

Highly Efficient Phosphorescent Materials Based on Platinum Complexes and Their Application in Organic Light-Emitting Devices (OLEDs)

Platinum complexes show promise for flat screens and energy efficient lighting

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Although numerous materials can be utilised as emitters in electroluminescent devices, platinum complexes bearing organic ligands are among the most promising for use as highly efficient phosphorescent materials in which the singlet and triplet states can be simultaneously harvested for emission. This article aims to give an overview of recent progress in Pt phosphors featuring ingeniously designed ligands and to summarise their impressive performances when incorporated into organic light-emitting devices (OLEDs). Such materials show great promise for applications such as flat screen displays and low-energy solid-state lighting.

1. Introduction

OLEDs have drawn much attention in the past two decades for their applications in new generation displays with unique advantages, such as low cost, high contrast, good colour range, wide viewing angle and flexibility (1–5). In addition, OLEDs emitting white light (white OLEDs or WOLEDs) are promising candidates for future energy-saving solid-state light sources due to their low driving voltage, high brightness and high efficiency (6–10). Emissive materials are the most critical functional component of OLEDs and have therefore been the subject of considerable research activity. However, traditional fluorescent (singlet) emitters employ only singlet excitons, which make up only *ca.* 25% of all generated excitons, and leave the remaining triplet excitons unharnessed. This results in low electroluminescence (EL) efficiency which has restricted the practical application of OLEDs, especially as solid-state lighting sources where high efficiency is a prerequisite.

This situation changed with the discovery of phosphorescent (triplet) emitters. This type of emitter is generally constructed by chelating transition metal ions with organic ligands. The introduction of heavier transition metal ions effectively triggers phosphorescent emission by spin-orbit coupling (11). Iridium(III),

platinum(II), osmium(II) and ruthenium(II) ions are highly effective for this purpose. Complexes of these metals can use both the singlet and triplet excitons when incorporated into OLEDs, which can achieve a maximum internal quantum efficiency (IQE) of 100% (12). Metallated phosphors have since been extensively investigated for use in WOLEDs as a practical avenue towards solid-state lighting sources.

Pt-based phosphors appear to have the highest potential for EL applications due to their higher triplet quantum yield (Φ_p), relatively short triplet state lifetime (τ_p), and tunable emission colour. Pt phosphors have been developed with both diverse structures and versatile properties. This review will highlight and critically discuss recent advances in Pt-based complexes as highly efficient phosphors for high performance OLEDs. Based on their structural features, these phosphors are classified into three main categories for discussion according to the dentation number of the main ligands chelated with the Pt centres:

- Tetradentate ligands;
- Tridentate ligands;
- Bidentate ligands.

2. Platinum Phosphors with Tetradentate Ligands

This type of triplet emitter mainly includes Pt(II) porphyrin and Schiff base complexes. The pioneering phosphor of this type was Pt(II) octaethylporphine (**PtOEP**) (**Figure 1**) which can show a peak IQE of

23% and an external quantum efficiency (EQE) of 4% with pure red EL at 650 nm. The quantum and power efficiencies are at least one order of magnitude higher than those of europium complexes (13). Due to the intrinsically long triplet lifetime of Pt phosphors with tetradentate ligands, bulky substituents can be introduced to block triplet–triplet (T–T) annihilation and enhance their EL efficiencies, especially at higher current densities. Even the near-infrared emitters Pt tetraphenyltetrabenzoporphyrin (**Pt-TPTBP**) and Pt tetraaryltetrabenzoporphyrins (**Pt-Ar₄TBP**) (**Figure 1**) can achieve high EQE values of 8.0% and 9.2% at 773 nm (14), respectively.

Che and coworkers have prepared many tetradentate Pt(II) Schiff base phosphors and tested their EL potentials in OLEDs as well as investigating their structure–property relationships (15–17). The first such complex, **PtSB-1** (**Figure 2**), showed promising EL efficiencies with a peak EQE of 11.0% and a current efficiency (CE) of 30.0 cd A⁻¹ (15). OLEDs based on **PtSB-2** (**Figure 2**) showed a maximum EQE of 9.4% and a lifetime of more than 20,000 h at a brightness of 100 cd m⁻² (16). Bis(pyrrole)-diimine Pt(II) complexes may also be good candidates for highly efficient OLEDs (17). A device using **PtSB-3** (**Figure 2**) as emitter gave a maximum brightness of 11,100 cd m⁻², an EQE of 6.5%, a CE of 9.0 cd A⁻¹, and a power efficiency (PE) of 4.0 lm W⁻¹. These promising results indicate that such tetradentate Pt(II) complexes may be competitive candidates for OLED applications.

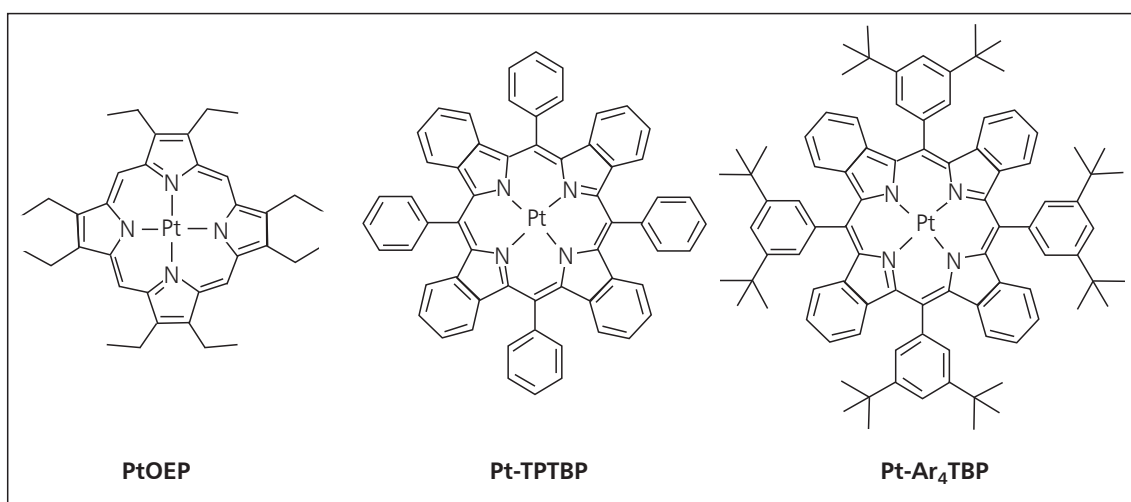


Fig. 1. Chemical structures of some Pt-porphyrin phosphors

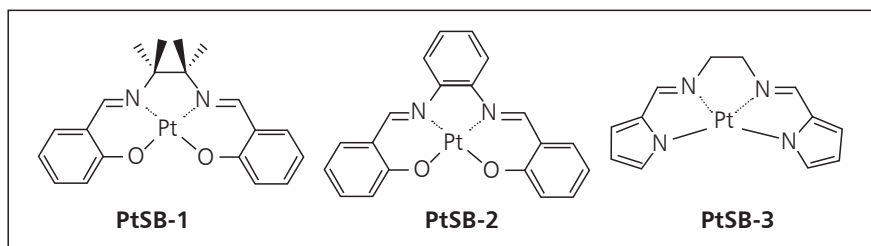


Fig. 2. Chemical structures of some Pt(II) Schiff base phosphors

3. Platinum Phosphors with Tridentate Ligands

Pt(II) phosphors with tridentate ligands typically bear rigid main ligands, including $N^{\wedge}N^{\wedge}C$ -, $N^{\wedge}C^{\wedge}N$ -, $N^{\wedge}N^{\wedge}N$ - and $C^{\wedge}N^{\wedge}C$ -coordinating ligands, to form cyclometalated complexes. These ligands are thought to improve the rigidity of the corresponding Pt(II) complexes by suppressing the D_{2d} distortion to induce higher Φ_p (18), hence promoting the performance of electrophosphorescent devices.

3.1 Platinum Phosphors with $N^{\wedge}N^{\wedge}C$ -coordinating Ligands

Much work on cyclometalated Pt(II) complexes based on $N^{\wedge}N^{\wedge}C$ -coordinating ligands (**PtNNC-1** to **PtNNC-9**, **Figure 3**) and their emitting characteristics have been reported by Che *et al.* (19, 20). In solution, tridentate Pt(II) complexes bearing σ -alkynyl auxiliary ligands can emit a variety of colours from 550 nm to 630 nm, induced by ligands with different steric and electronic properties. Although their EL performance is poor, these complexes have provided valuable information on tuning the emission colour of this type of phosphor.

Importantly, their performance was markedly improved by extending the π -conjugation of the ligands, for example **PtNNCCI-1** (**Figure 4**) had a Φ_p of 0.68 and a maximum CE of 20.2 cd A⁻¹ (21). The performance of this device was superior to those based on tetradentate Pt(II) Schiff base phosphors (15, 16).

