Two cyclometallated platinum(II) complexes, \(N^\text{\textdegree}C^\text{\textdegree}N^\text{\textdegree}-5\text{-fluoro-1,3-di(2-pyridyl)benzene platinum(II)}\) chloride, FPtCl, and \(N^\text{\textdegree}C^\text{\textdegree}N^\text{\textdegree}-5\text{-methyl-1,3-di(2-pyridyl)benzene platinum(II)}\) isothiocyanate, MePtNCS, have been synthesized and characterized. Both complexes are highly efficient phosphorescent green emitters which can also display excimer emission in the red region. They have been studied as triplet emitters in solution-processed, multilayer organic light-emitting diodes (OLEDs), together with the known complex of 5-methyl-1,3-di(2-pyridyl)benzene, MePtCl, for comparison. The trend in efficiencies of the OLEDs prepared correlates with the charge-trapping properties of the complexes. The most efficiently emitting complex, FPtCl, was used as the dopant in a solution-processed white OLED, employing monomer and excimer emission.

**Introduction**

To construct efficient organic light-emitting diodes (OLEDs), emitters possessing high quantum efficiencies under electrical operation are required. Since the introduction of phosphorescent metal complexes into this field, which utilize both singlet and triplet excitons to generate electroluminescence (EL),\(^1\) many new phosphorescent materials have been synthesized for potential OLED applications.\(^2,3\) Among them, a class of cyclometallated platinum(II) complexes with \(N^\text{\textdegree}C^\text{\textdegree}N^\text{\textdegree}\)-coordinated 1,3-di(2-pyridyl)benzene ligands is gaining increasing interest, owing to their high emission phosphorescence quantum yields.\(^4,5\) These compounds have been tested as phosphors in multilayer OLEDs, leading to high external quantum efficiencies.\(^6,9\) Additionally, owing to their propensity to form highly emissive bimolecular excimers or aggregates, they are of particular interest for the production of white OLEDs (WOLEDs). The combination of efficient triplet monomer and excimer emission to generate broad-band light across the visible spectrum has been put forward as an attractive route to single-dopant white-emitting devices.\(^10\) WOLEDs are expected to be more efficient and less expensive than fluorescent and incandescent illumination light sources.\(^11,12\)

They also offer useful properties like tunable correlated colour temperature (CCT) and can be obtained as completely flexible large area devices.\(^13,14\) Excimers possess a broad EL spectrum, a desirable feature for illumination purposes as it increases the colour rendering index (CRI). Moreover, among many strategies for obtaining white light from organic or organometallic molecular materials, excimer emission is of particular interest as it allows simplified device architectures to be used. This is because excimers lack a bound ground state and, as a result, energy transfer between multiple dopants is significantly reduced.\(^15\)

Most examples of devices with phosphorescent excimer emission use cyclometallated platinum(II) complexes with bidentate, \(N^\text{\textdegree}C^\text{\textdegree}\)-coordinating aryl-pyridines and \(\beta\)-diketonate co-ligands.\(^15,17\) Based on the same principle, WOLEDs with \(N^\text{\textdegree}C^\text{\textdegree}N^\text{\textdegree}\) coordinated platinum(II) complexes have since been created.\(^16\) Further improvements in device performance were recently achieved by combining the monomer and excimer emission of such complexes with exciplex emission involving the host material.\(^19\) However, until now, all such excimer WOLEDs have been vacuum-sublimed multilayer structures. Such fabrication methods, based on evaporation, are generally expensive...
processes, requiring precise control of evaporation rates when two or more compounds are in the same layer (e.g. host and dopant), and are less suitable for the production of large area devices due to the higher cost.

In this contribution, we present electroluminescent devices that use Pt(NC4H4N)X complexes as phosphors, built by a simple spin-coating technique. Two complexes have been investigated, as shown in Chart 1: N4C5N-5-fluoro-1,3-di(2-pyridyl)-benzene platinum(u) chloride, FPtCl, and N4C5N-5-methyl-1,3-di-(2-pyridyl)-benzene platinum(u) isothiocyanate, MePtNCS. The known chloro analogue of the latter complex, MePtCl, has also been studied for comparison. The synthesis and photophysical properties of the complexes are reported, together with studies of their use as phosphors in spin-coated diodes. Finally, the complex showing the best performance has been applied in a WOLED employing monomer and excimer emission mechanisms, in a simple solution-processed multilayer device.

