Another useful parameter is luminance (L) which indicates the intensity of the emitted light and is related to the brightness we perceive. On the other hand, the CIE (Commission Internationale de l'Eclairage) coordinates

(x,y) are generally used for the objective description of the emission colour. The essential components in full colour displays are red, green and blue, so that stable and efficient emitters with high colour purity are searched for these three colours.

The increasing demand for efficient phosphorescent emitters in OLEDs has led to intense research for luminescent heavy transition metal compounds, which, additionally are often useful for other applications such as bioimaging agents or optical sensors. Most OLEDs such as those used in mobile phones work at low luminance (100-400 cd m⁻²), however much higher luminance, up to 10,000 cd m⁻² are required for general illumination purposes. This is a challenge for phosphorescent OLEDs (PHOLEDs) since their efficiency tend to decrease as luminance increases, which is known as efficiency roll-off, due to triplet-triplet annihilation because of the long triplet state lifetimes of phosphorescent emitters.

Octahedral d⁶-Ir(III) complexes have been thoroughly studied and used as phosphorescent dopants in OLEDs leading to high EQE values. Further studies included octahedral d⁶ complexes of Re(I), Ru(II) or Os(II) and square-planar d⁸ complexes of Au(III), Pd(II) or Pt(II). In spite of the initial success of Ir(III) complexes, Pt(II) complexes can be considered nowadays as valuable alternative phosphorescent materials for OLEDs.^{6,11}

Pt(II) complexes are attractive as phosphorescent emitters in OLEDs because they adopt a square-planar geometry that allows them to aggregate through either Pt...Pt interactions or π ... π stacking of the ligands leading to formation of dimers (in the ground state) or excimers (in the excited state). Emission from both monomers and excimers or aggregates may cover the whole visible spectra since emission from excimers is red-shifted from that of isolated monomers. Moreover, square-planar Pt(II) complexes that emit from both monomer and excimer states are a good choice for developing white light emitting devices (WOLEDs) using a single metal complex as dopant. However, intermolecular interactions leading to aggregation should be controlled for monochromatic devices requiring high colour purity, and excimer formation may cause emission self-quenching at high doping levels.

Formation of excimers emitting at longer wavelengths than the monomers could also be useful for obtaining near-infrared (NIR) emitting devices.¹ NIR light is more suitable than shorter wavelengths for bioimaging and sensing applications since it can penetrate biological tissue to a greater extent.¹⁴

On the other hand, the development of efficient and stable Pt(II)-based blue emitters is more challenging than that of red or green ones. The tendency to form excimers and the distortion of the metal centre from square-planar geometry at the excited states limit the use of Pt compounds as blue emitters. Nevertheless, the use of strategies previously

reported for Ir compounds such as stabilise the highest occupied molecular orbital (HOMO) using electron withdrawing substituents or destabilise the lowest occupied molecular orbital (LUMO) by replacing pyridine for azole moieties, produced efficient blue phosphorescent Pt compounds.^{6,15-17}

3. CYCLOPLATINATED COMPOUNDS CONTAINING TETRADENTATE NITROGEN LIGANDS

The strong ligand field associated with cyclometallating ligands favours luminescence by raising the energy of the d-d states. Moreover, among cyclometallated compounds, those bearing tetradentate ligands usually exhibit higher phosphorescent efficiency than the analogues containing bi- or tridentate ligands since they benefit from a higher rigidity that decreases non-radiative vibrational pathways and reduces tetrahedral distortion of the excited state. In addition, tetradentate ligands confer high thermal stability to the compounds which is a desirable feature for the construction of efficient and robust OLEDs. Furthermore, these ligands can be easily modified by forming either 5- or 6-membered chelates or by introducing structural motifs or different substituents that may produce changes on the molecular rigidity or on the ligand electronics. Theoretical calculations are most useful to reveal the effect of these changes on the energies of the frontier orbitals and thus on the photo and electro-luminescence properties of these compounds.

Tetradentate cyclometallating ligands can be prepared by a sequence of organic synthesis steps generally involving C-C, C-N or C-O cross coupling, condensation reactions or nucleophilic substitutions. One-pot reaction of these ligands with K_2PtCl_4 in either acetic acid or acetic acid/chloroform mixtures under reflux in nitrogen atmosphere is the most common method to obtain cyclometallated Pt compounds with tetradentate ligands, although, in some cases the procedure involves the reaction of the tetradentate ligand with Pt precursors such as $[PtCl_2(PhCN)_2]$ or $[PtCl_2(COD)]$ in organic solvents.¹⁷ The most common types of such compounds are those containing [N,C,N,O], [N,C,C,N] or [C,N,N,C] ligands which are described below.

Pt(II) Compounds with [N,C,N,O] Ligands

In order to avoid the need of a fourth ligand, which is often a weakly coordinated ligand like chlorido, to complete the coordination sphere of Pt(II) compounds with terdentate [N,C,N] ligands, tetradentate [N,C,N,O] ligands leading to more rigid and stable compounds were developed. An interesting class of tetradentate cyclometallated Pt(II) compounds containing [N,C,N,O] ligands was reported by Che *et al.* in 2013¹⁸ and related studies have been pursued in the following years. In these compounds, the introduction of an O-donor in the cyclometallated ligand

produced rigid asymmetric tetradentate compounds which are stable, highly emissive and are often obtained with good yields from the corresponding ligand and K_2PtCl_4 . The compounds initially reported (see Figure 1, structure A) display a planar geometry around the Pt atom and extensive intermolecular $\pi \cdots \pi$ stacking but not Pt \cdots Pt interactions and were shown to be efficient for the fabrication of WOLED with a single emissive dopant.

