Dalton Transactions

PAPER

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Dalton Trans., 2013, 42, 13612

Received 5th February 2013, Accepted 9th July 2013 DOI: 10.1039/c3dt50364j

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Introduction

Phosphorescent platinum(π) complexes have gained increasing attention over the last few decades owing to their employment in chemosensors,¹ colorimetric oxygen sensors,² photovoltaics³ and electrophosphorescent devices.⁴ Phosphorescent transition-metal complexes⁵ are suitable for application in light-emitting devices⁶ due to the strong spin–orbit coupling induced by the heavy metal ion.⁷ This effect allows harvesting of both triplet and singlet excitons that are electrogenerated in a ratio of 3:1 according to simple spin statistics, leading to potentially achievable internal quantum efficiencies up to 100%.⁸ Most of the common triplet emitters are based on octahedral iridium(π)⁹ or square planar platinum(π)¹⁰ complexes. The latter often tends to form aggregates or excimers, causing shifts in the emission spectra.¹¹ Conventionally, this

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Photophysical properties and OLED performance of light-emitting platinum(II) complexes†

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The synthesis, photophysical properties and application as emitters in solution-processed multi-layer organic light-emitting diodes (OLEDs) of a series of blue-green to red light-emitting phosphorescent platinum(II) complexes are reported. These complexes consist of phenylisoquinoline, substituted phenyl-pyridines or tetrahydroquinolines as C^N cyclometalating ligands and dipivaloylmethane as an ancillary ligand. Depending on both the structure of the C^N cyclometalating ligands and the dopant concentration in the matrix, these platinum(II) complexes exhibit different aggregation tendencies. This property affects the photoluminescence spectra of the investigated compounds and colour-stability of the fabricated OLEDs. Using the blue-green to yellow-green emitting complexes, the best results were obtained with the 2-(4-trifluoromethylphenyl)-5,6,7,8-tetrahydroquinoline based platinum(II) complex. A maximum luminous efficiency of 4.88 cd A⁻¹ and a power efficiency of 4.65 lm W⁻¹, respectively, were achieved. Employing the red emitting phenylisoquinoline based complex as an emitter, colour-stable and efficient (4.71 cd A⁻¹, 5.12 lm W⁻¹) devices were obtained.

behaviour is ascribed to platinum–platinum or π - π interactions.¹² Although this property can be used to fabricate white light-emitting OLEDs¹³ with just one phosphorescent complex, it is not suitable for applications where colour purity is needed.

In the present investigation we discuss besides the photophysical and electro-optical characterisation of the platinum(π) compounds the synthesis of phenylisoquinoline^{14,15} and tetrahydroquinoline-type¹⁶ C^N ligands, leading to the blue-green through yellow-green to red light-emitting cyclometalated complexes, using dipivaloylmethane (dpmH) as an ancillary ligand. Contrary to the phenylisoquinoline ligand, which is received by a Suzuki coupling reaction,^{14,15,17} the tetrahydroquinoline ligands were obtained *via* a Mannich-reaction.¹⁶ The platinum(π) complexes were embedded in a matrix to study the optical properties in the solid state and were employed in solution-processed multi-layer phosphorescent OLEDs. Depending on both the structure of the ligands and the complex concentration, fabricated devices displayed dissimilar colour stability.

Results and discussion

Synthesis

The phenylisoquinoline ligand **L1** was synthesized from 1-chloroisoquinoline and phenylboronic acid using a

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 $[\]dagger Electronic supplementary information (ESI) available. See DOI: 10.1039/ c3dt50364j$



Scheme 1 Synthetic route of phenylisoquinoline ligand L1 obtained in 69% yield.

conventional palladium-catalyzed Suzuki cross-coupling reaction (Scheme 1).^{14,15,17}

The ligands 2-phenylpyridine (L2) and 2,4-difluorophenylpyridine (L3) were purchased. To prepare the tetrahydroquinoline based C^N ligands L4–L7, 1-morpholinocyclohexene and the corresponding Mannich-bases that were synthesized through aminomethylation of the respective phenylketone derivatives with N,N-dimethylmethylene-iminium-chloride were used to form the 1,5-diketones. These compounds were subsequently cyclised using NH₂OH·HCl in order to obtain the target C^N ligands L4–L7 (Scheme 2). The ligands L1–L7 were readily soluble in solvents of medium polarity.

Upon receipt of the ligands L1–L7 the platinum(II) complexes 1–7 were prepared in a two-step synthesis.^{13,16,18} The μ -chloro-bridged precursor dimers were synthesized by heating K₂PtCl₄ and the corresponding C^N ligand in a mixture of 2-ethoxyethanol and water (3/1) at 80 °C for 16 h and were obtained in yields between 66% and 84%. Subsequently, these dimers were heated with dpmH and Na₂CO₃ in 2-ethoxyethanol at 100 °C for 3–6 h to prepare the heteroleptic platinum(II) complexes 1–7 in yields of 55% to 84% (Scheme 3). The crude platinum(II) compounds 1–7 were chromatographically purified over silica gel. The structures of the synthesized emitters 1–7 are illustrated in Fig. 1.

