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# Sterically Hindered Luminescent Pt<sup>II</sup>–Phosphite Complexes for Electroluminescent Devices

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**Abstract:** Pt<sup>II</sup> complexes with one bulky, sterically demanding, tertiary phosphite ancillary ligand and a coordinating chromophore are herein presented. The phosphite ligand, tris(2,4-di-*tert*-butylphenyl) acts as a bidentate ligand coordinating the platinum ion through the central phosphorus atom and a cyclometalating carbon atom of one of the substituents. The two free phenoxy moieties lie above and below the coordination plane, leading to steric hindrance that avoids aggregation and provides solubility in organic solvents. The other two coordination sites on the central metal ion are occupied by a chromophoric ligand, which is

1. Introduction

For current applications of organic light-emitting diodes (OLEDs) in lighting and display technologies, not only the efficiency (photoluminescence quantum yield,  $\Phi_{\rm em}$ ) of the emitters are of major interest, but also their processability. Low reaction yields or issues in the purification process, which are related to a low solubility, lead to big losses of material. In fact, after the usual purification steps (column chromatography,

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	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405839.

responsible for the energy of the luminescent excited state. This separation of functions, on the two coordinated ligands, allows the use of a wider range of luminophores with good luminescent properties, maintaining the control of the intermolecular interactions with the non-chromophoric ligand. Based on this approach we were able to achieve a bright deep blue emission ( $\lambda = 444$  nm,  $\Phi_{em} = 0.38$ ) from a complex with a tailored ligand, which was then used for the fabrication of an electroluminescent device. In addition commercially available luminophores were also employed to synthesize green emitters.

crystallization), which precede the final sublimation step, it is necessary that the complexes have a purity of at least 99.5 %.<sup>[1]</sup> Besides the incidental intrinsic thermal instability of the emitter that might lead to decomposition upon heating, a low purity can further complicate the sublimation process.<sup>[2-4]</sup> For example, impurities can react with the material, thereby decreasing the yield of the sublimation process, and/or forming a glass phase that impedes the transition into the gas phase.<sup>[5]</sup> Intrinsic properties of the emitters can also restrict their processability. In the case of  $\mathsf{Pt}^{II}$  complexes, strong  $\pi$ -stacking and metalmetal interactions lead to the formation of aggregates that can inhibit or complicate the sublimation process.<sup>[6]</sup> The attachment of long aliphatic chains on the ligand(s) can improve the solubility, thus favoring the purification process, but at the same time can be disadvantageous to the evaporation process because it increases the sublimation temperature. In order to overcome this temperature rise, the use of fluorinated side chains can be advantageous.<sup>[7]</sup>

To address all these issues, we have designed and synthesized new  $Pt^{II}$  complexes, which are based on precursors already known for  $Pd^{II}$  and  $Pt^{II}$  in the field of homogenous catalysis.<sup>[8]</sup> As the use of organometallic species in catalysis requires good solubility, the introduction of similar ligands should lead to compounds that can be purified effectively by column chromatography. In addition, the peripheral substituents need to be relatively bulky to avoid aggregation. Thus, we have chosen a tris(2,4-di-*tert*-butylphenyl) phosphite as the bulky and spectroscopically transparent ligand for platinum(II). Indeed this chelate ligand offers three main advantages: 1) it has six *tert*butyl groups that provide a good solubility in a variety of sol-

Chem. Eur. J. **2015**, 21, 1–13

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vents, ranging from hexane to dichloromethane and dimethylsulphoxide, 2) the tert-butyl groups cannot scramble around the complex, which would isolate it from the surrounding matrix, and 3) the two uncoordinated phenyl groups on the sides inhibit the aggregation of the complexes, thereby allowing a straightforward processing of the material, without changes in the emission color at different concentrations.<sup>[9,10]</sup> All these features do not hinder the OLED performance because in our design the excessive shielding, which could result in a less efficient charge injection into the complex, is counterbalanced by charge hopping onto the emitter through the phenyl groups of the phosphite ligand. After having addressed the choice of the phosphite ligand, we have investigated two classes of luminophores for the design of our emitter. On the one hand, we have used tailored pyridine-azoles possessing a large HOMO-LUMO band gap to investigate the potential of our complexes as blue emitters. On the other hand, we have also tested commercially available phenoxy-azoles, yielding green emitters in only two synthetic steps, therefore making these complexes appealing for large-scale production.