In search of efficient red and near-infrared (NIR) OLEDs, the emission properties of compounds **1** and **2**, shown in Figure 1, with analogous [5,5,6] structures were studied in aggregation forms revealing the presence of significant intermolecular interactions. Thus, using neat **1** as the emitting layer, highly efficient NIR OLEDs were obtained while a device based on compound **2** as dopant produced deep red emission (see Table 1).¹⁴

On the other hand, in order to reduce the formation of excimers through intermolecular interactions, a spiro linkage was introduced incorporating a biphenyl moiety nearly perpendicular to the coordination plane.¹⁹ This strategy led to compounds **3** and **4**, shown in Figure 1, which are thermally stable and highly phosphorescent and for which the spiro linkage is effective in reducing aggregation and the tert-butyl substituents also contribute to reduce intermolecular interactions and enhance the solubility. Small variations in the ligand (electron deficient pyridine versus electron rich N-methylimidazole) produced variations in the energies of the frontier orbitals but did not produce significant changes in the photophysical properties. For both complexes the emission is similar in solution and in the solid state which indicates that the strategy to hinder aggregation is successful. OLEDs based on these compounds produced efficient yellow-green electro-phosphorescence.

Another study shows that devices obtained using a double-host emitting layer and compounds **5** and **6** containing a bridging tertiary amine or a bulky 2,6-dimethyl-4-tert-butylphenyl moiety were able to reduce the efficiency roll-off maintaining high EQE values at a luminance of 10,000 cdm^{-2} . Therefore, these compounds are well suited for OLEDs requiring high-brightness.²⁰ Compounds **5** and **6** are thermally stable as confirmed by thermogravimetric analyses and contain sterically hindered moieties in order to avoid aggregation.

In order to achieve a high photostability, which is a desirable property for using the compound as emitter in devices, compound **7** containing an acridinyl group and strong Pt-N bonds was prepared.⁷ This compound has a planar geometry and the distortion in the lowest triplet excited state (T_1) state compared to S_0 state is small. Compound **7** emits at room temperature with a high quantum yield and displays a long photo-stability lifetime. Recently, voltage-dependent colour-tuneable OLEDs were obtained using a single tetradentate [N,C,N,O]-Pt(II) compound as emitter. The reported compounds are able to

emit both high-energy and low-energy light with high efficiency and short emission lifetimes.²¹

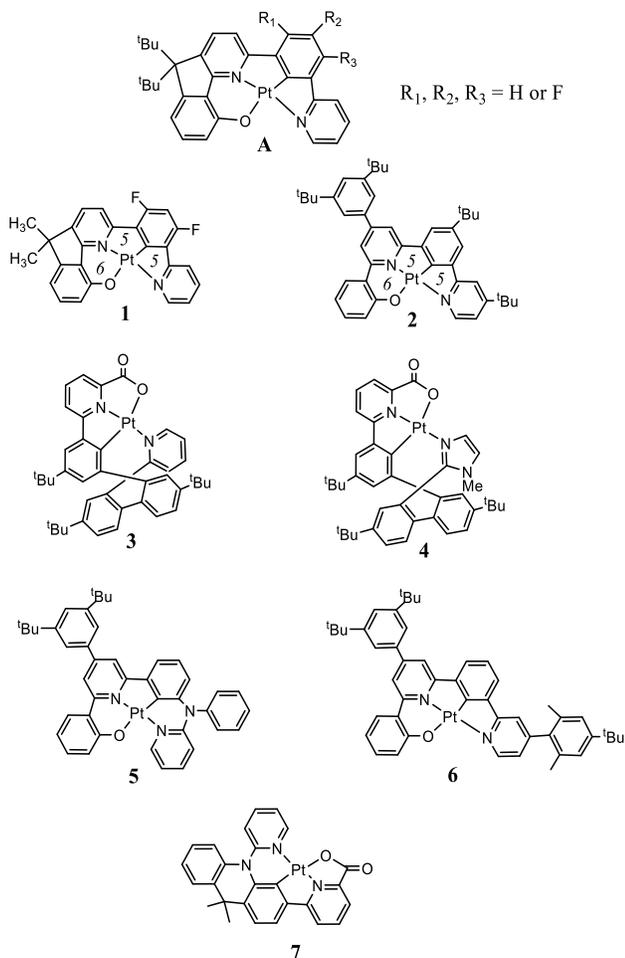


Figure 1. Selected examples of Pt(II) compounds with [N,C,N,O] ligands. Adapted from figures in the literature: **A** [ref.18], **1** and **2** [ref.14], **3** and **4** [ref.19], **5** and **6** [ref.20], and **7** [ref.7].

Pt(II) Compounds with [N,C,C,N] or [C,N,N,C] Ligands

Another strategy to obtain tetradentate ligands consists in linking two bidentate [C,N] cyclometallating moieties, so that these ligands may coordinate to Pt through two nitrogen and two carbon atoms to produce bis-cyclometallated compounds. The most common coordination pattern is [N,C,C,N] allowing for both symmetrical or unsymmetrical ligands. Initial work involved symmetric bis-cyclometallated tetradentate complexes that were obtained by linking with an amine or an oxygen two [C,N] moieties leading to compounds [Pt(N,C,C,N)] which are more stable and efficient than the corresponding bidentate bis-cyclometallated Pt complexes [Pt(C,N)₂]. The latter are unstable with respect to a distortion from square-planar to tetrahedral conformation in the excited state which facilitates non-radiative decay. In contrast, tetradentate coordination pattern minimises the

excited state distortions and decreases non-radiative pathways.²

In fact, several coordination patterns around Pt are possible by linking two [C,N] moieties however, in agreement with the anti-symbiotic effect,²² the presence of two C-donor ligands in mutually *trans* positions will have a destabilizing effect while [C,N,N,C] and [N,C,C,N] coordination sets in which the carbon atoms are *trans* to nitrogen atoms should lead to more stable compounds. As expected, these compounds show a high thermal stability when analysed by thermal gravimetry.^{23,24}