The complexes 1–7 were well soluble in solvents of medium polarity. The molecular ions $[M + H]^+$ (M = neutral complexes) were observed in the ESI mass spectra at m/z 583.2 (1), 533.2 (2), 569.2 (3), 587.2 (4), 655.2 (5), 605.2 (6) and 666.1 (7). The ¹H- and ¹³C-NMR spectra show the olefinic proton at 5.83–5.90 ppm and the characteristic splitting of the signals for ^tBu from the dpmH at 1.20–1.40 ppm. For 3, 5 and 6 ¹⁹F-NMR confirmed the aromatic fluorine and the aromatic



Scheme 2 Synthesis of 5,6,7,8-tetrahydroquinoline derivatives L4–L7. Yield of L4 98%, L5 54%, L6 50%, and L7 46%. R₁ = -H (L4), -CF₃ (L5), -F (L6), -Br (L7).



Scheme 3 Synthetic route of the ligands **1–7** *via* μ -chloro-bridged precursor dimers **1–7** to the platinum(1) complexes **1–7**.



Fig. 1 Molecular structures of the platinum(II) complexes 1–7.

 $-CF_3$ groups with the expected resonances. The complexes 1–7 were additionally characterized by FT-IR spectroscopy. The purity of the synthesized emitters 1–7 was confirmed by elemental analysis.

Optical properties in solution and electrochemical properties

In the following, we classify the investigated complexes in different categories: complex **1** differs from the greenish complexes **2–7** through its red emission colour and excellent colour-stability. The greenish phenylpyridine and tetrahydroquinoline based complexes **2–7** can be divided into two groups: the compounds **3** and **6** that were fluorinated at the aromatic system of the C^N cyclometalating ligand and show a strong tendency to form aggregates and the non-fluorinated complexes **2**, **4**, **5** and **7** that show a less pronounced aggregate formation.

The UV-vis absorption and emission data of the complexes in CH_2Cl_2 are summarized in Table 1, Fig. 2 and 3. The extinction coefficients of 6500–52 500 are in the same range as the values of similar compounds previously reported in the literature.^{16,19–22} The intense absorption for all complexes at 240–340 nm is assigned to spin-allowed intraligand transitions

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Table 1 UV-vis absorption, emission maxima of **1–7** in CH₂Cl₂ ($c = 1 \times 10^{-5}$ mol L⁻¹), PLQY (φ) in *n*-hexane or in CHCl₃ ($c = 1 \times 10^{-5}$ mol L⁻¹) at room temperature and redox properties (scan rate: 100 V s⁻¹, Pt-disk-electrode, CH₂Cl₂, TBAPF₆)

Complex	UV-vis [nm] $\{\varepsilon (dm^3 mol^{-1} cm^{-1})\}$	$\lambda_{\text{max-em.}} [\text{nm}]$	φ	$E_{1/2}^{\mathrm{Red}}\left[\mathrm{V} ight]$
1	255 (43 000), 274 (38 300),	597,639	0.15^{d}	-2.18^{a}
	345 (17 800), 408 (13 900)	,		
2	253 (52 600), 280 (37 300),	486, 518	0.19^{e}	-2.52^{b}
	315 (17 700), 367 (11 000)			
3	249 (46 900), 309 (15 900),	468, 498	0.09^{d}	-2.42^{b}
	323 (16 600), 364 (10 600)			
4	250 (27 600), 278 (25 100),	498, 528	0.08^{e}	-2.75^{c}
	317 (11 700), 367 (6500)			
5	251 (36 600), 280 (34 700),	501, 537	0.07^{d}	-2.37^{a}
	317 (15 800), 332 (15 500),			
	381 (8800)			
6	251 (26 000), 274 (25 900),	489, 523	0.05^{d}	-2.58^{c}
	330 (9500), 361 (7400)			
7	254 (39 000), 280 (40 600),	501, 535	0.10^{d}	-2.46°
	335 (16 100), 372 (10 200)			

^{*a*} Roughly reversible. ^{*b*} Partially reversible. ^{*c*} Irreversible. ^{*d*} In *n*-hexane. ^{*e*} In CHCl₃.



Fig. 2 UV-vis spectra of (a) 1–3 and (b) 4–7 dissolved in CH_2CI_2 (c = 1 × 10⁻⁵ mol L⁻¹) recorded at room temperature.