### Experimental

#### General comments

Reagents were purchased from Sigma-Aldrich or Fluorochem. Products were characterized by elemental analysis, mass spectrometry (FAB* and MALDI-TOF) and by 1H and 13C NMR spectroscopy (Bruker Avance DRX-400 instrument). 1H NMR spectra are referenced relative to residual proton solvent resonance; δ are in ppm and coupling constants in Hz. 5-Methyl-1,3-di(2-pyridyl)benzene for comparison (400 MHz, CDCl3): δH = 8.73 (2H, d, H6), 8.39 (1H, s, H2), 7.92 (2H, s, H6), 7.85 (2H, d, H4), 7.77 (2H, td, H4), 7.26 (2H, td, H4), 2.54 (3H, s, CH3). MS FAB+: 444 (M+ Cl)+. Anal. Calcd for C17H13ClN2Pt: C, 40.05; H, 2.10; N, 5.72% (Chart 3).

#### Synthesis of platinum(u) complexes

**MePtCl.** A solution of K2PtCl4 (337 mg, 0.815 mmol) in water (12.5 mL) was treated with a solution of 3,5-di(2-pyridyl)toluene (210 mg, 0.856 mmol) in acetonitrile (12.5 mL), and the mixture heated at reflux under N2 for 3 days. After cooling to room temperature, the orange residue formed was collected by filtration and washed with water (2 × 20 mL) and ethanol (2 × 20 mL). After being dried under reduced pressure, the product was obtained as an orange-yellow solid (259 mg, 67% yield). 1H NMR (400 MHz, CD2Cl2): δH = 8.39 (2H, d, H6), 8.00 (2H, d, J(195Pt) 38, H6), 7.93 (2H, td, H4), 7.66 (2H, d, J(195Pt) 6.3, H3), 7.29 (2H, s, H6), 7.28 (2H, not fully resolved due to overlap with the former signal and solvent, m, H3). 1H NMR data of 5-methyl-1,3-di(2-pyridyl)benzene for comparison (400 MHz, CDCl3): δH = 8.73 (2H, d, H6), 8.39 (1H, s, H2), 7.92 (2H, s, H6), 7.85 (2H, d, H4), 7.77 (2H, td, H4), 7.26 (2H, td, H4), 2.54 (3H, s, CH3) (Chart 2).

**Synthesis of 5-fluoro-1,3-di(2-pyridyl)benzene.**

A mixture of commercial 1,3-dibromo-5-fluorobenzene (0.279 g, 1.10 mmol), 2-(tri-n-butylstannyl)pyridine (1.00 g, 2.72 mmol), lithium chloride (0.074 g, 1.66 mmol) and bis(triphenylphosphine)-palladium(u) chloride (0.203 g, 0.287 mmol) in toluene (7 mL) was degassed via five freeze-pump-thaw cycles and then heated at reflux under an atmosphere of N2 for 72 h. After cooling, a saturated aqueous solution of potassium fluoride (10 mL) was added and the mixture stirred for 30 min. The insoluble residue formed was removed by filtration and washed with toluene. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was taken up into CH2Cl2 (3 × 50 mL) and washed with aqueous NaHCO3 (1 M, 2 × 50 mL). The organic phase was dried over anhydrous Na2SO4 and evaporated to dryness. The brown residue was purified by chromatography on a silica gel, gradient elution using hexane/diethyl ether 90/10, giving the product as a white solid (0.146 g, 53%). 1H NMR (400 MHz, DMSO-d6): δH = 8.83 (2H, d, H6), 8.68 (1H, s, H2), 8.39 (2H, dd, H4), 8.27 (2H, ddd, H3), 8.11 (2H, d, J(19F–1H) = 10, H4), 7.72 (2H, ddd, H4). Anal. Calcd for C16H10ClFN2Pt: C, 40.05; H, 2.10; N, 5.72%. Found: C, 40.12; H, 2.10; N, 5.76%.

**FPtCl.** FPtCl was prepared similarly, in 60% yield. 1H NMR (400 MHz, DMSO-d6): δH = 9.10 (2H, d, J(195Pt) 32, H6), 8.24 (2H, td, H4), 8.17 (2H, d, H2), 7.78 (2H, s, J(19F) 10, H4), 7.60 (2H, ddd, H4). 13C NMR (400 MHz, CD2Cl2): δ = 152.4, 139.2, 123.8, 119.8, 111.5 (quaternary not detected). MS FAB+: 444 (M – Cl)+. Anal. Calcd for C16H10ClIFN2Pt: C, 42.91; H, 2.75; N, 5.89%. Found: C, 43.10; H, 2.86; N, 5.72% (Chart 3).