Concerning the size of the fused rings, tetradentate [5,6,5] and [5,5,6] systems exhibit planar geometries that allow for excimer emission while [5,6,6] and [6,6,6] analogues display generally more distorted geometries that inhibit intermolecular interactions. For this reason, the former are ideally suited for single-doped white OLEDs and the latter for monochromatic emission.²⁵

An strategy involving unsymmetrical ligands was developed by Li *et al.* who obtained efficient blue-emitting tetradentate Pt complexes with a cyclometallated chromophore unit containing a pyrazole and linked through an oxygen to an auxiliary carbazolyl-pyridine group leading to a [5,6,6] fused system (see structure **B** in Figure 2).²⁶ In this compound, the presence of a pyrazole group, rather than a pyridine produced a blue shift of the emission since the energy of the lowest unoccupied molecular orbital (LUMO) is higher when pyridine is replaced for an azole group.¹⁵ This type of [N,C,C,N]-Pt compounds consists of a cyclometallated chromophore [C,N] unit connected to an auxiliary unit such as a carbazolyl-pyridine group and it generally displays a distortion from planarity that inhibit aggregation.²⁷ As recently reported for [5,6,6]-cyclometallated Pt compounds containing a pyrazolylpyridyl chelate, the control of the planarity and molecular distortions is decisive for tuning the emission and obtain efficient broad-spectrum OLEDs.²⁸ For analogous compounds, enhanced intramolecular distortion was achieved by incorporating a mesityl substituent in the pyridine which lead to a twisted structure which favours highly efficient blue emission.²⁹

Further work disclosed an alternative strategy to obtain deep blue emission which consists on breaking the conjugation by using a non-conjugated bridging group in the cyclometallated ligand, thus forming a [6,6,6] system (see compound **8** in Figure 2).¹⁵ Blue emission is then favoured since upon breaking the conjugation, the energy of the excited states increases. Moreover, as the number of six-member rings increases, the molecular geometry is more distorted since five-member rings are more planar, and as a result, formation of excimers is less favoured.

The effect of the modification of the ligands was further studied for compounds **9-11** containing either a 2-pyridylcarbazole, a 2-thiazolylcarbazole or a 2-oxazolylcarbazole connected to a 2-phenylbenzimidazole

through one oxygen atom to form [5,6,6] cyclometallated systems. In the three compounds, a diisopropylphenyl group lies nearly perpendicular to the coordination plane, thus hampering the formation of excimers so that the emission colour is maintained at different doping ratios.³⁰ Interestingly, the variation of the N-heterocycle did not affect significantly the frontier orbitals energies or the photophysical properties of the complexes and compound **9** containing a 2-pyridylcarbazole showed the best efficiency in the OLEDs based on these complexes.

Analogous compounds (**12-14**) were obtained from ligands containing a rigid imidazo[1,2-f]phenanthridine linked to either 9-(pyridine-2-yl)-9*H*-carbazole, 2-phenoxy-pyridine or 2-(9-phenyl-9*H*-fluoren-9-yl)-pyridine. The obtained compounds display a high thermal stability and a similar photoluminescence that arises mainly from ligand centred (LC) excited states. The presence of mesityl groups suppress the formation of excimers leading to small variations of the CIE coordinates of these blue emitters at different doping amounts in the corresponding OLEDs.²³ The effect of the nature of the linker in the cyclometallated fragment was studied for compounds **15-17**, shown in Figure 2, based on rigid pyrazolo[1,5-f]phenanthridine ligands which contain either oxygen, aniline or a carbazole unit in the pyridine fragment. As expected from the tetradentate coordination and the presence of a rigid pyrazolo[1,5-f]phenanthridine moiety, these compounds display high thermal stabilities. Upon photoexcitation at room temperature these compounds show highly structured emission spectra that could arise mainly from ligand centred (LC) excited states and the OLEDs based on them displayed electroluminescence in the blue to yellow-green region. For **15** and **17** intermolecular interactions produce a red shift of the electroluminescence spectra relative to the photoluminescence spectra in solution, while for **16** the presence of the 4-(*tert*-butyl)phenyl group reduces these interactions and leads to similar electro- and photoluminescence properties.²⁴

Modification of the substituents on the pyridyl ring of the parent compound **B** (see Figure 2), produces important effects on the photophysical properties of the complexes. These compounds, in which two cyclometallated units (3,5-dimethyl-1-phenyl-pyrazole and carbazolylpyridine) are linked by an oxygen atom, display distortions from planarity on the carbazolylpyridine fragment and although substituents in the *meta* and *para* positions of the pyridine do not affect the geometry, substitution on the *ortho* position increases distortion from ideal square-planar geometry. Introduction of electron-donating groups (Me, *tert*-Bu, NMe₂) at the *para* position of the pyridyl ring increases the emission energy and the luminescence lifetime, while electron-withdrawing groups (CF₃) or aryl groups decrease the emission energy and the luminescence lifetime. In contrast, substituents at the *ortho* or *meta* positions do not produce significant effects.³¹ In addition,

it was found that emission width can be modulated by the substituents since narrow emission can be obtained by reducing the contribution of the metal to ligand charge transfer (MLCT) to the excited state.³¹