 $(\pi \to \pi^*)$ that show similar absorption bands in this region.^{23,24} The metal-to-ligand charge transfer (MLCT) and ligand-toligand charge transfer (LLCT) transitions are located between 350 nm and 450 nm.¹⁸

The emission of 1–7 is ascribed to a mixed ³LC-MLCT state and the specific effects of the substituent at the C^N ligands



Fig. 3 Photoluminescence spectra of (a) **1–3** and (b) **4–7** dissolved in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol L⁻¹) recorded at room temperature.

can directly be seen in the emission spectra (Fig. 3) that exhibit a characteristic pattern, which reveals two maxima and ranges from the green-blue to the red spectral region. The higher the electronegativity of the substituent, the larger is the resulting blue-shift of emission. In contrast, the higher the aromatic conjugation of the C^N ligand, the larger is the observed red-shift in the photoluminescence (PL) spectra.

The photoluminescence quantum yields (PLQY) of 1–7 in CHCl₃ or *n*-hexane vary between 0.05 and 0.19 (Table 1) and are in the same range as that for structurally related complexes reported in the literature.¹⁸

The electrochemical properties of the platinum(II) complexes were investigated by cyclic voltammetry (CV) using the redox couple ferrocene/ferrocenium as a reference. The CVmeasurements showed that the oxidation of 1-7 is completely irreversible. It is reported that this is due to a nucleophilic attack of the solvent on the platinum centre of the complex, since the oxidation takes place at the metal centre, whereas the reduction occurs at the C^N ligand.¹⁸ The best results concerning reversibility of the reduction of 1-7 were obtained using a fast scan rate of 100 V s^{-1} . The reduction was roughly reversible for 1 and 5, partially reversible for 2 and 3 and irreversible for 4, 6 and 7. The position of the reduction wave ranges from -2.18 V for 1 to -2.75 V for 4. The estimation of the LUMO of the electron transporting material OXD-7 is based on a measurement with a scan rate of 100 mV s^{-1} . Regardless of the reduced reversibility of the values of 1-7,

which were obtained under identical measurement conditions, we use them to discuss the capability of these compounds as traps for electrons. The reduction potential for both scan rates and the estimated LUMOs are summarized in Table S1 in the ESI.[†]

Optical properties in the solid state

Due to the significant influence of the emitter concentration on the electroluminescence spectra of the devices based on 2–6, the effect of the dopant concentration on the photoluminescence of films containing various amounts of these complexes was investigated. To be consistent with OLED measurements, a mixture of poly(vinyl)carbazole (PVK) and 1,3-bis(*N*,*N*-*t*-butyl-phenyl)-1,3,4-oxadiazole (OXD-7) served as the host and equimolar amounts of **1–6** were embedded into the matrix. For comparison, all photoluminescence data of the films are summarized in Table S2[†] and the PL spectra of the samples containing equimolar amounts of **2–6** are shown in Fig. S1 in the ESI.[†]

Unlike octahedral six-fold coordinated osmium(π), ruthenium(π) or iridium(π) complexes,^{6,25} four-fold coordinated platinum(π) complexes¹⁶ exhibit a square planar coordination geometry.²⁶ For this reason, platinum(π) compounds with sterically undemanding substituents are basically flat. This allows intermolecular interactions that are mandatory for aggregates like dimers²⁷ in the ground state or excimers^{27,28} in the excited state. The tendency to aggregate depends on various parameters such as the steric demand of the substituents^{13,29,30} and the concentration of the compound in the matrix or solution.²⁷

For low dopant concentrations, the PL spectra of the films are comparable to the emission spectra of the complexes in solution. However, as the concentration of the dopants 2–6 in the matrix is raised, an increase of the intensity of the energetically low-lying emission band is observed. In contrast, the PL spectrum of the red emitting complex 1 is not affected by the dopant concentration. The degree of this concentrationinduced red-shift of the emission colour depends highly on the substituent at the C^N cyclometalating ligands and is most distinct for the fluorinated compounds 3 and 6, whereas it is much less pronounced for the non-fluorinated greenish emitting compounds 2, 4 and 5.

To illustrate the dissimilar concentration dependence of the PL spectra of films containing the fluorinated and nonfluorinated greenish complexes, exemplary PL spectra of films containing various concentrations of the non-fluorinated compound **2** and fluorinated compound **3** are depicted in Fig. 4.

The comparison of the concentration-dependent PL spectra of films doped with the fluorinated compounds 3 and 6 (Fig. S1[†]) shows that the concentration-induced red-shift is less pronounced for 6. The higher steric demand of ligand L6 compared to L3 might be one possible reason for this behaviour.