**MePtNCS.** Sodium thiocyanate (18 mg, 0.210 mmol) was added to a suspension of MePtCl (50 mg, 0.105 mmol) in methanol/acetonitrile (5/20 v/v). The reaction mixture was stirred at room temperature for 1 day. The crude compound was dissolved in CH2Cl2, filtered, and precipitated twice from dry pentane, giving the pure product as a red solid (26 mg, 50% yield). 1H NMR (400 MHz, CD2Cl2): δH = 8.77 (2H, d, J(195Pt) 40, H6), 8.27 (2H, d, J(195Pt) 32, H6), 8.02 (2H, td, H4), 7.83 (2H, ddd, H4), 7.60 (2H, ddd, H4). 13C NMR (400 MHz, CD2Cl2): δ = 152.4, 139.2, 123.8, 119.8, 111.5 (quaternary not detected). MS FAB+: 440 (M – Cl)+. Anal. Calcd for C16H10ClIFN2Pt: C, 42.05; H, 2.10; N, 5.83%. Found: C, 42.12; H, 2.10; N, 5.76%.

[Chart 1] Structures of the complexes investigated (top) and of the unsubstituted and difluorinated analogues.

[Chart 2] Numbering system for 1H NMR assignment of ligands.
The luminescence lifetimes of the complexes were determined relative to MePtCl₅ as a secondary standard emitting in the same region. The luminescence lifetimes of the complexes were determined from the lifetimes in degassed and air-equilibrated solution, taking the concentration of oxygen in CH₂Cl₂ at 0.21 atm O₂ to be 2.2 mmol dm⁻³.²⁰

**Photophysical measurements**

Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrophotofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube (PMT); the spectra shown are corrected for the wavelength dependence of the PMT. Photophysical measurements

**Device fabrication and characterization**

Glass substrates coated with indium tin oxide (ITO) were cleaned ultrasonically in distilled water, acetone and 2-propanol. Subsequently, a 50 nm layer of poly(3,4-ethylentioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) (H.C. Starck Clevis P VP.AI 4083) was spin-coated from a water solution filtered through nylon (pore size 0.45 µm), and annealed at 100 °C for 10 min under a N₂ atmosphere. In the case of the green-emitting OLEDs (5% dopant in the emissive layer), a film of poly(N-vinylcarbazole) (PVK-h, average Mₙ = 10⁶ g mol⁻¹) was then spin-coated from CH₂Cl₂ solution (12 mg mL⁻¹) onto the layers prepared as above. The samples were annealed at 150 °C for 30 min. The emitting layer, consisting of PVK-l (Mₙ = 42 000 g mol⁻¹),²¹ 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and either FPFCl, MePtNCs or MePtCl, was then spun-coated from a deaerated CH₂Cl₂ solution (8 mg mL⁻¹) comprised of 65% PVK-l:30% PBD:5% Pt complex by mass. The average total thickness of PVK-h and the emitting layer was equal to 165 nm for all three devices. Finally barium (5 nm layer) and aluminium (60 nm layer) were deposited by thermal vacuum evaporation at 10⁻⁶ mbar.

For the WOLED, a film of PVK-h mixed with poly(9,9-dioctylfluorenyl-2,7-diyil) end-capped with N,N-bis(4-methylphenyl)-4-aniline (PFO, American Dye Source), with ratio 52% PVK-h:48% PFO by mass, was then spin-coated from toluene solution (15 mg mL⁻¹) onto the PEDOT:PSS-covered ITO substrates. Samples were successively annealed at 100 °C for 30 minutes. Then the second layer, comprised of 40% PVK-l:20% PBD, 40% FPFCl by mass, was then spin-coated from CH₂Cl₂ solution (2 mg mL⁻¹). Finally calcium (10 nm layer) and aluminium (60 nm) were deposited by thermal vacuum evaporation at 10⁻⁶ mbar.