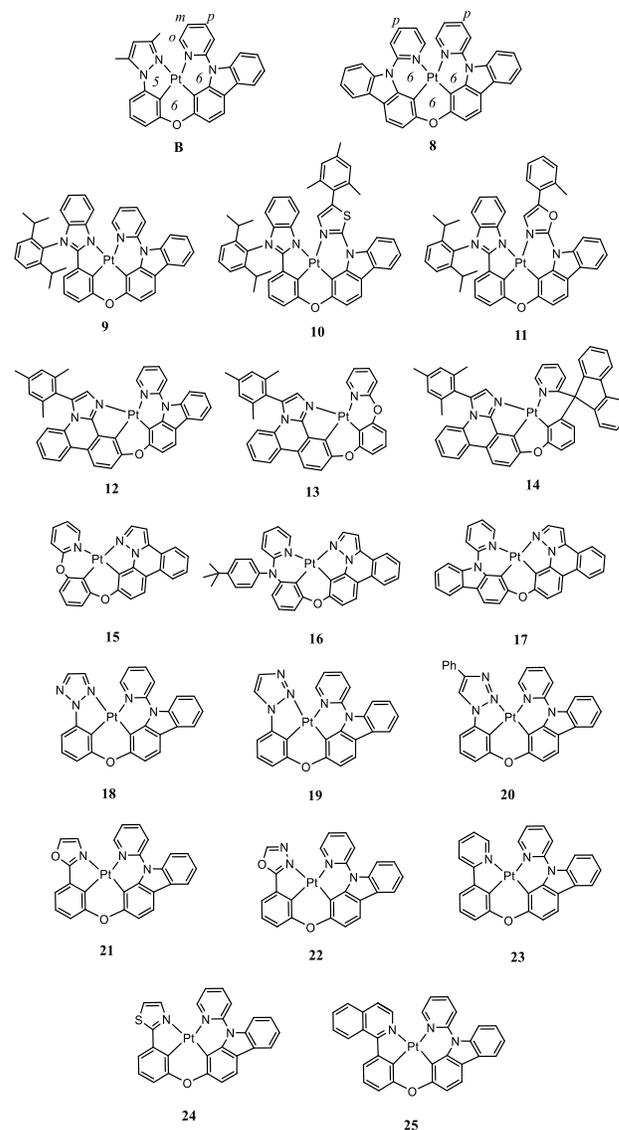


Figure 2. Selected examples of Pt(II) compounds with [N,C,C,N] ligands containing an oxygen atom as linker between the two carbon donor atoms. Adapted from figures in the literature: **B** [ref.26], **8** [ref.15], **9-11** [ref.30], **12-14** [ref.23], **15-17** [ref.24] and **18-25** [ref.33].

The effect of electron-donating (Me or MeO) or withdrawing (CF₃) substituents was also studied on compound **8** that was reported as a deep blue phosphor due to its [6,6,6] structure as indicated above. Interestingly, both the colour and the emission width can be tuned by introducing these substituents at the positions *para* to the nitrogen atoms of the pyridines. The compound containing electron withdrawing CF₃ substituents emits from the MLCT state leading to a broad emission, while compound

with OMe substituents emits predominantly from the LC state giving a narrow emission spectrum.³²

Another study aimed at investigating the structure-properties relationships of [5,6,6] fused systems, involved compounds containing triazole, oxazole, oxadiazole, thiazole, pyridine or isoquinoline groups as the heteroaromatic ring (compounds **18-25** in Figure 2). It was found that the emission spectra were affected by the geometry and the nature and position of the substituents and that the whole visible region could be covered by modification of the ligand. Devices based on the Pt compounds containing triazole groups were fabricated and their efficiency was tested.³³

The effect of the nature of the linker connecting the two C-donor was also addressed in a study involving symmetric compounds **26-32**, shown in Figure 3, in which two phenyltriazole groups are connected by either an oxygen, a methylene or a ketone group. In addition, for compounds **31** and **32**, a linker between two N atoms of the triazole was introduced so that more rigid tetradentate macrocyclic ligands were obtained. The thermogravimetric analyses carried out for these compounds confirmed a higher stability for the macrocyclic structures. These are the first examples of macrocyclic Pt(II) compounds displaying deep blue emission and efficient devices have been fabricated.¹⁶

Compounds **33** and **34** with the same framework based on two triazolyl-phenyl units linked by an oxygen atom were shown to display a reversible emission colour change from blue (arising from the monomer) to red (arising from the excimers) that can be controlled by different external stimulus such as temperature, pressure or UV irradiation under air since the excimer emission is much more sensitive towards oxygen quenching than the monomer emission. These compounds act as ³O₂ sensitizers, converting it into ¹O₂ and present a remarkable potential as O₂ sensors and photooxidation catalysts.³⁴

A strategy to preserve blue electrophosphorescence consists on avoiding intermolecular interactions that lead to bathochromically shifted emissions. With this aim, compounds **35-37**, shown in Figure 4, containing a bis(1-pyrazolylphenyl)methane ligands were prepared. In these compounds, the use of a methylene rather than an ether bridge lowers the energy of the highest occupied molecular orbital (HOMO) which favours blue emission. Moreover, the presence of 3-methyl substituent in compound **37** produces helical distortion and suppress excimer formation. While devices using **37** as dopant produced pure blue emission, the emission from **35** and **36** was contaminated with excimer emission.³⁵