By cooling films containing various amounts of 3 and 6, which show the most pronounced concentration-dependent



Fig. 4 Photoluminescence spectra of films consisting of PVK/OXD-7 doped with various equimolar amounts of complexes (a) **2** and (b) **3** recorded 720 ns after excitation with a laser pulse and normalized to the highest energy emission peak. Arrows indicate the effect of increasing dopant concentration.

shift of the emission colour, down to 80 K, this red-shift could be significantly reduced for both compounds (Fig. S2⁺).

Based on the literature^{12,13,26–28} we assume that the increase in intensity of the low-energy emission band of the greenish complexes 2-6 arises from aggregates and is caused by dimer and/or excimer emission.

Investigations on platinum(II) complexes with pyridylazolate based chelates showed that cyclometalated complexes with very asymmetric electronic properties tend to display a strong tendency for the formation of aggregates.³¹ Considering that the complexes 2–7 consist of an electron poor pyridine fragment and a comparable electron rich substituted phenyl fragment, this effect might also contribute to the observed dimer or excimer emission.

Time-resolved PL measurements of a film doped with 39.1 wt% 3 showed that at least for this compound, the redshift can be assigned to excimer emission. The intensity of the monomer signal ($\lambda_{max} = 470$ nm) decays after the excitation pulse, whereas the intensity of the excimer emission ($\lambda_{max} =$ 592 nm) increases (Fig. 5). These data are in good agreement with the literature, since the excimer emission of a structurally related complex with a sterically less demanding ancillary ligand is reported to be located at 598 nm.²⁷

According to these results, the aggregate emission, which can result from dimers in the ground state or excimers in the excited state, cannot be absolutely prevented by introducing a Paper



Fig. 5 Photoluminescence spectra of a film containing 39.1 wt% 3 in a PVK/ OXD-7 matrix 20 ns and 708 ns after excitation, recorded at 295 K.

dpmH as an ancillary ligand. Nevertheless, the concentration induced red-shift is less pronounced compared to platinum(II) complexes with identical or structurally related C^N cyclometalating ligands and sterically less demanding ancillary ligands.¹³ Moreover, the introduction of dpmH enhances the solubility of the complexes in non-polar solvents compared to compounds with simple acetylacetones as ancillary ligands.

The photoluminescence decay of the monomer emission of 1-6 was observed at the highest energy emission wavelength and exhibits a mono-exponential kinetic for the red light-emitting complex 1 and a bi-exponential kinetic for 2-6. Due to self-quenching an increase of the dopant concentration causes a significant decrease of the (averaged) photoluminescence lifetime.

Depending on the concentration, the photoluminescence lifetime of **1** varies between 4.49 and 3.94 μ s and the average lifetime of the **2–6** monomers between 1.49 and 5.56 μ s (Table S2[†]).

The PLQY of **1–6** in a PVK/OXD-7 matrix varies depending on the dopant and its concentration between 0.69 for **2** and 0.07 for **6** (Table S2[†]). Due to concentration quenching, high amounts of the greenish platinum(II) complexes cause a decrease in PLQY. For the red platinum dopant **1** only a slight concentration-induced decrease in PLQY was observed in the investigated concentration range.

OLED performance

To investigate the electroluminescence properties of the platinum(II) emitters **1–7** various equimolar amounts were blended in a PVK/OXD-7 matrix (70 wt% PVK, 30 wt% OXD-7). The electron transporting material OXD-7 was used in order to improve the bipolar charge-transport properties of the host. The chemical structure of the materials used for device fabrication is given in Fig. S3.[†] The devices comprise the following layout:

ITO//PEDOT:PSS (32 nm)//QUPD (18 nm)//OTPD (10 nm)// PVK+OXD-7+ 1–7 (30 nm)//TPBi (30 nm)//CsF (3 nm)//Al (120 nm) (Fig. S4†).

The HOMO and LUMO levels of the materials used in the devices are schematically depicted in Fig. S5 in the ESI.[†] As can be seen in Fig. S5,[†] all dopants apart from 4 and 6 act as

traps for electrons, due to the energy difference to the lowest unoccupied molecule orbital (LUMO) of the electron transporting component OXD-7. The LUMOs of **4** and **6** correspond, within the limits of accuracy of the CV measurement, nearly to the LUMO of OXD-7.

The two hole transporting layers consisting of cross-linked QUPD and OTPD were used to enhance the hole injection and for their electron blocking capabilities. To improve the charge balance and hence for better positioning of the recombination zone, an additional 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene (TPBi) layer was introduced, acting as an exciton/ hole blocking and electron transport layer. The OLED containing 8.9 wt% of the red-emitting dopant **1** achieved a high maximum luminous efficiency and power efficiency of 4.71 cd A⁻¹ and 5.12 lm W⁻¹, respectively.