Extending the π -conjugation of the $N^{\wedge}N^{\wedge}C$ ligands with a fluorene unit has been shown to play a critical role in increasing phosphorescent emission and EL efficiency, in devices based on complexes **PtNNCCI-2** to **PtNNCCI-6** (22). The Φ_p for **PtNNCCI-2** was 0.07 and that for **PtNNCCI-3** was 0.16, while **PtNNCCI-4** and **PtNNCCI-5** exhibited Φ_p values of 0.35 and 0.73, respectively. Owing to its high Φ_p , **PtNNCCI-5** was used in a vacuum deposition fabricated device which exhibited very attractive EL efficiencies with an EQE of 5.5%, a CE of 14.7 cd A⁻¹ and a PE of 9.2 lm W⁻¹. The

moderate EL performance of **PtNNCCI-6** is thought to be due to the method of solution-processed device fabrication.

3.2 Platinum Phosphors with $N^{\wedge}C^{\wedge}N$ -Coordinating Ligands

As noted earlier, higher rigidity of the molecular skeleton generally leads to higher Φ_p . J. A. G. Williams *et al.* reported that the platinum–carbon bond lengths in Pt($N^{\wedge}C^{\wedge}N$) complexes are around 1.90 Å, about 0.14 Å shorter than those in typical Pt($N^{\wedge}N^{\wedge}C$) complexes (23). Furthermore, the shorter Pt–C bond length is expected to deactivate the d-d states by raising their energy, and hence lead to superior performance. This can be seen in a new series of Pt($N^{\wedge}C^{\wedge}N$) complexes bearing various aryl substituents (**Figure 5**) (24). All of the new phosphors display Φ_p values from 0.46 to 0.65 with emission maxima from 481 nm to 588 nm. Additionally, the introduction of 4-(dimethylamino)-phenyl to $N^{\wedge}C^{\wedge}N$ ligands can suppress the self-quenching and aggregation/excimer formation which would otherwise hamper the EL efficiencies. OLEDs employing complexes **PtL¹Cl** to **PtL⁹Cl** as emitters (25) can achieve maximum EQE values from 4 to 16% and CE values from 15 to 40 cd A⁻¹, accompanying extremely low EL efficiency roll-off with increased driving voltage.

The EL performance of these phosphors can also be optimised by changing the auxiliary ligand and the host materials in devices. Replacing the ancillary chloride (–Cl) ligand in **PtL³Cl** with a phenoxy (–OPh) group gives **PtL³OPh** (26), which can provide very admirable green-emitting OLEDs with a maximum EQE of 16.5% and a CE of 67.1 cd A⁻¹. By adopting a two-host system to optimise the energy levels between charge-transport layers and confining the emissive zone, the EL efficiencies for **PtL¹⁰Cl**-based devices have been almost doubled with respect to those of their single-host counterparts, to give an EQE of 11.5%, a CE of 38.9 cd A⁻¹ and a PE of 27.2 lm W⁻¹ (27).

Jabbour *et al.* constructed a highly efficient blue phosphor **PtL¹¹Cl** (28) with a maximum Φ_p of 0.8 in

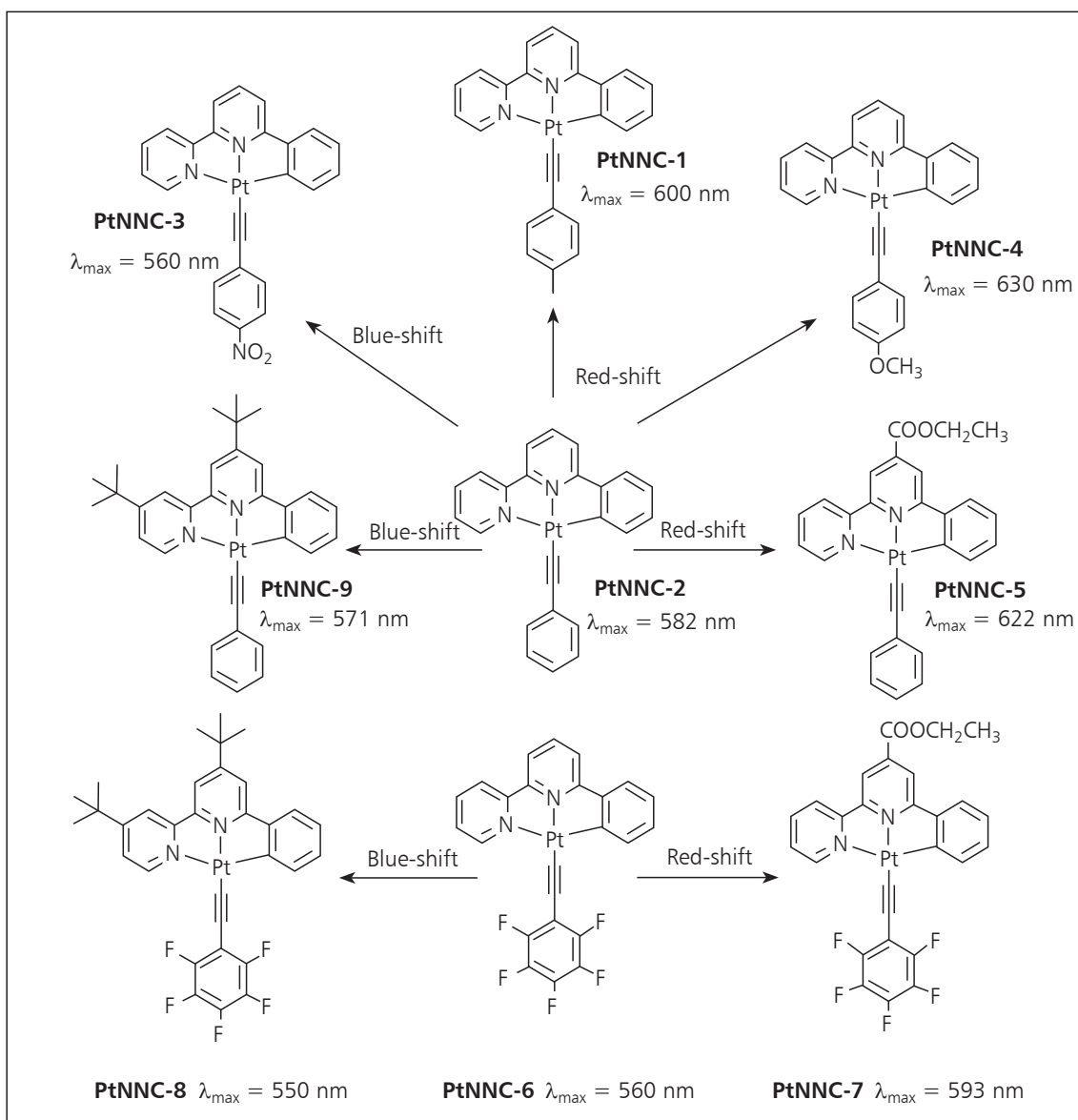


Fig. 3. Chemical structures of typical Pt(II) complexes with N^N^C-coordinating ligands and their emission maximum in CH₂Cl₂ solution at 298 K

degassed dichloromethane (CH₂Cl₂) (29), which was ascribed to both its rigid triplet state configuration and very high ligand-field strength giving a strong destabilisation to the metal-centred d-d excited states. A deep-blue device based on **PtL¹¹Cl** doped in a co-host gave a maximum EQE of 16% and a PE of 20 lm W⁻¹. A WOLED based on 8 wt% **PtL¹¹Cl** doped in 1,3-bis(*N*-carbazolyl)benzene (mCP) exhibited a maximum EQE of 9.3%, a PE of 8.2 lm W⁻¹ and Commission Internationale de l'Éclairage (CIE)

coordinates of (0.33,0.35) at 1300 cd m⁻², very close to the pure white point at (0.33,0.33).