A new series of symmetrical and unsymmetrical compounds containing a rigid fused [6,5,6] system in which two cyclometallated units are connected by a biphenyl moiety were prepared (see compounds **38-45** in Figure 4). These compounds display a very high

photostability and are promising candidates for stable and efficient Pt(II)-based emitters.^{7,36}

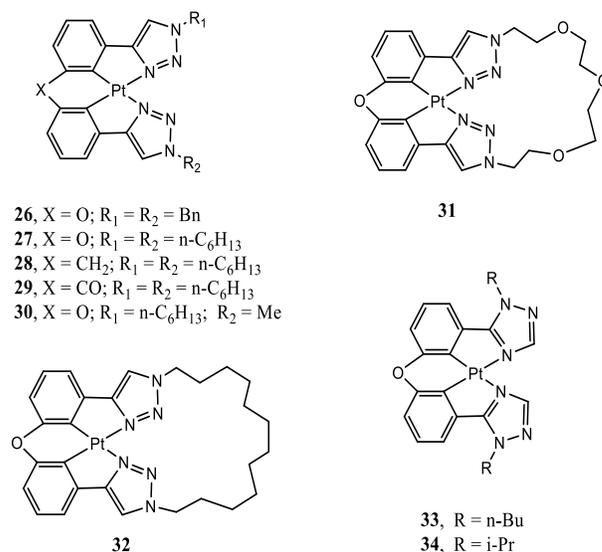


Figure 3. Selected examples of Pt(II) compounds with open chain and macrocyclic [N,C,C,N] ligands. Adapted from figures in the literature: **26-32** [ref.16] and **33-34** [ref.34].

A comparison of the features of Pt(II) compounds with [N,C,N,O] or [N,C,C,N] ligands was recently reported by Li based on compounds **7** and **43-45**.⁷ Compound **7** with a [N,C,N,O] coordination set displays a high quantum efficiency arising from a higher ³MLCT character of the lowest triplet excited state (T₁) while for compounds **43-45** containing a [N,C,C,N] coordination set the T₁ state has a dominant ³LC character resulting in relatively low quantum efficiency but higher colour purity.

Compounds containing fused [6,6,6] or [6,6,5] platinacycles were also obtained using azacarbazolylcarbazole based ligands (see compounds **46-48** in Figure 4). These compounds are green to yellow phosphorescent emitters and a green OLED was developed using compound **47** as dopant (10% in 2,6-bis(N-carbazolyl)pyridine host).³⁷ In dichloromethane at room temperature compounds **46** and **47** containing a [6,6,6] system display lower quantum efficiencies than compound **48** with a more rigid [6,6,5] structure, however the quantum yields of **46** and **47** increase in rigid surrounding such as poly(methylmethacrylate) (PMMA) film.³⁷

Novel Pt(II) compounds in which the two [C,N] moieties are linked through the nitrogen atoms leading to a [C,N,N,C] arrangement were also prepared with the aim of achieving blue phosphorescence (see compounds **49-52** in Figure 5). These compounds, in particular those containing strong C–F bonds, exhibit high thermal stability as expected from a coordination set in which the C and N atoms are mutually *trans*. The two nitrogen atoms are linked by a bulky group so that excimer formation is

inhibited. The emission is influenced by the nature of the substituents of the pyridine rings while the nature of the linker does not affect the luminescence properties. Electron-withdrawing fluorine substituents stabilize the HOMO energies leading to bright blue phosphorescence while methoxy substituents lead to blue-green emission.¹⁷

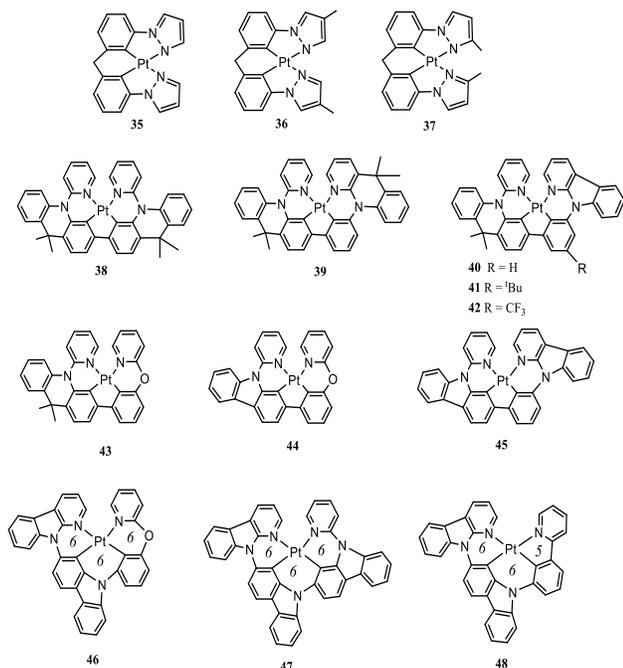


Figure 4. Selected examples of Pt(II) compounds with [N,C,C,N] ligands containing methylene, biphenyl or carbazolyl linkers between the two carbon donor atoms. Adapted from figures in the literature: **35-37** [ref.35], **38-42** [ref.36], **43-45** [ref.7], **46-48** [ref.37].

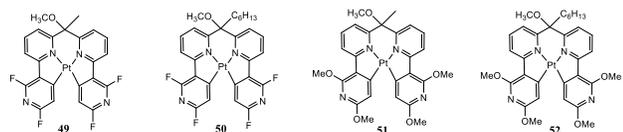


Figure 5. Selected examples of Pt(II) compounds with [C,N,N,C] ligands. Adapted from figures in the literature: **49-52** [ref.17].