For OLEDs employing a structurally related emitter based on phenylisoquinoline, efficiencies up to 1.88 cd A^{-1} are reported.³² Possibly our more complex device architecture might contribute to the enhanced performance. However, more efficient vacuum-processed OLEDs based on red emitting platinum(II) complexes with efficiencies up to 24.6 cd A^{-1} have been reported.³³

Using the non-fluorinated greenish light-emitting dopants 2, 4, 5 and 7, the highest maximum luminous efficiency of 4.88 cd A⁻¹ and power efficiency of 4.65 lm W⁻¹ were achieved with devices containing 10.0 wt% 5. However, the devices based on complex 2 showed a slightly better performance at higher device brightness. In the literature, OLEDs using structurally related emitters based on non-fluorinated 2-phenylpyridines are described that achieved efficiencies up to 1.5 cd A⁻¹.²⁹ It is possible that also our more complicated device architecture might result in higher efficiency. For vacuum-processed OLEDs employing a complex structurally related to 2 chelating a 2-pyridylhexafluoropropoxide as ancillary ligand efficiencies up to 13.5 cd A⁻¹ were achieved.³⁴ For structurally non-related greenish platinum(II) complexes efficiencies up to 50.0 cd A⁻¹ have been reported.³⁵ However, the comparison of solution- and vacuum-processed devices is difficult, since we cannot exclude aggregate formation of the Pt(II) complexes during the spin coating process.

The performance data (Table S3[†]) show that for all investigated platinum(II) emitters, apart from 7, the optimum dopant concentration corresponds to an equimolar amount of 10.0 wt% 5. The luminance-, current-, and voltage-characteristics of the devices with emitter concentrations that correspond to an equimolar amount of 10.0 wt% of complex 5 are depicted and summarized in Fig. S6[†] and Table 2, whereas the external quantum efficiencies (EQE) of these devices are summarized in Table S4.[†] The most efficient OLED using dopant 7 as an emitter contained only 5.1 wt% of this complex. Indeed, complex 7 is not suitable as an emitter in OLEDs since only a very low maximum device brightness of 248 cd m⁻² was achieved. One possible explanation for the poor performance of the devices that employed 7 as an emitter could be the quenching of luminance due to heat generation during device operation, since previous investigations showed that 7 displays

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Table 2	Performance of t	ne investigated OLEDs	s containing equimolar	amounts of 1-7
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Comp	lex [wt%]	PL emission colour	CIE-coordinates @ 500 cd m ⁻² [X/Y]	Max. luminous efficiency [cd A ⁻¹]	Max. power efficiency [lm W ⁻¹]	Luminous efficiency (a) 500 cd m ⁻² [cd A ⁻¹] (a) [V]
1	8.9	Red	0.63/0.36	4.71	5.12	1.98 @ 6.6
2	8.1	Green	0.27/0.51	4.52	3.73	3.52 (a) 5.8
3	8.7	Blue-green	0.31/0.42	1.71	1.57	0.95 @ 7.5
4	9.0	Green	0.32/0.47	3.09	3.02	1.86 (a) 6.7
5	10.0	Yellow-green	0.34/0.51	4.88	4.65	2.39 (a) 6.6
6	9.2	Green	0.34/0.44	2.08	2.25	0.95 (a) 7.0
7	10.2	Yellow-green	_	1.66	1.31	_

a strong temperature quenching effect.^{16,36} Furthermore, the irreversibility of the reduction of 7 that was observed during the CV measurement indicates that this complex might degrade during device operation.

Employing the fluorinated compounds 3 and 6 as emitters, comparable efficiencies for both emitters were obtained: 1.71 cd A^{-1} for 3 and 2.08 cd A^{-1} for 6.

Similar to the PL spectra of the dopants 2-6, the Electroluminescence (EL) spectra are also sensitive to the emitter concentration and, moreover, to the driving voltage. An increase in dopant concentration as well as an increase in driving voltage contributes to the growth of the low-energy emission. In analogy to the PL, this red-shift is most pronounced for the fluorinated compounds 3 and 6, whereas this effect is less distinct for the devices based on the non-fluorinated complexes 2, 4 and 5. The concentration-dependent shift in the EL spectra is ascribed to an increase in aggregate emission. We assume that the current dependence might be ascribed to the formation of excimers, since an increase in driving voltage causes an increase in the number of excited platinum(II) complexes that can potentially form excimers. It is also possible that other effects like field dependent shifts of the recombination zone contribute to the growth of the low-energy emission band. To illustrate the dissimilar current- and concentrationdependent EL spectra of devices based on the fluorinated and non-fluorinated greenish emitters, the corresponding EL spectra of devices based on 2 and 3 are shown in Fig. 6 and 7, exemplarily. The detailed spectra of all dopants are shown in Fig. S7 and S8 in the ESI.[†]

The OLEDs based on the red light-emitting complex **1** exhibit excellent colour-stability even at various emitter concentrations and driving voltages.