Another highly efficient phosphor **PtL¹²Cl** (Figure 5) with a Φ_p of 0.87 was incorporated into OLEDs at doping levels of 10, 15, 20 and 25 wt%, respectively. By varying the doping level, the EL colour of the devices could be tuned from bluish-green to red with very high EQE values up to 18.3% (30). It is worth mentioning that the electron-donating groups attached to the lateral pyridyl rings of the Pt complexes resulted

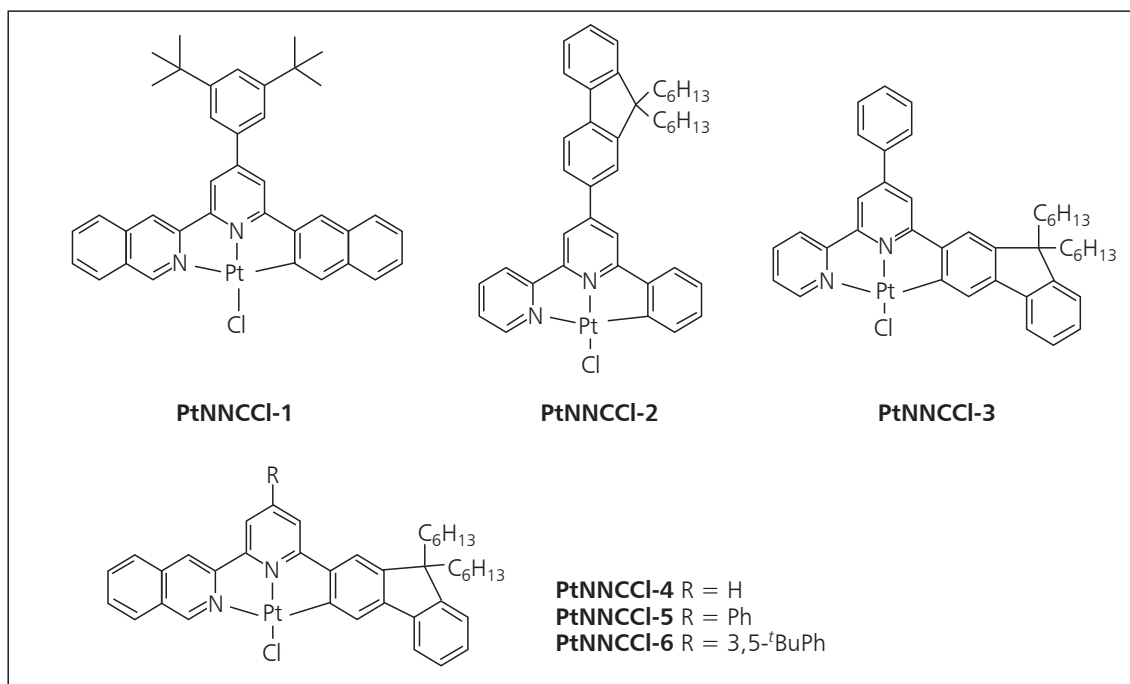


Fig. 4. Chemical structures of phosphors **PtNNCCI-1** to **PtNNCCI-6**

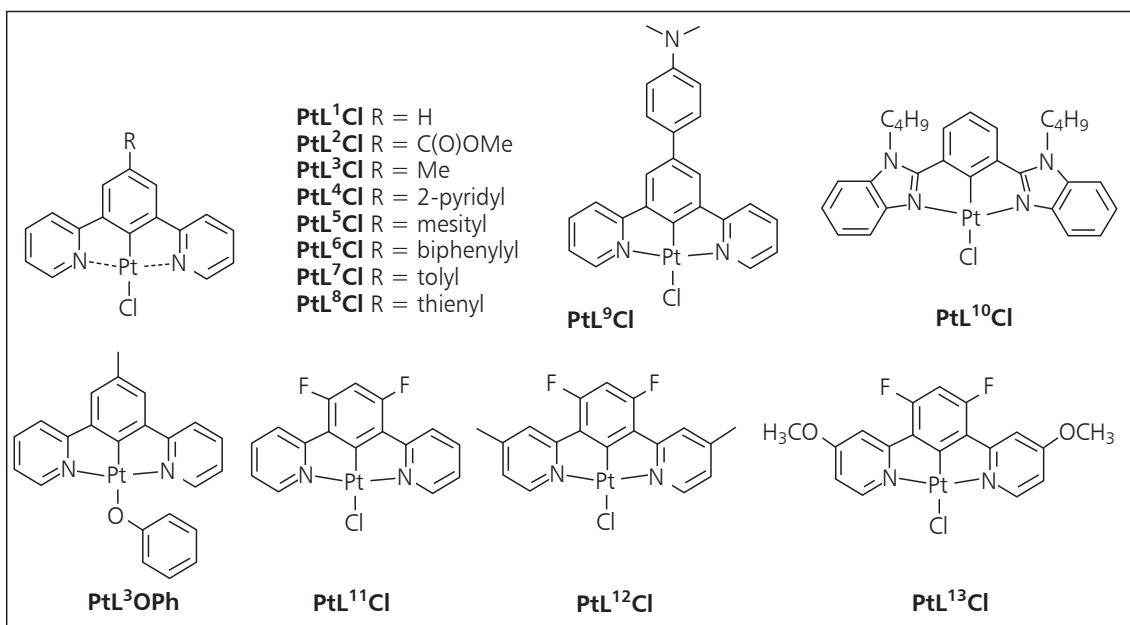


Fig. 5. Chemical structures of high performance $Pt(N^C^N)$ phosphors

in a blue-shift in the monomer emission, as well as excimer emission resulting from the interactions between emitter molecules (29). Accordingly, **PtL¹³Cl** (31) showed a blue-shift emission compared with that of **PtL¹²Cl** due to the stronger electron-donating

ability of the methoxy group ($-OCH_3$) compared to the methyl group ($-CH_3$). By tuning the doping concentration from 5 wt% to 35 wt%, OLEDs based on **PtL¹³Cl** could be made to emit nearly any colour from blue to yellowish red. The dependence of emission

colour on doping concentration offers a very simple and practical way to regulate OLED emission colour by adjusting the contributions of monomer and excimer emission.

3.3 Platinum Phosphors with N[^]N[^]N- Coordinating Ligands

Chen *et al.* introduced a trifluoromethyl-pyrazolyl group to 2,2'-bipyridine to form a neutral tridentate cyclometalated ligand, 6-(5-trifluoromethyl-pyrazol-3-yl)-2,2'-bipyridine, and investigated the photophysical properties of the resulting complexes (Figure 6) (32). These complexes emit phosphorescence between 524 nm for **PtNNN-1** and 604 nm for **PtNNN-2**. The bathochromic effect in emission may lie in the stronger donor ability of acetamide and the larger π -conjugation involving the nitrogen and the carbonyl group of acetamide in **PtNNN-2**. An optimised device doped with 28 wt% **PtNNN-1** exhibited a maximum EQE of 8.5%, corresponding to a CE of 18.5 cd A⁻¹ and a maximum brightness of 47,543 cd m⁻² at 18.5 V.

Cola *et al.* also reported several Pt(N[^]N[^]N)-type complexes displaying Φ_P values of up to 0.73 in

deaerated chloroform solution (33), which are among the highest found for tridentate chelates (21, 22, 27, 34). A multilayer vapour deposited device doped with 6% **PtNNN-3** (Figure 6) generated a green emission peak at 510 nm with a second peak at 544 nm and gave a maximum CE of 15.2 cd A⁻¹ and a PE of 6.8 lm W⁻¹, which is comparable with the performance of devices based on the well-established green emitter, Ir(ppy)₃, in a similar architecture.

3.4 C[^]N[^]C-Coordinating Ligands Based Platinum Phosphors

Though several Pt(II) complexes with C[^]N[^]C type ligands were reported in 2002 (35), they drew little attention due to their poor emission (35, 36). Recently, Kui *et al.* reported the first examples of complexes of these ligands with intense phosphorescence in solution at room temperature (Figure 7) (37). By functionalising with carbazole, fluorene, or thiophene heterocyclic unit(s) at the periphery, they can show Φ_P values up to 0.26 in solution at room temperature. This emission performance has been ascribed to both the σ -donating ability of the C \equiv NR ancillary

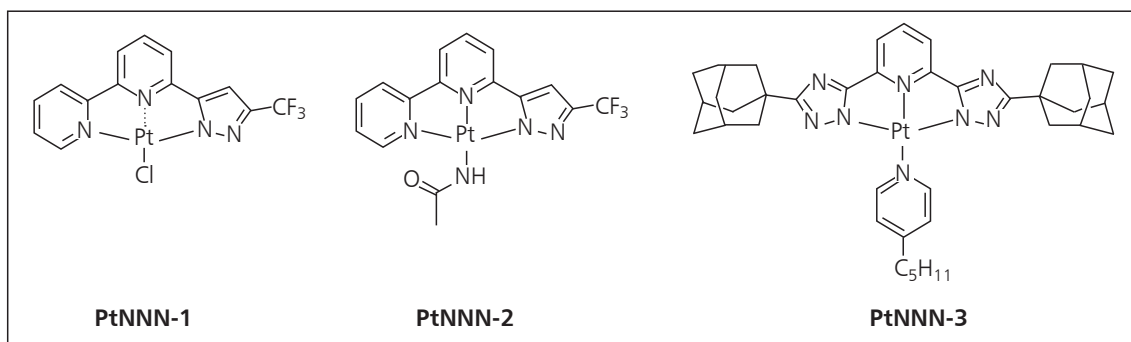


Fig. 6. Chemical structures of **PtNNN-1** to **PtNNN-3**

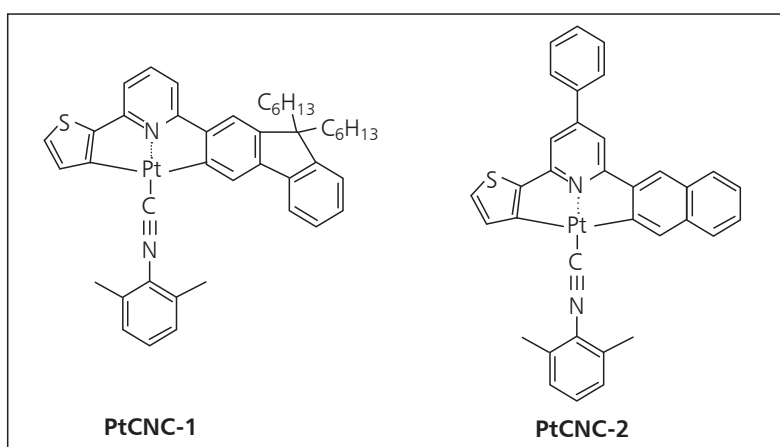


Fig. 7. Chemical structures of **PtCNC-1** and **PtCNC-2**

ligand and the rigidity of the triplet state due to the carbazole, fluorene or thiophene heterocyclic units in the main ligand. Red-emitting OLEDs based on this ligand system can give very decent EL performance. For example, a device based on **PtCNC-1** displayed a maximum EQE of 12%, a PE of 10.9 lm W^{-1} and a CE of 13.9 cd A^{-1} , while a device doped with 6 wt% **PtCNC-2** achieved a maximum EQE, PE and CE of 12.6%, 10.5 lm W^{-1} and 13.4 cd A^{-1} , respectively.