Pt(II) Compounds with Tetradentate Ligands Containing a N-heterocyclic Carbene

Metal complexes containing N-heterocyclic carbenes (NHCs) have a great potential as emitters in OLEDs. The NHC carbon has a strong σ -donating and weak π -accepting ability leading to strong Pt–C_{NHC} bonds and stable compounds.³⁸ Neutral Pt(II) compounds with a [C,C,C,N] coordination set (compounds **53** and **54** in Figure 6), in which the asymmetric tetradentate ligands contain a cyclometallated moiety linked to an auxiliary chelate such as phenoxy pyridine or carbazolylpyridine, display

distorted geometries that inhibit aggregation.²⁶ In an attempt to reduce even more the intermolecular interactions bulky groups such as adamantyl were introduced (see compounds **55-57** in Figure 6) and OLEDs based on these compounds exhibit deep blue emission.³⁹ A series of Pt compounds with [5,6,6] tetradentate ligands derived from N-heterocyclic carbene, benzocarbene and pyridine carbene (compounds **58-61** in Figure 6) have been recently studied. The distorted geometry of the compounds and the introduction of a bulky tert-butyl group prevents aggregation. The photophysical properties of these compounds were studied and an OLEDs based on compound **59** display a very high maximum brightness (L_{\max}).³⁸ The results obtained suggest that tetradentate Pt(II) compounds with N-heterocyclic carbene are stable emitters with a high potential for OLEDs fabrication.

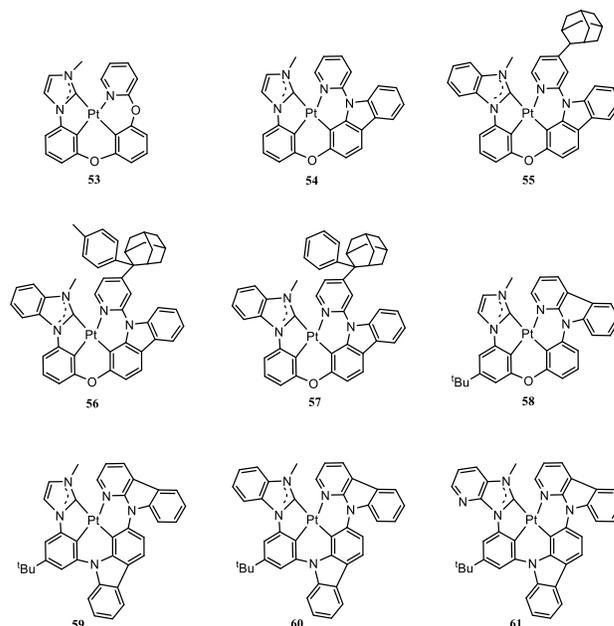


Figure 6. Selected examples of Pt(II) compounds with tetradentate ligands containing a N-heterocyclic carbene. Adapted from figures in the literature: **53-54** [ref.26], **55-57** [ref.39], **58-61** [ref.38].

Pd(II) Versus Pt(II) Compounds with Tetradentate Ligands

While a large number of luminescent Pt(II) compounds with tetradentate cyclometallating ligands have been reported, studies for analogous square-planar Pd(II) are scarce which can be related to the fact that d-d excited states are more accessible for Pd than for Pt compounds which favours non-radiative pathways.⁴⁰ Some comparative studies between tetradentate cyclopalladated and cycloplatinated compounds have been recently reported.^{5,6,40}

Table 1. OLED performances for selected examples of cycloplatinated compounds reviewed in this work^a

Compound	Emissive layer	Doping wt %	CE/(cd A ⁻¹)	PE/(lm W ⁻¹)	EQE/(%)	CIE coordinates	Emission colour	Ref.
2	TCTA/B3YMPPM	26	16.18	11.30	22.02	(0.63;0.37)	Red	14
3	26mCPy	15	83.0	63.8	22.9	(0.36;0.60)	Yellow-Green	19
6	TCTA/B3YMPPM	12	86.4	104.3	24.5	-	Yellow-green	20
7	26mCPy	10	-	-	18.5	(0.298;0.634)	Green	7
9	26mCPy	15	78.5	66.4	22.3	(0.31;0.62)	Yellow-Green	30
12	26mCPy	10	36.5	33.1	16.2	(0.18;0.32)	Blue	23
15	CBP	30	58.0	51.6	16.4	(0.33;0.57)	Yellow-Green	24
19	26mCPy	8	27.3	20.4	14.5	(0.16;0.28)	Blue	33
32	BCPO	10	11.0	10.8	9.7	(0.14;0.14)	Blue	16
37	mCBP	8	-	12.7	8.5	(0.16;0.24)	Blue	35
49	mCPPO1	5	-	24.9	17.6	(0.15;0.29)	Blue	17
50	mCPPO1	50	-	7.8	8.5	(0.32;0.34)	White	17

^aSee the corresponding references for the device structure description.

Abbreviations: CE = current efficiency; PE = Power efficiency; EQE = external quantum efficiency; CIE = Commission Internationale de l'Éclairage. 26mCPy = 2,6-bis(N-carbazolyl)pyridine; CBP = 4,4'-Di(9H-carbazol-9-yl)-1,1'-biphenyl; mCBP = 4,4'-Di(9H-carbazol-9-yl)-1,1'-biphenyl; BCPO = 9,9'-(4,4'-(phenylphosphoryl)bis(4,1-phenylene))bis(9H-carbazole); mCPPO1 = (9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)diphenylphosphine oxide; TCTA = 4,4',4''-tris(N-carbazolyl)-triphenylamine; B3YMPPM = bis-4,6,(3,5-di-3-pyridylphenyl)-2-methylpyrimidine.