Conclusions

The synthesis of the platinum(II) complexes 1–7 and their photo- and electroluminescence properties are reported. The red-shifts in the PL and EL spectra of the greenish phenylpyridine and tetrahydroquinoline based compounds 2–6 are ascribed to aggregate formation in the ground or excited state. Time-resolved measurements of films consisting of 39.1 wt% 3



Fig. 6 Electroluminescence spectra (normalized to the highest energy emission peak) of devices with various concentrations of (a) **2** and (b) **3** recorded at a current density of 20 mA cm⁻². Arrows indicate the effect of increasing dopant concentration.

doped in PVK/OXD-7 showed that, at least for this complex, the growth of the low-energy emission band can be assigned to the formation of excimers. The degree of the observed red-shifts depends on the substituent at the C^N ligands and the concentration of the complex in the matrix, whereas this effect is most distinct for the fluorinated compounds **3** and **6**.

Using the non-fluorinated greenish complexes the most efficient and colour-stable device was obtained using compound 5 as an emitter. A maximum luminous efficiency of 4.88 cd A^{-1} and a power efficiency of 4.65 lm W^{-1} were achieved. The most efficient devices using the fluorinated compounds as emitters were based on 6, whereas a maximum



Fig. 7 Electroluminescence spectra (normalized to the highest energy emission peak) of devices containing (a) 8.1 wt% **2** and (b) 8.7 wt% **3** driving at various voltages. Arrows indicate the effect of increasing voltage.

luminous efficiency of 2.08 cd A^{-1} and a power efficiency of 2.25 lm W^{-1} were achieved.

As opposed to the phenylpyridine and tetrahydroquinoline based complexes 2–6, the red-emitting complex 1 did not show any concentration induced red-shift of the emission colour and the application of this dopant in OLEDs results in colour stable and efficient (4.71 cd A^{-1} , 5.12 lm W^{-1}) devices.

We showed that it was possible to enhance the device performance compared to structurally related red and green emitting platinum(π) complexes with sterically less demanding ancillary ligands previously used in OLEDs with a simpler device architecture.^{29,32} However, it is possible to fabricate significantly more efficient green and red light-emitting OLEDs through vapour deposition that employs other classes of platinum(π) complexes as emitters.^{33,35}

Experimental section

General remarks

All reagents were used as purchased from commercial suppliers without further purification. All reactions were carried out by using standard Schlenk techniques under an atmosphere of dry argon. Solvents were used as purchased without further purification. ¹H-NMR and ¹³C-NMR spectra were recorded using a BRUKER ARX 125, ARX 200 and ARX 500 as well as using a

BRUKER III AVANCE 600; ¹⁹F-NMR spectra were recorded using a BRUKER AVANCE 400. Chemical shifts were referenced relative to the internal standard tetramethylsilane (Me₄Si) in CDCl₃ solutions. For ${}^{1}H$ (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), ¹³C-NMR data, J values are given in hertz (Hz). Mass spectrometry was carried out using electron impact (EI, 70 eV) and electrospray ionization (ESI) techniques on a Finnigan MAT 8230 and a Bruker Daltonics MICROTOF instrument, respectively. Fourier transform infrared (FT-IR) spectra were recorded using a JASCO FT/IR-4200 as well as a Nicolet 510 P FT-IR spectrometer. Elemental analysis (EA) was measured using a Perkin Elmer 240 B and a HEKAtech EuroEA 3000 (CHNS) setup, correspondingly. UV-vis spectra were measured with a JASCO V-550 UV-vis spectrometer (1 cm cuvettes) at concentrations of 1×10^{-5} mol L⁻¹. The emission spectra were performed using a CARY Eclipse fluorescence spectrophotometer at a concentration of 1×10^{-5} mol L⁻¹. Chromatography: separations were carried out using Geduran Si 60 (0.063-0.200 mm). Thin layer chromatography (TLC) was done on Analtech uniplate silica gel GF plates (500 micron, 20 × 20 cm) and developed with (*n*-hexane–ethyl acetate: 10/3).

Methyleneiminiumchloride,^{37,38} the enamine³⁹ and 1-morpholinocyclohexene,⁴⁰ phenylisoquinoline,^{14,15} as well as the dimers^{13,16,41} **D1** and **D2** and complexes^{13,16,41} **1** and **2** were synthesized conforming to partly modified literature procedures. Besides phenylisoquinoline, **D1** and complex **1**, all synthetic procedures can be found in the ESI.[†]

Photoluminescence quantum yields were measured with a Hamamatsu Photonics Absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C10027 photonic multichannel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics Ltd., Shizuoka, Japan).