4. Platinum Phosphors with Bidentate Ligands

4.1 Conventional ($\text{N}^{\wedge}\text{C}$ Pt($\text{O}^{\wedge}\text{O}$) Phosphors

Complexes with one $\text{N}^{\wedge}\text{C}$ main ligand (2-phenylpyridine-type or ppy-type) and one ancillary β -diketonato ligand (acetyl acetone or its derivatives) represent the first and most developed type of EL phosphors, with good emission and tunable colour.

J. Brooks *et al.* reported a series of this type of phosphor, **Ptppy-1** to **Ptppy-8** (Figure 8), which show intense phosphorescence at room temperature (38). They also show distinct emission colour tuning properties. Introducing electron-withdrawing groups to the phenyl moiety and electron-donating groups to the pyridyl ring in the ppy ligand can induce a blue-shift in the emission maxima ($\lambda_{\text{max}} = 486 \text{ nm}$ for **Ptppy-1**, $\lambda_{\text{max}} = 484 \text{ nm}$ for **Ptppy-3** and $\lambda_{\text{max}} = 466 \text{ nm}$ for **Ptppy-2**, $\lambda_{\text{max}} = 456 \text{ nm}$ for **Ptppy-6** and $\lambda_{\text{max}} = 440 \text{ nm}$ for **Ptppy-7**), while electron-donating groups on the phenyl ring of the ligand will cause a red-shift ($\lambda_{\text{max}} = 525 \text{ nm}$ for **Ptppy-4** and $\lambda_{\text{max}} = 480 \text{ nm}$ for **Ptppy-5**). Theoretical calculations indicate that this colour tuning behaviour can be explained in terms of the highest occupied molecular orbitals (HOMOs), contributed mainly by the π orbitals of the phenyl ring and the d_{π} orbital of the Pt centre, and

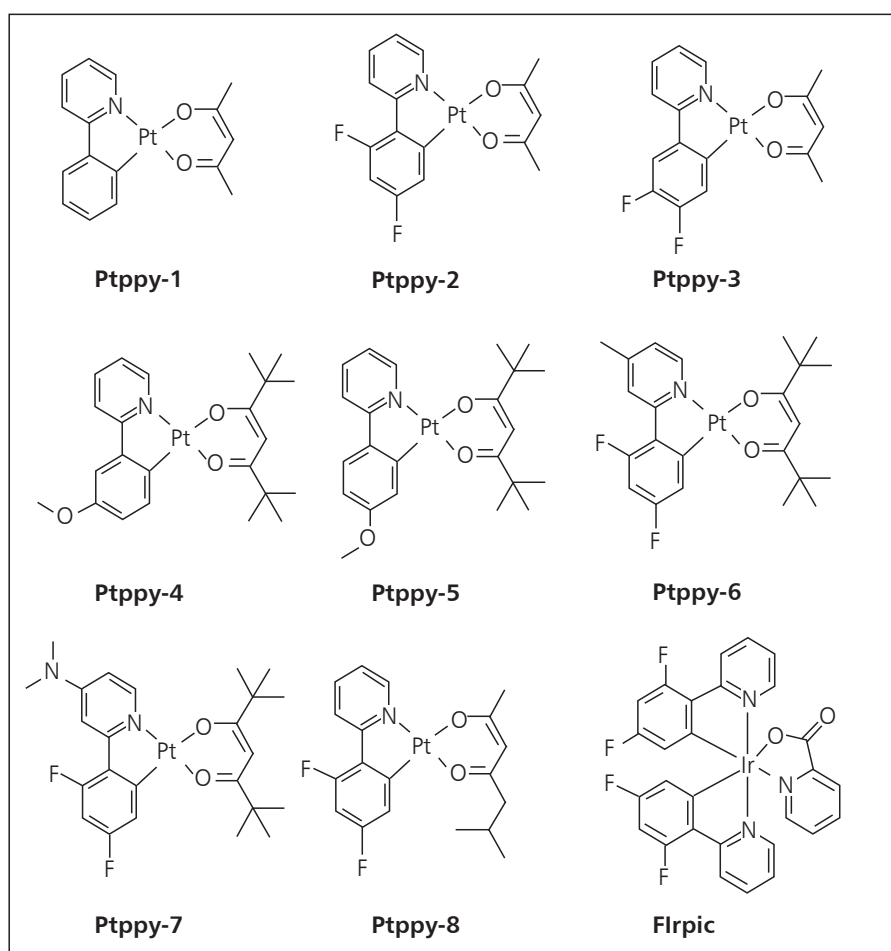


Fig. 8. Chemical structures of **Ptppy-1** to **Ptppy-8** plus **Flrpic**

the lowest unoccupied molecular orbitals (LUMOs), located mainly on the π orbitals of the pyridyl ring in the ligands.

The excimer emission in the orange or red region caused by interaction among molecules means that blue-emitting phosphors can be used to fabricate simple WOLEDs by a blue-orange 'colour complementary' strategy. Co-doping **Ptppy-2** and **Flrpic** (**Figure 8**) in a single layer allows the blue monomer emission from **Flrpic** and the orange excimer emission from **Ptppy-2** to be combined, providing white light for simple WOLEDs with a single emissive layer (EML) (39). Based on the same strategy, the single phosphor **Ptppy-8** can also be used to create simple WOLEDs with just one EML (40).

Importantly, the performance of these simple WOLEDs can easily be improved by inserting an electron blocking layer (EBL), selecting the proper host materials, and optimising the energy levels of the functional layers, thus balancing the carrier injection in the device. In single EML WOLEDs with **Ptppy-2** as the emitter, the EL efficiencies could be improved to a peak EQE of 6.4%, a CE of 17.0 cd A⁻¹ and a PE of 12.2 lm W⁻¹ by inserting an Irppz EBL. The host 2,6-bis(*N*-carbazolyl)pyridine (mCPy) could guarantee a more efficient energy transfer to **Ptppy-2** than conventional mCP. Simple WOLEDs with **Ptppy-2** doped into mCPy could thereby furnish better device efficiencies with an EQE of 6.9% and a CE of 15.7 cd A⁻¹ at 500 cd m⁻². Taking poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) as the hole injecting layer (HIL) and poly(*N*-vinylcarbazole) (PVK) as the hole transport layer (HTL) as well as the EBL, the efficiencies of simple WOLEDs could be maximised to an EQE of 18%, a PE of 29 lm W⁻¹ and a CE of 42.5 cd A⁻¹ (41), corresponding to an IQE of nearly 100% (42). These dramatic enhancements may be attributed to the smoother interface of PEDOT:PSS/PVK compared to that of PEDOT:indium tin oxide (ITO)/PVK, resulting in a smaller interfacial surface area and lower leakage current. Furthermore, ITO/PVK has an injection barrier 0.6 eV larger than that of ITO/*N,N'*-di-[(1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl-4,4'-diamine (NPD) (the HOMOs for PVK and NPD are 5.8 eV and 5.2 eV, respectively) and PVK has a much lower hole mobility than NPD, which can effectively reduce the number of holes injecting to the emissive layer, leading to a more balanced ratio of holes and electrons.

Some phosphors with substituted β -diketonato ligands (**Ptppy-9** and **Ptppy-10**) (**Figure 9**) were

also obtained (43). Although the substituents can exert only limited electronic effects on the complex cores, they can evidently influence the molecular packing in the crystals and the thin films to facilitate the fabrication of simple non-doped devices. The attractive EL performance of non-doped devices based on **Ptppy-10**, with a peak EQE of 9.76%, a CE of 28.1 cd A⁻¹ and a PE of 9.91 lm W⁻¹ at 500 cd m⁻² indicates the great potential of these phosphors for simplifying device fabrication, since traditional phosphorescent OLEDs generally possess doped EMLs which are much more complicated to construct.