Electroluminescence (EL) and photoluminescence (PL) spectra of the devices were recorded using a liquid-nitrogen-cooled CCD camera in conjunction with a monochromator (Spex 270M). The light source for PL was a monochromated xenon lamp. The spectra were corrected for the instrument response functions. Current–voltage (I–V) device characterization was performed with a Keithley 2602 source meter combined with a calibrated photodiode. External quantum efficiency (EQE) was calculated by measuring the light emitted in the forward direction with Lambertian source assumption.²² Device preparation and characterization was performed under a N₂ atmosphere inside a M-Braun glovebox system. CCT was evaluated according to ref. 23. Luminance (L), luminance efficiency (LE) and power efficiency (PE) were calculated using formulae from ref. 24.

AFM investigations were performed with a NT-MDT NTEGRA instrument in non-contact mode under ambient conditions.

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**Chart 3**

Numbering system for ¹H NMR assignment of complexes.

8.04 (2H, td, H²), 7.73 (2H, d, J(¹⁹Pt) 6, H¹), 7.36 (2H, ddd, H¹), 7.33 (2H, s, H⁶), 2.42 (3H, s, CH₃). ¹³C NMR (400 MHz, CD₂Cl₂): δ = 152.3, 140.2, 124.9, 123.1, 119.1, 22.1 (CH₃) (quaternary not detected). IR (v/cm⁻¹): for SCN⁻, 2096 and 2089 in CHCl₃ and Nujol, respectively. MS FAB⁺: 440 (M – NCS)⁺; MS MALDI-TOF (with LiCl): 505 (M + Li)⁺. Anal. Calcd for C₁₈H₁₃N₃PtS: C, 43.37; H, 2.63; N, 8.43%. Found: C, 43.57; H, 2.70; N, 8.52%.
Results and discussion

Synthesis of ligands and complexes

The ligand 5-fluoro-1,3-di(2-pyridyl)benzene was easily obtained by a Stille reaction of 1,3-dibromo-5-fluorobenzene with 2-(tri-n-butylstannyl)pyridine (molar ratio 1 : 2.5) in the presence of lithium chloride and bis(triphenyolphosphate)-palladium(II) chloride as the catalyst, in toluene at reflux under N₂. Further reaction with K₂PtCl₄ in refluxing CH₃CN/H₂O (v/v) affords FPtCl. Reaction of the known complex MePtCP with NaSCN gives the new isothiocyanate Pt(II) complex, MePtNCS. The bonding of the SCN⁻ ligand to the Pt ion through the N atom is confirmed by the strong, sharp peak at 2096 cm⁻¹ in CHCl₃ (2089 cm⁻¹ in Nujol) a value typical of the ν(SCN) stretching mode of metal N-bonded isothiocyanate ligands (see Experimental section and Scheme 1).

Photophysical and electrochemical properties in solution

Photophysical and electrochemical data for FPtCl, MePtNCS and MePtCl in solution are reported in Table 1. Their electronic absorption and photoluminescence spectra in diluted dichloromethane are complex, we attribute the intense absorption bands at λ < 300 nm to π→π* transitions localized on the ligands, while those between 320 nm and 450 nm correspond to transitions of mixed charge-transfer/ligand-centred character. A very weak band appears at around 504 nm, due to the formally forbidden S₀→S₁ transition facilitated by the high spin–orbit coupling (2089 cm⁻¹ compared to the unsubstituted complex HPtCl). The PL spectrum of complex MePtCl is essentially identical to that of MePtCl. It displays a vibrationally structured spectrum, ν ≈ 1300 cm⁻¹, with the 0,0 vibrational component at 504 ± 1 nm, representing a red-shift of 13 nm compared to the unsubstituted complex HPtCl. This contrasts with the effect of fluorine atoms at the positions meta to the Pt ion in m-F₂PtCl (structures in Chart 1), as opposed to the para-disposed F atom in FPtCl. In m-F₂PtCl, the emission is blue-shifted by 20 nm compared to HPtCl.

These contrasting effects of the F atoms can be understood in terms of the frontier orbitals in such complexes. Thus, time-dependent density functional theory calculations on HPtCl have revealed that the T₁ state has predominantly HOMO–LUMO character. The HOMO is based primarily on the aryld ring, the metal ion and the chloride co-ligand, whilst the LUMO is predominantly localised on the pyridyl rings. The inductive electron-withdrawing effect of F atoms, irrespective of whether they be meta or para to the metal, should lower the energy of both HOMO and LUMO, as found, for example, with iridium (III) complexes containing related fluoride-substituted terdentate ligands. However, when the F atom is para to the metal as in FPtCl, the mesomeric electron-donating effect of F through the π orbitals will slightly attenuate the inductive effect. In contrast, there is no such possibility in m-F₂PtCl, in which the F atoms are meta to the metal, so the HOMO is expected to drop further in energy in this case. On the other hand, the extent to which the LUMO is stabilised in the latter complex may be expected to be slightly less than in the former, owing to the pyridyl rings (on which the LUMO is localised) being ortho to the F atoms, and therefore subject to the opposing mesomeric effect. These combined effects—which are represented schematically in Fig. S6 of the ESI—lead to the net trend in energies: FPtCl < HPtCl < m-F₂PtCl.