Since Pd(II) has a smaller spin-orbit coupling than Pt(II) ($\xi = 1412$ vs. 4481 cm^{-1}), the tetradentate Pd(II) complexes show a decreased metal-to-ligand charge transfer (³MLCT) and enhanced ligand centred (³LC) character in the T₁ states leading to longer excited-states lifetimes than those of Pt(II) analogues.⁵ In contrast, the Pt(II) complexes possess more metal-to-ligand charge transfer (³MLCT) character in their T₁ states leading to higher quantum efficiencies and shorter excited-state lifetimes.⁵

For [N,C,C,N]-Pd(II) compounds analogous to Pt(II) compounds **46-48** described above,³⁷ a blue shift was observed compared to Pt(II) compounds that are green to yellow phosphorescent emitters. Moreover, a decrease in ³MLCT character and enhanced ³LC character in their T₁ states was deduced for Pd versus Pt compounds, which results in longer excited-state lifetimes. For this reason, Pd(II) complexes display efficient reverse intersystem crossing (RISC) from T₁ to S₁, then to S₀ and exhibit delayed fluorescence. Pd(II) analogues of **46** and **47** display both metal-assisted delayed fluorescence and phosphorescence in PMMA films at room temperature.

4. ELECTROLUMINESCENT DEVICES OBTAINED FROM CYCLOPLATINATED COMPOUNDS WITH TETRADENTATE LIGANDS

OLED devices based on cycloplatinated compounds with tetradentate ligands as dopants were fabricated in order to investigate the electroluminescence properties of these compounds. Descriptions of the multilayer device structures are given in each contribution and a constant current source combined with a photometer is used to measure the electroluminescence spectra, the CIE coordinates and the current-voltage characteristics.

In general, different host materials and dopant concentrations were tested to achieve the best performance. Independence of the CIE coordinates with doping concentration is related to a weak interaction between

dopant molecules in the emitting layer while concentration quenching is generally observed for heavily doped devices. OLED performances for selected cycloplatinated compounds with tetradentate ligands are given in Table 1. These compounds display excellent photophysical properties and are very promising for the fabrication of OLEDs.

5. CONCLUSIONS

Cyclometallated Pt(II) compounds containing tetradentate nitrogen ligands display interesting features that makes them valuable in the development of stable and efficient OLEDs. These compounds are highly stable and the tetradentate ligands provide the required rigidity to maintain the square planar coordination of Pt(II). In addition, the cyclometallating ligands allow diverse molecular designs combining the presence of five and six-member rings. The photophysical properties of these complexes can be tuned by modifying their frontier orbitals which can be achieved by introducing different substituents on the cyclometallating ligand. Moreover, the propensity of these complexes to engage in intermolecular interactions can also be controlled either from the bulk of the substituents or from deviations of the planarity of the molecules.

As a result of their interesting features, cycloplatinated compounds with tetradentate ligands constitute a very promising class of materials whose emission properties can be tuned by rational design. These compounds are able to emit with high efficiency and high colour quality across the visible spectra and are suitable for a range of devices including those capable of efficient pure blue emission, aggregation-based red and NIR OLEDs, and single-dopant WOLEDs.

CONFLICTS OF INTEREST

The authors have declared that there is no conflict of interest.