Ptppy-2 can be attached to a random terpolymer backbone containing hole-transport (HT) and electron-transport (ET) moieties, leading to a range of phosphorescent terpolymers (44) (**Figure 10**). The polymeric phosphor **Ptppy-P** was employed to prepare a simple solution-processed OLED, with a maximum EQE of 4.6% and CIE coordinates of (0.33, 0.50). **Ptppy-2** has also been attached to a polyhedral oligomeric silsesquioxane (POSS) core (45) (**Figure 10**). The carbazole moieties provided efficient HT character as well as diluting the concentration of the Pt complex bonded to the POSS, thus controlling the emission contributions from the monomer and excimer states. The maximum EQE was 8.4% for a **Ptppy-POSS** based solution-processed WOLED. Although its CIE coordinates of (0.46, 0.44) deviate slightly from the ideal white point at (0.33, 0.33), the EL spectrum of the device was voltage-independent, indicating good colour stability.

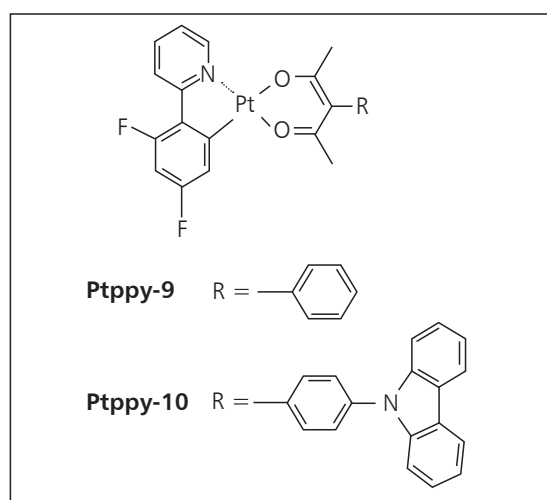


Fig. 9. Chemical structures of **Ptppy-9** and **Ptppy-10**

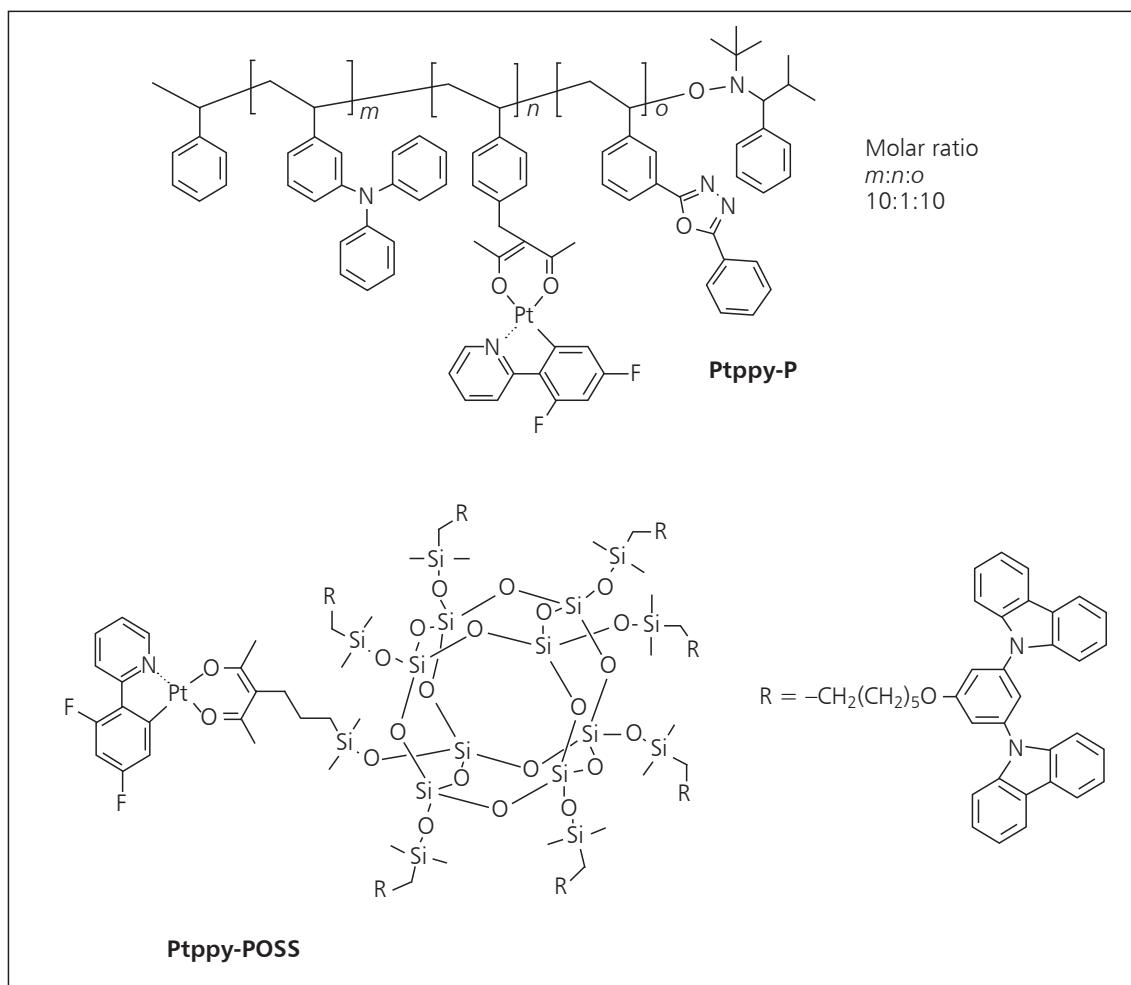


Fig. 10. Chemical structures of **Ptppy-P** and **Ptppy-POSS**

4.2 Functionalised (N[^]C)Pt(O[^]O) Phosphors

Besides the Pt phosphors described above, functionalised analogues have also been developed to address some critical issues in OLEDs, including carrier injection/transport, emission colour tuning and T-T annihilation.

A series of Pt phosphors functionalised with main group elements have been designed and synthesised (**Figure 11**) (46–49). Some of these might represent the highest Φ_p values ever reported for Pt phosphors, at 0.93 for **Pt-PO** and 0.95 for **Pt-SO₂**. The diphenylamino group (NPh₂) has been shown to add HI/HT functionality to **Pt-N**, while dimesitylboron B(Mes)₂, diphenylphosphoryl (POPh₂) and phenylsulfonyl (SO₂Ph) moieties can provide EI/ET functionality to **Pt-B**, **Pt-PO** and **Pt-SO₂**, respectively

(48). It is well known that carrier injection/transport are very important to the EL process. Hence, **Pt-B**, **Pt-N**, **Pt-PO** and **Pt-SO₂** exhibit much better EL efficiencies (with CE values of 30.00 cd A⁻¹, 29.74 cd A⁻¹, 22.06 cd A⁻¹ and 19.59 cd A⁻¹, respectively) than do other congeners (8.47 cd A⁻¹ for **Pt-Si**, 8.49 cd A⁻¹ for **Pt-Ge**, 11.42 cd A⁻¹ for **Pt-O** and 16.77 cd A⁻¹ for **Pt-S**, for example), indicating the great potential of such functionalisation for enhancing the EL performance of Pt phosphors.

Inspired by the success of **Pt-B**, other efficient Pt phosphors bearing B(Mes)₂ were also prepared (**Figure 11**). **Pt-pyB** can show outstanding EL performance with an EQE of 20.9%, a CE of 64.8 cd A⁻¹ and a PE of 79.3 lm W⁻¹ (50). This complex also shows comparable HI/HT and EI/ET properties to those