Meanwhile, the change in the monomeric co-ligand from chloride in MePtCl to isothiocyanate in MePtNCS is seen to have essentially no significant effect, probably reflecting the rather small participation of the co-ligand in such complexes, and the similar positions of the NCS and Cl ligands in the spectrochemical series.

The relatively long lifetimes of several microseconds (Table 1) are typical of the phosphorescence of complexes of this class. The quantum yields of FPtCl and MePtNCS in degassed dichloromethane at room temperature were 0.47 and 0.60, comparable with those of MePtCl (see Table 1) and other complexes of this type. That such high quantum yields arise despite the relatively long lifetimes (which are indicative of relatively low radiative rate constants) indicates that non-radiative decay processes in these complexes are particularly ineffective, probably reflecting the high rigidity of the system and high ligand-field strength associated with the N⁶C⁶N-coordinated ligand. The radiative k_r and non-radiative Σk_n decay constants can be estimated from the lifetimes and quantum yields, assuming that the emitting state is formed with unitary efficiency (see footnote to Table 1). The rates of both processes are smaller than those typically found for more commonly studied iridium(m)-based OLED emitters, for example, but the fact that the values are comparable to one another leads to the PL quantum yields of around 0.5.

The influence of increasing concentration on the absorption and PL spectra of FPtCl in dichloromethane is shown in Fig. 1 for example, but the fact that the values are comparable to one another leads to the PL quantum yields of around 0.5.

The influence of increasing concentration on the absorption and PL spectra of FPtCl in dichloromethane is shown in Fig. 1 (b). While the shape of the absorption spectrum does not change, the PL spectra of all three complexes at higher concentrations reveal the appearance of a broad, structureless band at longer wavelengths, due to emission from an excimer, as observed for other members of this family of complexes. The associated self-quenching rate constants of the monomer emission, k_Q, are of...
Table 1  Photophysical and electrochemical parameters at 298 K in dichloromethane

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption λ_{max}/nm (ε/L mol^{-1} cm^{-1})</th>
<th>Emission λ_{max}/nm</th>
<th>Φ_{em}</th>
<th>r_{0} [1/μs] degassed (aerated)</th>
<th>k_{Q}/[10^{10}] M^{-1} s^{-1}</th>
<th>k_{Q}/[10^{10}] M^{-1} s^{-1}</th>
<th>E_{ox}/V</th>
<th>E_{red}/V</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MePtCl</td>
<td>335 (5710), 381 (6900), 412 (6780), 460 (190), 495 (130)</td>
<td>505, 539, 578</td>
<td>0.68</td>
<td>7.8 (0.3)</td>
<td>3.3</td>
<td>16</td>
<td>8.7 (4.1)</td>
<td>-2.27</td>
<td>0.36</td>
<td>-5.16</td>
</tr>
<tr>
<td>FPtCl</td>
<td>322 (6170), 377 (7740), 422 (8270), 486 (312)</td>
<td>504, 542, 580</td>
<td>0.47</td>
<td>6.3 (0.6)</td>
<td>5.6</td>
<td>7.4</td>
<td>7.4 (8.5)</td>
<td>-2.19</td>
<td>0.56</td>
<td>-5.36</td>
</tr>
<tr>
<td>MePtNCS</td>
<td>333 (4760), 357 (2800), 382 (3890), 406 (3820), 499 (188)</td>
<td>501, 533, 580</td>
<td>0.60</td>
<td>8.6 (0.7)</td>
<td>8.9</td>
<td>6.2</td>
<td>7.0 (4.6)</td>
<td>-2.21</td>
<td>0.24</td>
<td>-5.04</td>
</tr>
</tbody>
</table>