Fabrication of OLEDs

The OLEDs were prepared on pre-cleaned, UV-ozone-treated ITO-coated glass substrates. A layer of 32 nm PEDOT:PSS (Clevios P, AI4083, Heraeus) was spin coated onto the substrates under clean-room conditions and baked at 120 °C for 3 minutes to remove residual water. To deposit the hole-transporting layers QUPD⁴² (N,N'-bis(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexyloxyphenyl]-N,N'-bis(4-methoxyphenyl)biphenyl-4,4'-diamine)) and OTPD⁴² (N,N'-bis(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexylphenyl]-N,N'-diphenyl-4,4'-diamine)) were dissolved in toluene and 1.5 wt% of the photoinitiator OPPI (4-octyloxydiphenyliodonium-hexafluoroantimonate, Organica Feinchemie) was added. After spin coating, the films were exposed to UV-light (360 nm) for 10 s, annealed at 110 °C for 90 s to promote crosslinking and non-cross-linked residues were removed with THF. The platinum(II) emitters 1-7 were mixed with PVK (poly(vinyl)carbazole, Sigma Aldrich) and OXD-7 (1,3-bis(N,N-t-butylphenyl)-1,3,4-oxadiazole, Sensient) in a THF solution, whereas the PVK: OXD-7-ratio was 70 wt% PVK and 30 wt% OXD-7. TPBi (1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene, Sensient) was evaporated in a K. J. Lesker spectros evaporator at a rate of 0.2 Å s⁻¹ at a base pressure of 2×10^{-7} mbar. The cathode, consisting of 3 nm CsF (Alfa Aesar) and 120 nm of Al (Alfa Aesar), was deposited by thermal evaporation in a Leybold high-vacuum chamber at a base pressure of 2×10^{-6} mbar. The structures of all the used materials are shown in Fig. S3.[†]

The current density-voltage-luminescence (J-V-L) characteristics were measured with a source-measure unit (Keithley 2400) and a calibrated photodiode under an argon atmosphere. The EL spectra were measured with a calibrated CCD spectrometer (Ocean Optics).

Time-resolved spectroscopy

A detailed description of the experimental setup for the timeresolved photoluminescence measurements can be found elsewhere.⁴³ In short, the photoluminescence (PL) was excited with the third harmonic (355 nm) of a Nd:YAG laser operated at a repetition rate of 10 Hz. The PL was collected and focused onto the entrance slit of the monochromator and detected by an intensified gateable CCD camera. The spectral resolution was set to 2 nm. The instrument response function is about 1.7 ns. Time resolved measurements have been done at 295 K under a continuous flow of nitrogen.

Electrochemistry

The cyclic voltammetry was carried out in a one-compartment cell fitted with a Luggin capillary under an argon atmosphere at room temperature using an Ecochemie Autolab PGSTAT302N as a potentiostat/galvanostat. For all measurements a Pt-disk electrode was used as a working electrode and an Ag-wire, finally calibrated with the redox-system ferrocene/ferrocenium, as a counter electrode. CH_2Cl_2 was used as a solvent and tetrabutyl-ammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte (0.1 M). The denoted potentials are the arithmetic average of the peak potential of corresponding waves of the semi-derivatives of the current-density-curves.

Synthesis of phenylisoquinoline^{14,15}



1-Chloroisoquinoline (3 g, 18.303 mmol) was stirred with tetrakis(triphenylphosphine)palladium(0) (1.057 g, 0.915 mmol) in toluene (90 mL) at room temperature. Phenylboronic acid (2.232 g, 18.303 mmol) in ethanol (60 mL) and aqueous saturated Na₂CO₃ solution (60 mL) were added. The mixture was heated under reflux for 2 h, cooled down to room temperature and poured into 2 N HCl (150 mL). The crude product was collected with dichloromethane (3 × 100 mL). The combined organic layers were washed with a saturated NaHCO₃ solution (75 mL) and water (15 mL), dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexaneethylacetate 10/3 as an eluent). Yield: 2.606 g (69%) colourless powder. $\nu_{\text{max}}/\text{cm}^{-1}$ 3047, 1678, 1578, 1562, 1398, 1117, 863, 834, 807, 783, 648. ¹H-NMR (600 MHz; CDCl₃) δ = 7.51–7.58^{h,i,j,d} (m, 4H), 7.67–7.68^b (d, ³J = 5.7 Hz, 1H), 7.70–7.74^{e,g,k} (m, 3H), 7.90–7.91^f (d, ³J = 8.3 Hz, 1H), 8.13–8.14^c (d, ³J = 8.3 Hz, 1H), 8.64–8.65^a (d, ³J = 5.7 Hz, 1H). ¹³C-NMR (100 MHz; CDCl₃): δ = 119.9, 126.7, 127.0, 127.2, 127.6, 128.4, 128.6, 129.9, 130.2, 136.8, 139.6, 142.3. *m/z* (ESI): 206.1 (M⁺ – C₁₅H₁₁N requires 205.09). C₁₅H₁₁N (205.09): calcd C 87.77, H

General procedure for the platinum (11)- μ -dichloro-bridged dimers ^{13,16,41}

5.40, N 6.82; found C 87.76, H 5.38, N 6.88.