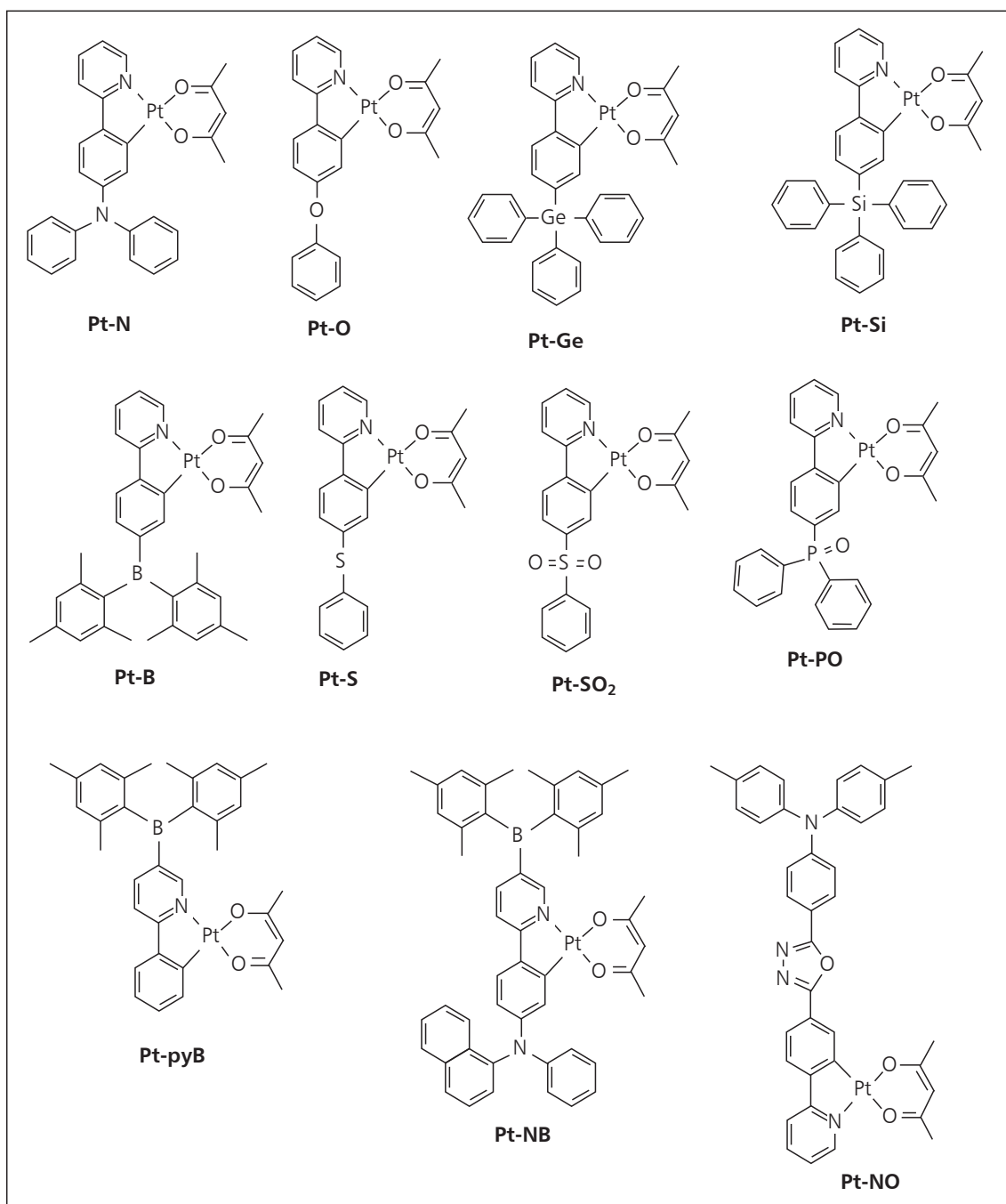


Fig. 11. Chemical structures of some functionalised Pt phosphors

of the analogous **Pt-NO** and **Pt-NB**, and has decent efficiencies with an EQE of 10.6%, a CE of 33.2 cd A⁻¹ and a PE of 34.8 lm W⁻¹ (51).

Additionally, these phosphors can exhibit unique colour tuning behaviours. **Pt-B** ($\lambda_{em} = 542$ nm), **Pt-PO** ($\lambda_{em} = 500$ nm) and **Pt-SO₂** ($\lambda_{em} = 503$ nm) bearing

electron-withdrawing main group moieties on the phenyl ring of their ppy ligands show a bathochromic (red-shift) effect in their emission maxima with respect to that of their parent complex **Ptppy-1** ($\lambda_{em} = 486$ nm). These results are in conflict with traditional colour tuning theory, which predicts a

hypsochromic (blue-shift) effect in the emission wavelength when electron-withdrawing moieties are introduced to the phenyl ring of the ppy ligands (38). Time-dependent density functional theory (TD-DFT) calculations show that the electrons in the metal-to-ligand charge transfer (MLCT) process mainly go to the main group moieties B(Mes)₂, POPh₂ and SO₂Ph in **Pt-B**, **Pt-PO** and **Pt-SO₂** rather than to the pyridyl ring in the ligand as in their conventional counterparts (38). This means that the electron-withdrawing main group moieties have changed the direction of the MLCT process compared to the unfunctionalised pyridyl ring complexes, an effect which is not seen with other electron-withdrawing groups such as F or CN which cannot host electrons. The stronger electron-withdrawing properties of the main group moieties compared to the pyridyl ring in the ligand allows them to stabilise the MLCT states. The phosphorescence from triplet MLCT states in **Pt-B**, **Pt-PO** and **Pt-SO₂** can therefore be expected to show red-shift. Similar colour tuning behaviour was also observed in fluorenone-based Pt phosphors, indicating the universality of this effect (52). The importance of this new colour tuning strategy lies in that it makes possible the design and synthesis of long wavelength phosphors with EI/ET properties.

The high LUMO levels for **Pt-Si**, **Pt-Ge**, **Pt-O** and **Pt-S** mean that electrons can leak into the 4,4'-bis-[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) layer, resulting in blue emission which provides a chance to generate white light by mixing with the green monomeric emission and orange/red excimer emission from the Pt phosphors. This could provide another route towards simple WOLEDs emitting good quality white light. **Pt-Ge** and **Pt-O** have been employed in OLEDs with the simple configuration indium tin oxide/NPB/x%Pt:4,4'-bis(N-carbazolyl)-1,1'-biphenyl/bathocuproine/tris(8-hydroxyquinolino)-aluminium/lithium fluoride/aluminium (ITO/NPB/x%Pt:CBP/BCP/Alq₃/LiF/Al) (49). As expected, these simple devices can emit high quality white light with a blue component from NPB and green and orange/red components from the monomer and excimer of the Pt phosphor, respectively. **Pt-Ge** based devices can reach an exceptionally high colour rendering index (CRI) of up to ca. 97 at brightness > 15,000 cd m⁻², a correlated colour temperature (CCT) of 4719 K and CIE coordinates of (0.354, 0.360) at a doping level of 10 wt%. A 6 wt% **Pt-O** doped WOLED produced white light with a CRI of ca. 94, a CCT of 6606 K and a CIE of (0.320, 0.340), perhaps the best quality white light

ever produced by WOLEDs, comparable with natural sunlight and therefore most suitable for artificial lighting applications.

Typically, Pt phosphors suffer from efficiency roll-off due to T-T annihilation induced by their inherent square-planar structure geometry favouring strong molecular interaction, as well as their relatively long τ_p (13, 30). This undesired T-T annihilation has been successfully hindered by attaching bulky triphenylamine moieties to the Pt phosphor ligands (**Figure 12**) (53). **Pt-F2TPA** has a τ_p of 8.2 μ s, and T-T annihilation can only occur at very high current densities of 360 mA cm⁻². Triphenylamine can also enhance its HI/HT characteristics.

4.3 N[^]N-Coordinating Ligands Based Platinum Phosphors

Chi *et al.* have synthesised a series of Pt(N[^]N)₂ phosphors bearing N-heterocycle substituted pyrazole ligands (**Figure 13**). A device doped with 20 wt% **PtNN-1** showed a maximum brightness of 40,973 cd m⁻² at 15 V, a peak EQE of 5.96%, a CE of 19.70 cd A⁻¹ and a PE of 6.44 lm W⁻¹ (54). The optimal device based on **PtNN-2** achieved a maximum luminescence of 20,296 cd m⁻² at 16 V, a peak EQE of 5.78%, a CE of 12.19 cd A⁻¹ and a PE of 6.12 lm W⁻¹ (55). Similarly to other congeners, they also undergo self-aggregation at high doping levels in devices.

M. A. Omary *et al.* reported a turquoise-blue Pt(N[^]N)₂ complex, **PtNN-3** (**Figure 13**), in which the N[^]N represents a pyridyltriazolate derivative (56, 57). This complex features intense Pt⁺Pt⁺ intermolecular