* Estimates of radiative k_{r} and non-radiative (Σk_{nr}, in parenthesis) decay constants are made as follows: k_{r} = Φ_{em}/r_{0}. Σk_{nr} = (1/r_{0}) − k_{r}. All processes were electrochemically irreversible, hence E_{ox} and E_{red} refer to peak potentials of oxidation and reduction, respectively; values are reported relative to a ferrocene/ferrocene (Fc+/Fc) redox couple used as an internal reference (E_{Fc}/Fc = +0.42 V vs. saturated calomel electrode SCE); at 298 K, in the presence of 0.1 M [Bu₄N][PF₆] as the supporting electrolyte, scan rate 200 mV s^{-1}. Energies of the highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO as calculated from the redox potentials. Data from ref. 5 and 6. Data from the present work.

a Luminescence quantum yield in degassed solution. b t_{0} is the lifetime at infinite dilution and k_{Q} the self-quenching rate constant, determined from the intercept and slope, respectively, of a plot of the measured emission decay rate constant against concentration. c Bimolecular rate constant for quenching by molecular oxygen, estimated using the lifetimes in degassed and air-equilibrated solutions, and taking [O2] = 2.2 × 10^{-3} M in CH₂Cl₂ at 1 atm pressure of air. d Estimates of radiative s_{r} and non-radiative (Σk_{nr}, in parenthesis) decay constants are made as follows: k_{r} = Φ_{em}/r_{0}. Σk_{nr} = (1/r_{0}) − k_{r}. All processes were electrochemically irreversible, hence E_{ox} and E_{red} refer to peak potentials of oxidation and reduction, respectively; values are reported relative to a ferrocene/ferrocene (Fc+/Fc) redox couple used as an internal reference (E_{Fc}/Fc = +0.42 V vs. saturated calomel electrode SCE); at 298 K, in the presence of 0.1 M [Bu₄N][PF₆] as the supporting electrolyte, scan rate 200 mV s^{-1}. Energies of the highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO as calculated from the redox potentials. Data from ref. 5 and 6. Data from the present work.

a comparable magnitude in each case, as are the bimolecular oxygen quenching rate constants, which show only small differences amongst the three complexes.

A comparison of the cyclic voltammetry data for complexes FPtCl, MePtNCS and MePtCl is given in Table 1. As expected for the higher electron withdrawing effect of F with respect to a methyl group, FPtCl is more easily reduced and more difficult to oxidize with respect to MePtCl. The first oxidation and reduction potentials can be used to estimate the HOMO and LUMO energy levels by means of equations E_{HOMO} (eV) = -(E_{ox} + 4.8) and E_{LUMO} (eV) = -(E_{red} + 4.8), which involve the use of the internal ferrocene standard value of -4.8 eV with respect to the vacuum level. The HOMO–LUMO gap is 2.45, 2.63, and 2.75 eV for MePtNCS, MePtCl, and FPtCl, respectively (Table 1).

Spin-coated OLEDs using new Pt(II) complexes

Using complexes FPtCl and MePtNCS as phosphorescent dopants, we fabricated solution-processed multilayer electroluminescent devices with a typical composition of 100% PVK-h in the first layer and 65% PVK-l:30% PBD:5% Pt complex in the emissive layer. The PEDOT:PSS layer, which is standardly used in polymer based OLEDs, is considered as a part of the substrate. The chemical structures of the organic materials used are shown in Chart 4. The multilayer OLED approach has many advantages in comparison to single layer devices, but usually requires the use of thermal evaporation which is generally an expensive process. Here, we combined the simplicity of the low-cost spin-coating technique with the advantages of multilayer architecture. A PVK-h layer, directly deposited on PEDOT:PSS, plays a multiple role in our OLEDs. This polymer is well known as a hole transporting material, and additionally is able to block the radiative excitons from direct quenching by PEDOT:PSS, removing a non-radiative decay channel introduced by this latter material. High molecular weight PVK-h (M_w = 10^6 g mol^{-1}), with diminished solubility upon thermal treatment, allows us to fabricate multilayer architecture by successive solution deposition, as verified by AFM investigation. The top (emissive) layer is composed of the platinum complex dispersed in a host matrix comprised of PVK-l:PBD. PBD is an electron-transporting material, introduced in order to improve the balance between charges.

The EL spectra of OLEDs prepared in this way are shown in Fig. 2 together with HOMO and LUMO levels of used materials, and device performance data are compiled in Table 2. The EL spectra are similar to the corresponding PL spectra of dilute solutions. However, an additional long-wavelength component is evident, around 600 nm, superimposed on the emission of the complex and increasing in intensity in the order FPtCl < MePtCl < MePtNCS. This low-energy emission is attributed to a PVK electron emitter, rather than to complex luminescence. The order of increasing intensity of the electron can be explained by the charge-trapping properties of the complexes.