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REFERENCES

1. J. A. G. Williams, S. Develay, D. L. Rochester, L. Murphy, *Coord. Chem. Rev.*, **2008**, *252*, 2596-2611.
2. J. Kalinowski, V. Fattori, M. Cocchi, J. A. G. Williams, *Coord. Chem. Rev.*, **2011**, *255*, 2401-2425.
3. A. Haque, L. Xu, R. A. Al-Balushi, M. K. Al-Suti, R. Ilmi, Z. Guo, M. S. Khan, W. Y. Wong, P. R. Raithby, *Chem. Soc. Rev.*, **2019**, *48*, 5547-5563.
4. C. Gourlaouen, C. Daniel, *Dalt. Trans.*, **2014**, *43*, 17806-17819.
5. G. Li, H. Guo, X. Fang, Y. F. Yang, Y. Sun, W. Lou, Q. Zhang, Y. She, *Chinese J. Chem.*, **2022**, *40*, 223-234.
6. T. Fleetham, G. Li, J. Li, *Adv. Mater.*, **2017**, *29*, 1601861.
7. G. Li, G. Shen, X. Fang, Y. F. Yang, F. Zhan, J. Zheng, W. Lou, Q. Zhang, Y. She, *Inorg. Chem.*, **2020**, *59*, 18109-18121.
8. H. H. Zhang, S. X. Wu, Y. Q. Wang, T. G. Xie, S. S. Sun, Y. L. Liu, L. Z. Han, X. P. Zhang, Z. F. Shi, *Dye. Pigment.*, **2022**, *197*, 109857.
9. R. J. Ortiz, J. D. Braun, J. A. G. Williams, D. E. Herbert, *Inorg. Chem.*, **2021**, *60*, 16881-16894.
10. S. Huo, J. Carroll, D. A. K. Vezzu, *Asian J. Org. Chem.*, **2015**, *4*, 1210-1245.
11. M. C. Tang, A. K. W. Chan, M. Y. Chan, V. W. W. Yam, *Top. Curr. Chem.*, **2016**, *374*, 1-43.
12. C. Cebrián, M. Mauro, *Beilstein J. Org. Chem.*, **2018**, *14*, 1459-1481.
13. D. Chen, W. Li, L. Gan, Z. Wang, M. Li, S. J. Su, *Mater. Sci. Eng. R Reports*, **2020**, *142*, 100581.
14. G. Cheng, Q. Wan, W. H. Ang, C. L. Kwong, W. P. To, P. K. Chow, C. C. Kwok, C. M. Che, *Adv. Opt. Mater.*, **2019**, *7*, 1801452.
15. T. B. Fleetham, L. Huang, K. Klimes, J. Brooks, J. Li, *Chem. Mater.*, **2016**, *28*, 3276-3282.
16. X. Wang, T. Peng, C. Nguyen, Z. H. Lu, N. Wang, W. Wu, Q. Li, S. Wang, *Adv. Funct. Mater.*, **2017**, *27*, 1604318.
17. C. Lee, R. Zaen, K. M. Park, K. H. Lee, J. Y. Lee, Y. Kang, *Organometallics*, **2018**, *37*, 4639-4647.
18. S. C. F. Kui, P. K. Chow, G. S. M. Tong, S. L. Lai, G. Cheng, C. C. Kwok, K. H. Low, M. Y. Ko, C. M. Che, *Chem. - A Eur. J.*, **2013**, *19*, 69-73.
19. G. Liu, F. Liang, Y. Zhao, H. Hu, J. Fan, L. S. Liao, *J. Mater. Chem. C*, **2017**, *5*, 1944-1951.
20. M. Mao, J. Peng, T. L. Lam, W. H. Ang, H. Li, G. Cheng, C. M. Che, *J. Mater. Chem. C*, **2019**, *7*, 7230-7236.
21. M. Mao, T. L. Lam, W. P. To, X. Lao, W. Liu, S. Xu, G. Cheng, C. M. Che, *Adv. Mater.*, **2021**, *33*, 1-8.
22. R. G. Pearson, *Inorg. Chem.*, **1973**, *12*, 712-713.
23. W. Zhang, J. Ma, G. J. Liu, X. Y. Liu, J. Fan, L. S. Liao, *J. Mater. Chem. C*, **2017**, *5*, 9496-9503.
24. D. Zhao, X. Tang, X. Y. Liu, J. Fan, L. S. Liao, *Org. Electron.*, **2017**, *50*, 473-479.
25. Y. Wang, Q. Peng, Z. Shuai, *Mater. Horizons*, **2022**, *9*, 334-341.
26. X. C. Hang, T. Fleetham, E. Turner, J. Brooks, J. Li, *Angew. Chemie - Int. Ed.*, **2013**, *52*, 6753-6756.
27. H. Li, T. -L. Lam, L. Yan, L. Dai, B. Choi, Y. -S. Cho, Y. Kwak, C. -M. Che, in *Liquid Crystals and Display Technology*, ed. G. Morteza Sasani, **2020**.
28. D. Wu, K. Qin, X. Gao, S. Cheng, A. Wu, C. Sha, H. Ma, Z. Sun, C. Zhang, X. -C. Hang, *J. Mater. Chem. C*, **2022**, *10*, 1365-1370.
29. Y. Chen, C. Qian, K. Qin, H. Li, X. Shi, Z. Lu, H. Ma, T. Qin, X. C. Hang, W. Huang, *ACS Appl. Mater. Interfaces*, **2021**, *13*, 52833-52839.
30. J. Li, F. Liang, Y. Zhao, X. Y. Liu, J. Fan, L. S. Liao, *J. Mater. Chem. C*, **2017**, *5*, 6202-6209.
31. G. Li, A. Wolfe, J. Brooks, Z. Q. Zhu, J. Li, *Inorg. Chem.*, **2017**, *56*, 8244-8256.
32. T. Fleetham, J. H. Golden, M. Idris, H. M. Hau, D. S. Muthiah Ravinson, P. I. Djurovich, M. E. Thompson, *Inorg. Chem.*, **2019**, *58*, 12348-12357.
33. G. Li, X. Zhao, T. Fleetham, Q. Chen, F. Zhan, J. Zheng, Y. F. Yang, W. Lou, Y. Yang, K. Fang, Z. Shao, Q. Zhang, Y. She, *Chem. Mater.*, **2020**, *32*, 537-548.
34. L. Liu, X. Wang, N. Wang, T. Peng, S. Wang, *Angew. Chemie - Int. Ed.*, **2017**, *56*, 9160-9164.
35. Y. K. Moon, J. S. Huh, S. Kim, S. Kim, S. Y. Yi, J. J. Kim, Y. You, *ACS Appl. Electron. Mater.*, **2020**, *2*, 604-617.
36. G. Li, F. Zhan, J. Zheng, Y. F. Yang, Q. Wang, Q. Chen, G. Shen, Y. She, *Inorg. Chem.*, **2020**, *59*, 3718-3729.
37. Y. She, K. Xu, X. Fang, Y. F. Yang, W. Lou, Y. Hu, Q. Zhang, G. Li, *Inorg. Chem.*, **2021**, *60*, 12972-12983.
38. G. Li, S. Liu, Y. Sun, W. Lou, Y. F. Yang, Y. She, *J. Mater. Chem. C*, **2022**, *10*, 210-218.
39. J. S. Huh, M. J. Sung, S. K. Kwon, Y. H. Kim, J. J. Kim, *Adv. Funct. Mater.*, **2021**, *31*, 2100967.
40. I. Maisuls, C. Wang, M. E. Gutierrez Suburu, S. Wilde, C. G. Daniliuc, D. Brünink, N. L. Doltsinis, S. Ostendorp, G. Wilde, J. Kösters, U. Resch-Genger, C. A. Strassert, *Chem. Sci.*, **2021**, *12*, 3270-3281.