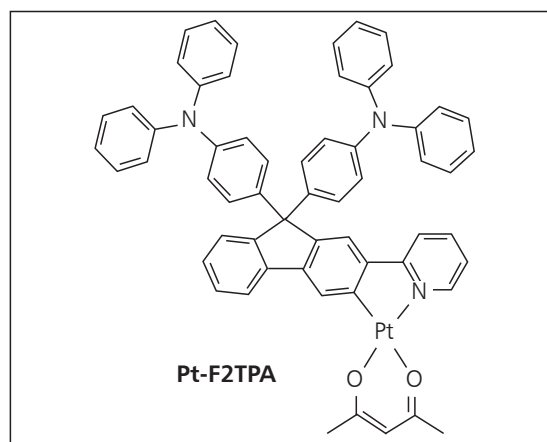


Fig. 12. Chemical structure of **Pt-F2TPA**

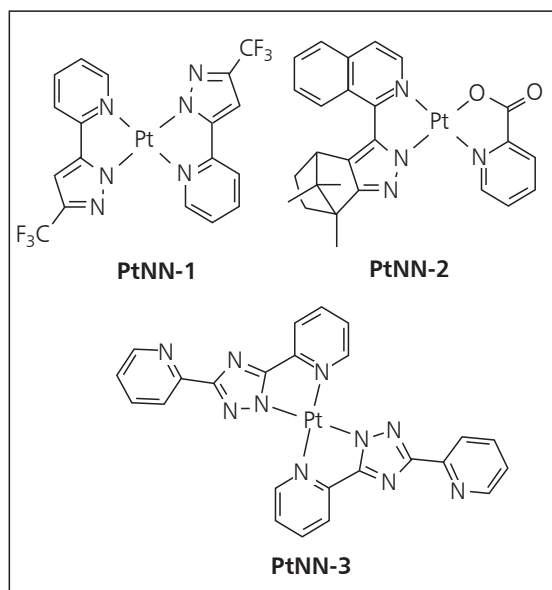


Fig. 13. Chemical structures of **PtNN-1** to **PtNN-3**

interactions due to the strong polarity induced by pyridyltriazolate as well as its square-planar geometry. Generally, interactions among the phosphor molecules will decrease EL efficiency. However, EL efficiencies could be enhanced by increasing the doping level of **PtNN-3** and a maximum EQE of 19.7%, a PE of 44.7 lm W^{-1} and a CE of 62.5 cd A^{-1} were achieved at a doping level of 65%. This interesting result may be attributed to energy-level matching among the functional layers within the devices to balance the hole/electron ratio and confine the recombination zone in the EML. Furthermore, the short lifetime of **PtNN-3** in the solid film may play a critical role in reducing T-T annihilation and thus enhancing the device efficiencies. These results might provide valuable information on how to cope with the problem of intermolecular interactions associated with Pt phosphors.

4.4 Platinum Phosphors with C[^]C-Coordinating Ligands

Carbene-type ligands have also been employed to prepare novel Pt phosphors. Y. Unger *et al.* prepared some homoleptic Pt(II) biscarbene complexes which were emissive in the deep blue region (58). The complex **PtCC-1** (Figure 14) gave intense photoluminescence at 386 nm with a Φ_p of 0.45 under a nitrogen atmosphere. Due to its emission energy being in the ultraviolet (UV) region, the **PtCC-1** phosphor is less suitable for fabricating OLEDs. However, a

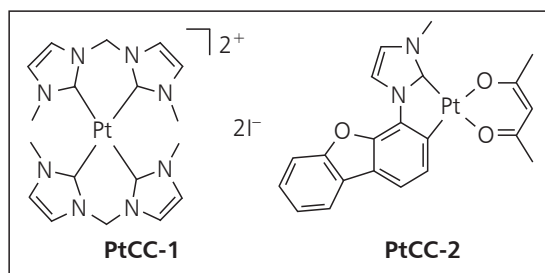


Fig. 14. Chemical structures of **PtCC-1** and **PtCC-2**

new series of carbene-type Pt(II) phosphors were subsequently constructed using modified structures (59). The complex **PtCC-2** (Figure 14) had a Φ_p of 0.9 under a nitrogen atmosphere, qualifying it as a triplet emitter for EL devices. A device based on **PtCC-2** had a maximum brightness of 6750 cd m^{-2} and a peak EQE of 6.2% at 13.2 V.

4.5 Platinum Phosphors with Bridged N[^]C-Coordinating Ligands

Recently, K. Feng *et al.* reported some interesting Pt phosphors with bridged ligands (**PtbNC-1** and **PtbNC-2**) and their copolymers (**PtbNC-P1** and **PtbNC-P2**) (Figure 15) (60). These Pt complexes exhibit peak emissions around 525 nm with a maximum Φ_p around 0.55 in degassed CH_2Cl_2 and their corresponding polymers display almost identical photoluminescence spectra in PVK films. The investigation of the EL properties of these green-lighting polymers shows that the novel phosphorescent polymers can show a maximum brightness of ca. 1000 cd m^{-2} and a peak EQE of 2.5% (61).

Vezzu *et al.* also synthesised some $\text{Pt}(\text{N}^{\wedge}\text{C})_2$ complexes (Figure 15) emitting between 474 nm and 613 nm with Φ_p values ranging from 0.14 to 0.75 (62). Doping 4% **PtbNC-3** into a 2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBI)-4,4',4''-tris(*N*-carbazolyl)triphenylamine (TCTA) co-host produced a bright green emitting device ($\lambda_{\text{max}} = 512 \text{ nm}$) with a peak EQE of 14.7% and a maximum CE of 50.0 cd A^{-1} . When the current density was increased to 10 mA cm^{-2} , the brightness rose to 3698 cd m^{-2} with significant efficiency roll-off (EQE of 10.6% and CE of 37 cd A^{-2}), implying the occurrence of T-T annihilation in the device.

5 Concluding Remarks

Platinum-based phosphors have unique properties which give them great potential for electroluminescent

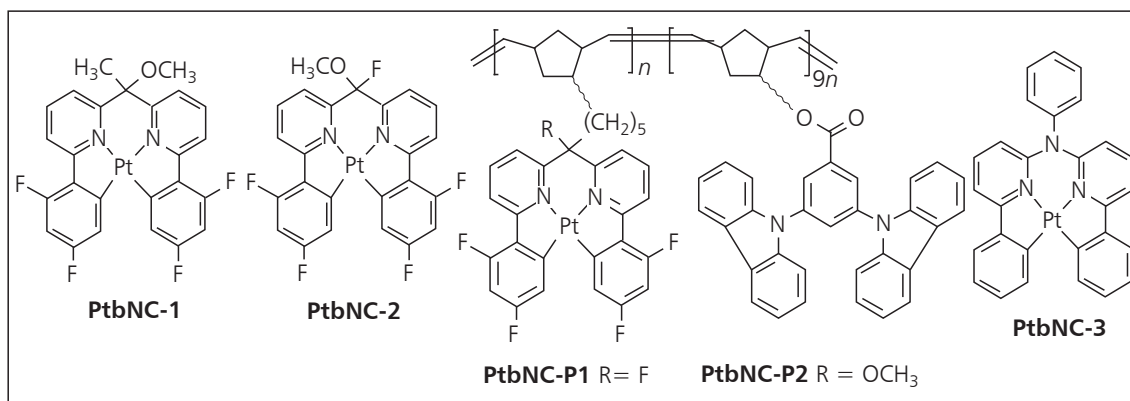


Fig. 15. Chemical structures of typical Pt phosphors with bridged ligands

applications. Modifying the chemical structures of their ligands has allowed advanced emitters to be generated which have addressed many of the critical issues in OLED research, including improved photoluminescence and electroluminescence efficiencies, carrier injection/transport, novel colour tuning strategies, overcoming the problem of T-T annihilation, and the fabrication of simple WOLEDs emitting good quality white light. These developments and the associated performance enhancements may soon allow Pt-phosphor based EL devices to begin moving from the laboratory into the commercial market. More and increasingly sophisticated triplet

emitters based on Pt will continue to be developed, leading to further improvements in the field.

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Glossary

Term	Definition	Term	Definition
τ_p	triplet state lifetime	HI	hole injection
Φ_p	triplet quantum yield	HIL	hole injection layer
CCT	correlated colour temperature	HOMO	highest occupied molecular orbital
CE	current efficiency	HT	hole transport
CIE	Commission Internationale de l'Éclairage	HTL	hole transport layer
CRI	colour rendering index	IQE	internal quantum efficiency
EBL	electron blocking layer	LUMO	lowest unoccupied molecular orbital
EI	electron injection	MLCT	metal-to-ligand charge transfer
EL	electroluminescence	OLED	organic light-emitting diode
EML	emissive layer	PE	power efficiency
EQE	external quantum efficiency	T-T	triplet-triplet
ET	electron transport	WOLED	white organic light-emitting diode