If a complex does not trap the charge carriers efficiently, they can travel into the host more freely and the probability that they will recombine on PVK-l:PBD matrix increases.

Poorer trapping ability of a complex will lead to a more intense electron band being observed. In contrast, efficient trapping on a complex emitting centre will favour high EQE of devices and also should decrease leakage current. In the present case, FPtCl doped in PVK-l:PBD host matrix has the best trapping abilities while MePtNCS has the poorest (see inset in Fig. 2), according to the trend in electron intensities, and indeed this order is reflected in the EQE values in Table 2.
It is remarkable that the EQE values obtained for the various devices (Table 2), although unsurprisingly lower than those obtained for OLEDs based on complexes of the same family built by evaporation techniques, are one order of magnitude higher than for a recently reported OLED based on a substituted 4,4'-stilbenoid N^C^N platinum(II), also built by the spin-coating technique.  

![Fig. 1](image1.png)  

**Fig. 1** (a) Absorption and PL spectra of FPtCl, MePtNCS and MePtCl in dichloromethane; (b) Absorption and PL spectra of FPtCl in dichloromethane at concentrations 4.15 × 10^{-5} M (solid line), 2.075 × 10^{-4} M (dashed line), 4.15 × 10^{-4} M (circles), and 2.075 × 10^{-3} M (squares).

![Chart 4](image2.png)  

**Chart 4** Molecular structures of PBD, PVK and PFO.

![Fig. 2](image3.png)  

**Fig. 2** EL spectra of PVK-h/65% PVK-l:30% PBD:5% Pt complex diodes: FPtCl (solid), MePtCl (dash), MePtNCS (circle). In the inset HOMO and LUMO levels of used materials are shown.

![Table 2](image4.png)  

**Table 2** Electroluminescence performance of devices based on FPtCl, MePtNCS and MePtCl with the device structure PVK-h/65% PVK-l:30% PBD:5% Pt complex

<table>
<thead>
<tr>
<th></th>
<th>FPtCl</th>
<th>MePtNCS</th>
<th>MePtCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_{on}/V</td>
<td>12</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>EQE (%)</td>
<td>0.28</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>L/ cd m^{-2}</td>
<td>91</td>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>LE/ cd A^{-1}</td>
<td>0.94</td>
<td>0.62</td>
<td>0.68</td>
</tr>
<tr>
<td>PE/ lm W^{-1}</td>
<td>0.18</td>
<td>0.11</td>
<td>0.097</td>
</tr>
<tr>
<td>L_{max}/ cd m^{-2}</td>
<td>755</td>
<td>161</td>
<td>195</td>
</tr>
<tr>
<td>CIE (x, y)</td>
<td>(0.32, 0.61)</td>
<td>(0.39, 0.55)</td>
<td>(0.37, 0.58)</td>
</tr>
</tbody>
</table>

a Maximum external quantum efficiency at the forward direction. b At a maximum external quantum efficiency.

![Fig. 3](image5.png)  

**Fig. 3** EL spectra of single layer devices with different concentrations of FPtCl dispersed in PVK-h:PBD matrix.
By increasing the concentration of the FPtCl complex in the PVK-l:PBD matrix, we were able to tune the emission of the single layer devices (in this case without PVK-h bottom layer) from green to red (see Fig. 3), owing to the appearance of an excimer band centred at 700 nm. For the diode with the composition 40% PVK-l:20% PBD:40% FPtCl, balanced green and red emission was observed, and the same composition was therefore employed for the construction of a multilayer WOLED, as described in the next section.

**WOLED**

In this section, we present a multilayer WOLED prepared using a simple solution-processing technique. As diodes with a bottom layer consisting of PVK-h or PVK-h:PBD did not emit in the blue region, we introduced PFO (Chart 4) as an efficient blue emitter.\(^{34}\) The selected structure for the device was: ITO/PEDOT:PSS/52% PVK-h:48% PFO/40% PVK-l:20% PBD:40% FPtCl/Ca/Al. A schematic diagram illustrating the HOMO and LUMO levels of each of the materials used is shown in Fig. 4. The bottom layer consists of a mixture of PVK-h and PFO, and serves as a blue-emitting and hole-transporting layer. PFO is known to provide good hole mobility.\(^{35}\) Additionally, the HOMO level of PVK-h is lower compared to the PEDOT:PSS level, which facilitates injection of holes from the anode to PFO. The top layer is composed of the platinum complex FPtCl dispersed in PVK-l:PBD matrix. FPtCl is an effective hole-trapping centre (Fig. 4), collecting holes that arrive from the bottom layer and preventing their migration towards the cathode, automatically decreasing leakage current.