 K_2PtCl_4 and the corresponding ligand HC^N (2.2 equiv.) were stirred in a Schlenk flask for 16 h at 80 °C in a mixture of 2ethoxyethanol and water (3:1). After cooling down to room temperature, the respective dimeric complexes were precipitated after the addition of water (20 mL), filtered, and washed with water and ethanol. The precursor complexes were dried under reduced pressure.

Dimer D1.^{14,15} Phenylisoquinoline (205 mg, 1 mmol) and K_2 PtCl₄ (189 mg, 0.455 mmol). Yield: 130 mg (66%) ochre powder.

General procedure for the platinum(II) complexes^{13,16,41}

The respective dimer complexes were stirred in a Schlenk flask with dipivaloylmethane (3 equiv.) and Na₂CO₃ (10 equiv.) in 2ethoxyethanol at 80 °C for 3–6 h. The crude complexes were collected by filtration and purified using thin layer chromatography (*n*-hexane–ethyl acetate) or column chromatography (CH₂Cl₂–*n*-hexane) and re-crystallized, correspondingly.

Complex 1.



Dimer D1 (128 mg, 0.147 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (81 mg, 0.441 mmol) and Na₂CO₃ (156 mg, 1.470 mmol). Purification by column chromatography on silica gel (CH₂Cl₂–*n*-hexane 1/3 as an eluent) yielded red crystals (95 mg, 55%). (Found C 53.56, H 5.13, N 2.56; C₂₆H₂₉NO₂Pt requires C 53.60, H 5.02, N 2.40); ν_{max} /cm⁻¹ 3049, 2953, 2925, 2899, 2858, 2368, 2346, 2314, 1579, 1544, 1541, 1523, 1496, 1477, 1452, 1436, 1420, 1391, 1382, 1353, 1312, 1277, 1245, 12223, 1188, 1175, 1153, 1140, 1099, 1057, 1038; ¹H-NMR (600 MHz; acetone-d₆; Me₄Si): δ = 1.33^m (s, 9H, CH₃), 1.34^k (s, 9H, CH₃), 5.96^l (s, 1H, CH), 7.16–7.21^h (m, 1H, ArH), 7.24ⁱ (td, J = 7.3, 1.3 Hz, 1H, ArH), 7.78^b (d, J = 6.5 Hz, 1H, ArH), 7.84^{dij} (ddd, J = 15.2, 7.7, 1.3 Hz, 2H, ArH), 7.92^e (ddd, J = 8.1, 7.0, 0.9 Hz, 1H, ArH), 8.08^f (d, J = 8.1 Hz, 1H, ArH), 8.22^g (d, J = 7.3 Hz, 1H, ArH), 9.04^c (d, J = 8.7 Hz, 1H, ArH), 9.05–9.12^a (m, 1H, ArH); ¹³C-NMR (100 MHz; acetone-d₆; Me₄Si): δ = 29.3, 29.6, 42.4, 42.9, 94.6, 121.7, 124.6, 127.4, 127.5, 129.4, 130.1, 130.5, 130.6, 132.4 133.2, 139.1, 140.5, 144.8, 147.8, 170.0, 193.9, 195.4 ppm; C 53.60, H 5.02, N 2.40; *m/z* (ESI): 583.2 (M⁺ – C₂₆H₂₉NO₂Pt requires 582.18); $\lambda_{max-absorption}$ (CH₂Cl₂)/nm 255 (ε /dm³ mol⁻¹ cm⁻¹ 43 000), 274 (38 300), 345 (17 800), 408 (13 900); $\lambda_{max-emission}$ (CH₂Cl₂)/nm 597, 639.

Acknowledgements

The authors acknowledge the DFG (Deutsche Forschungsgemeinschaft) for financially supporting this work with grant applications ME1246/18-1, HE5577/2-1, HO3911/3-1, HO3911/ 6-1 and RI449/9-1. K.M., D.H. and D.K. acknowledge funding by the State of Northrhine-Westfalia and the Europäischer Fonds für Regionale Entwicklung (EFRE) through the PROTECT project, which is part of the Centre of Organic Production Technologies COPT.NRW. E.H. acknowledges Prof. Ullrich Scherf for granting access to the tools of the Macromolecular Chemistry at the University of Wuppertal (BUW).

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