References

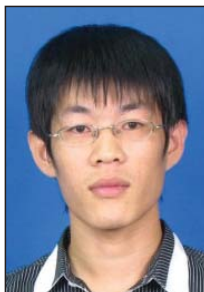
- 1 C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirm, P. Rudati, H. Frohne, O. Nuyken, H. Becker and K. Meerholz, *Nature*, 2003, **421**, (6925), 829
- 2 E. Holder, B. M. W. Langeveld and U. S. Schubert, *Adv. Mater.*, 2005, **17**, (9), 1109
- 3 W.-Y. Wong and C.-L. Ho, *J. Mater. Chem.*, 2009, **19**, (26), 4457
- 4 L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong and J. Kido, *Adv. Mater.*, 2011, **23**, (8), 926
- 5 G. Zhou, W.-Y. Wong and X. Yang, *Chem. Asian J.*, 2011, **6**, (7), 1706
- 6 J. Kido, M. Kimura and K. Nagai, *Science*, 1995, **267**, (5202), 1332
- 7 Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, (7086), 908
- 8 G. Zhou, W.-Y. Wong and S. Suo, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2010, **11**, (4), 133
- 9 G. M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, **40**, (7), 3467
- 10 H. Sasabe and J. Kido, *Chem. Mater.*, 2011, **23**, (3), 621
- 11 P.-T. Chou and Y. C. Chi, *Chem. Eur. J.*, 2007, **13**, (2), 380
- 12 Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2010, **39**, (2), 638
- 13 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, (6698), 151
- 14 K. R. Graham, X. Yang, J. R. Sommer, A. H. Shelton, K. S. Schanze, J. Xue and J. R. Reynolds, *Chem. Mater.*, 2011, **23**, (24), 5305
- 15 C.-M. Che, S.-C. Chan, H.-F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Commun.*, 2004, (13), 1484
- 16 C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu and H. Yersin, *Chem. Eur. J.*, 2010, **16**, (1), 233
- 17 H.-F. Xiang, S.-C. Chan, K. K.-Y. Wu, C.-M. Che and P. T. Lai, *Chem. Commun.*, 2005, (11), 1408
- 18 J. A. G. Williams, S. Develay, D. L. Rochester and L. Murphy, *Coord. Chem. Rev.*, 2008, **252**, (23–24), 2596
- 19 W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, N. Zhu, S.-T. Lee and C.-M. Che, *Chem. Commun.*, 2002, (3), 206
- 20 W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu and S.-T. Lee, *J. Am. Chem. Soc.*, 2004, **126**, (15), 4958
- 21 S. C. F. Kui, I. H. T. Sham, C. C. C. Cheung, C.-W. Ma, B. Yan, N. Zhu, C.-M. Che and W.-F. Fu, *Chem. Eur. J.*, 2007, **13**, (2), 417
- 22 M.-Y. Yuen, S. C. F. Kui, K.-H. Low, C.-C. Kwok, S. S.-Y. Chui, C.-W. Ma, N. Zhu and C.-M. Che, *Chem. Eur. J.*, 2010, **16**, (47), 14131
- 23 J. A. G. Williams, A. Beeby, E. S. Davies, J. A. Weinstein and C. Wilson, *Inorg. Chem.*, 2003, **42**, (26), 8609
- 24 S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard and J. A. G. Williams, *Inorg. Chem.*, 2005, **44**, (26), 9690
- 25 M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester and J. A. G. Williams, *Adv. Funct. Mater.*, 2007, **17**, (2), 285
- 26 W. Sotoyama, T. Satoh, N. Sawatari and H. Inoue, *Appl. Phys. Lett.*, 2005, **86**, (15), 153505
- 27 A. Y.-Y. Tam, D. P.-K. Tsang, M.-Y. Chan, N. Zhu and V. W.-W. Yam, *Chem. Commun.*, 2011, **47**, (12), 3383
- 28 X. Yang, Z. Wang, S. Madakuni, J. Li and G. E. Jabbour, *Adv. Mater.*, 2008, **20**, (12), 2405
- 29 A. F. Rausch, L. Murphy, J. A. G. Williams and H. Yersin, *Inorg. Chem.*, 2012, **51**, (1), 312
- 30 M. Cocchi, J. Kalinowski, V. Fattori, J. A. G. Williams and L. Murphy, *Appl. Phys. Lett.*, 2009, **94**, (7), 073309
- 31 M. Cocchi, J. Kalinowski, L. Murphy, J. A. G. Williams and V. Fattori, *Org. Electron.*, 2010, **11**, (3), 388
- 32 J.-L. Chen, S.-Y. Chang, Y. Chi, K. Chen, Y.-M. Cheng, C.-W. Lin, G.-H. Lee, P.-T. Chou, C.-H. Wu, P.-I. Shih and C.-F. Shu, *Chem. Asian J.*, 2008, **3**, (12), 2112
- 33 C. A. Strassert, C.-H. Chien, M. D. G. Lopez, D. Kourkoulos, D. Hertel, K. Meerholz and L. D. Cola, *Angew. Chem. Int. Ed.*, 2011, **50**, (4), 946
- 34 G. S.-M. Tong and C.-M. Che, *Chem. Eur. J.*, 2009, **15**, (29), 7225
- 35 V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, X.-X. Lu, K.-K. Cheung and N. Zhu, *Chem. Eur. J.*, 2002, **8**, (17), 4066
- 36 S. C. F. Kui, S. S.-Y. Chui, C.-M. Che and N. Zhu, *J. Am. Chem. Soc.*, 2006, **128**, (25), 8297
- 37 S. C. F. Kui, F.-F. Hung, S.-L. Lai, M.-Y. Yuen, C.-C. Kwok, K.-H. Low, S. S.-Y. Chui and C.-M. Che, *Chem. Eur. J.*, 2012, **18**, (1), 96
- 38 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, **41**, (12), 3055
- 39 C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 2001, **79**, (13), 2082
- 40 B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, **14**, (15), 1032
- 41 E. L. Williams, K. Haavisto, J. Li and G. E. Jabbour, *Adv. Mater.*, 2007, **19**, (2), 197
- 42 C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, (10), 5048
- 43 C.-H. Chen, F.-I. Wu, Y.-Y. Tsai and C.-H. Cheng, *Adv. Funct. Mater.*, 2011, **21**, (16), 3150
- 44 P. T. Furuta, L. Deng, S. Garon, M. E. Thompson and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, (47), 15388
- 45 X. Yang, J. D. Froehlich, H. S. Chae, B. T. Harding, S. Li, A. Mochizuki and G. E. Jabbour, *Chem. Mater.*, 2010, **22**, (16), 4776
- 46 W.-Y. Wong, Z. He, S.-K. So, K.-L. Tong and Z. Lin, *Organometallics*, 2005, **24**, (16), 4079
- 47 Z. He, W.-Y. Wong, X. Yu, H.-S. Kwok and Z. Lin, *Inorg. Chem.*, 2006, **45**, (26), 10922

- 48 G. Zhou, Q. Wang, X. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang and Z. Lin, *J. Mater. Chem.*, 2010, **20**, (35), 7472
- 49 G. Zhou, Q. Wang, C.-L. Ho, W.-Y. Wong, D. Ma and L. Wang, *Chem. Commun.*, 2009, (24), 3574
- 50 Z. B. Wang, M. G. Helander, Z. M. Hudson, J. Qiu, S. Wang and Z. H. Lu, *Appl. Phys. Lett.*, 2011, **98**, (21), 213301
- 51 M. Velusamy, C.-H. Chen, Y. S. Wen, J. T. Lin, C.-C. Lin, C.-H. Lai and P.-T. Chou, *Organometallics*, 2010, **29**, (17), 3912
- 52 G.-J. Zhou, Q. Wang, W.-Y. Wong, D. Ma, L. Wang and Z. Lin, *J. Mater. Chem.*, 2009, **19**, (13), 1872
- 53 G.-J. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, *J. Mater. Chem.*, 2008, **18**, (15), 1799
- 54 S.-Y. Chang, J. Kavitha, S.-W. Li, C.-S. Hsu, Y. Chi, Y.-S. Yeh, P.-T. Chou, G.-H. Lee, A. J. Carty, Y.-T. Tao and C.-H. Chien, *Inorg. Chem.*, 2006, **45**, (1), 137
- 55 S.-Y. Chang, J. Kavitha, J.-Y. Hung, Y. Chi, Y.-M. Cheng, E. Y. Li, P.-T. Chou, G.-H. Lee and A. J. Carty, *Inorg. Chem.*, 2007, **46**, (17), 7064
- 56 U. S. Bhansali, E. Polikarpov, J. S. Swensen, W.-H. Chen, H. Jia, D. J. Gaspar, B. E. Gnade, A. B. Padmaperuma and M. A. Omary, *Appl. Phys. Lett.*, 2009, **95**, (23), 233304
- 57 M. Li, M.-T. Lin, W.-H. Chen, R. McDougald Jr., R. Arvapally, M. Omary and N. D. Shepherd, *Phys. Status Solidi A*, 2012, **209**, (1), 221
- 58 Y. Unger, A. Zeller, S. Ahrens and T. Strassner, *Chem. Commun.*, 2008, (28), 3263
- 59 Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Münster, G. Wagenblast and T. Strassner, *Angew. Chem. Int. Ed.*, 2010, **49**, (52), 10214
- 60 K. Feng, C. Zuniga, Y.-D. Zhang, D. Kim, S. Barlow, S. R. Marder, J. L. Brédas and M. Weck, *Macromolecules*, 2009, **42**, (18), 6855
- 61 K. Feng, Y. Zhang, S. Barlow, D. Kim, S. R. Marder, J.-L. Brédas, M. Weck, B. Kippelen and S.-J. Kim, Solvay SA, 'Phosphorescent Platinum Complexes, Their Monomers and Copolymers, and Uses in Organic Electronic Devices', *World Patent* 2011/000,873
- 62 D. A. K. Vezzu, J. C. Deaton, J. S. Jones, L. Bartolotti, C. F. Harris, A. P. Marchetti, M. Kondakova, R. D. Pike and S. Huo, *Inorg. Chem.*, 2010, **49**, (11), 5107

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