Fig. 5(a) shows the EL spectrum of the device, with Commission Internationale de l’Eclairage (CIE) coordinates \(x = 0.28, y = 0.35\) and CCT equal to 8145 K, CRI equal 74 and EQE of about \(4 \times 10^{-4}\%\). The shoulder around 400–420 nm is most likely due to the residual emission of PFO \(\alpha\)-phase,\(^{36–38}\) almost eliminated after thermal treatment of the PVK-h:PFO layer (see Experimental part). The sharp peaks at 438 nm and 465 nm are due to the vibrational \(0 \rightarrow 0\) and \(0 \rightarrow 1\) components of the emission of the newly formed \(\beta\) phase PFO. In our diode, the emitted blue light can exit the device immediately or after reflection from the cathode. In the second case, partially absorbed light is used to excite the Pt(II) complex by an energy transfer process,\(^{39,40}\) enabled by the overlap of the absorption of the complex and blue emitter’s emission spectrum (Fig. 5(b)). Two-colour emission was obtained with a high concentration of FPtCl in the top layer. Bands at 509 nm and 544 nm, together with a shoulder at 590 nm, originate from the phosphorescence of single FPtCl molecules. The tail at low energy is due to complex excimer emission. The lower intensity of the excimer band observed in this WOLED in comparison to the single-emitting-layer device with the same concentration of the complex, described in the previous section, is probably caused by the partial dissolution of the bottom layer during preparation on the second film, as confirmed by AFM investigation. In this process, the effective dispersion of the complex at the interface is increased, changing the balance between accessible monomer and dimer states. The combined EL from the two layers creates white light, since green-red light emitted from the top layer is not absorbed by polymers in the bottom layer and thus exits the device freely, along with blue light from the bottom layer.

The corresponding PL spectrum of the device is also shown in Fig. 5(a). A difference in the green-red region can be noticed, with reversed intensities of monomer and excimer emission...
compared to EL. Such a discrepancy between EL and PL originates from the different mechanisms responsible for the exciton and excimer generation in two types of luminescence. In PL, energy transfer is the dominant phenomenon, while in EL, the charge trapping properties of the system are the main contributor. PFO emission recorded in EL suggests that electrons may enter into the bottom layer and bind there some holes on emitting centres localized on PFO. In devices with a bottom layer consisting of PVK-h or PVK-h:PBD, blue EL is not observed. This is due to the good transporting properties of both materials, preventing efficient trapping of charge carriers on emitting centres, and to their emission quantum yields being only modest.41 On the other hand, PFO is an efficient emitter and is able to trap electrons in the PFO/PVK-h system in the bottom layer (see Fig. 4).

Conclusions

We have synthesized two phosphorescent green-emitting N,C,N-coordinated platinum(II) complexes, FpCl and MePtNCs, and we have compared their properties with those of MePtCl. Photophysical measurements revealed that, in addition to green emission, the complexes also display an excimer band centred around 700 nm. The emitters were tested in simple-to-build, solution-processable OLEDs as dopants in a PVK:PBD matrix. The obtained external quantum efficiencies were ten times higher than for a recently reported OLED based on a substituted 4,4'-stilbened N,C,N platinum(II), also built by the spin-coating technique. The more promising FpCl, thanks to its double emission color, was used as a single dopant in solution processed multilayer WOLED. Green and red light originated from the monomer and excimer emission of the complex, respectively, while blue came from the bottom layer. Application of highly concentrated dopant displaying excimer emission allows the device structure to be simplified, as energy transfer between multiple dopants is reduced. Additionally we combined the facility of the low-cost spin-coating technique with the advantages of multilayer architecture. The study reveals that the Pt(N,C,N) class of emitters are amenable to the production of solution-processed OLEDs, in addition to the vacuum-sublimed systems mostly investigated to date for such compounds, which are more costly and therefore less suitable for large areas.

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20 PDF applied in bottom and top layers has the same optical and electrical properties, and differs only in molecular weight.