## 2. Results and Discussion

## 2.1 Synthesis

The luminophoric ancillary ligands presented herein are divided into three groups (Figure 1). One group is constituted of pyridine-pyrazoles (HL1, HL2), a second one includes pyridine-1,2,4-triazoles (HL3, HL4), and the last one is constituted of phenoxy-benzoxazoles and phenoxy-benzothiazoles (HL5, HL6).

The last two ligands in the series are commercially available, and only the synthesis of the first two groups is therefore described. The synthetic steps towards the pyridine-pyrazoles are shown in Scheme 1. The intermediate diketone is formed in an aldol reaction starting from methylpicolinate and an appropriately substituted methyl ketone, either trifluoromethyl methyl ketone or adamatyl methyl ketone, to yield the ligand precursors PL1 or PL2, respectively. These intermediates are then further reacted with hydrazine in a ring-closure reaction to give the pyrazole-based ligands HL1 and HL2.

The synthetic procedure leading to the pyridine-1,2,4-triazole-based ligands consists of more reaction steps. In the first

step, 2-cyanopyridine is reacted with hydrazine to yield the amidrazone precursor PL3, as shown in Scheme 2. This is then reacted with either adamantanecarbonyl chloride to yield PL4, or with tolylcarbonyl chloride to yield PL5. These intermediates are then further reacted in a condensation reaction to yield the 1,2,4-triazole derivatives HL3 and HL4.



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Figure 1. Structures of the ancillary ligands used for the preparation of Pt<sup>II</sup> complexes.



Scheme 1. Synthetic route for the preparation of the pyridine-pyrazolebased ligands HL1 and HL2 via the ligand precursors PL1 and PL2.

plexes is the chloro-bridged dimer P1, which can be easily obtained from tris(2,4-di-tert-butylphenyl) phosphite and potassium tetrachloroplatinate(II) by following a known procedure,<sup>[8,11]</sup> as schematically shown in Scheme 3. The dimer is a mixture of cis and trans isomers (only the trans isomer is shown in Scheme 3 for clarity). This mixture of the cis and trans precursors can be treated in analogy to the  $[(ppy)_2 lr(\mu-Cl)_2 lr(ppy)_2]$ (ppy=4-pyrrolidinopyridine) dimer known in the synthesis of iridium(III) emitters.[12]

The phosphite dimer P1 can be reacted with a number of different ligands under mild conditions (Scheme 4). For our complexes the P1 precursor is reacted overnight with a suitable



Scheme 2. Synthetic route for the preparation of the 1,2,4-triazole-based ligands HL3 and HL4 via the ligand precursors PL3-PL5

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Scheme 3. Preparation of the chloro-bridged Pt<sup>II</sup> phosphite dimer P1.



Scheme 4. Generalized preparation of complexes 1–6 from the  $\mathsf{Pt}^{II}$  phosphite dimer P1.

chromophoric chelate at 50 °C in a 1:1 mixture of dichloromethane and methanol to yield the desired product, which can be purified through column chromatography on silica by using a dichloromethane/cyclohexane mixture as eluent. The final product can then be re-crystallized from hexane, in which the solubility of the complexes is generally much lower.

As mentioned above, there is no need for the chromophoric ligands to fulfill other requirements than providing highly emissive excited states. Therefore, the possibility to tune the



color with commercially available ligands was investigated, in addition to the use of tailored ligands (Figure 2).

Generally, when pyridine-azole ligands are employed, the LUMO is mainly localized on the pyridine ring, and the HOMO spread over the metal center and the five-membered ring.<sup>[13]</sup> Therefore, the design strategy was aiming at tuning the energy level of the HOMO of the compounds by changing the substitution pattern on the five-membered ring on the one hand, and by varying its nitrogen content on the other. At the same time, the pyridine ring was left unchanged to keep the LUMO unaffected. The phosphite ancillary ligand is expected to play a minor role, both for the HOMO and for the LUMO. Furthermore, we used the commercially available ligands HL5 and HL6 to prove the potential of the design strategy, even with non-optimized ligands. These chromophores have already been employed on Ir<sup>III</sup> and Sc<sup>III</sup> complexes in the past, showing reasonable properties ( $\Phi_{em}$  up to 0.29).<sup>[14,15]</sup> The resulting complexes were characterized by high-resolution mass spectrometry, <sup>1</sup>H NMR spectroscopy, and elemental analysis (see the Experimental Section).

#### 2.2 Structure analysis

To confirm the structure of the two kinds of families, the coordination geometry of the complexes were studied by X-ray diffraction or by <sup>1</sup>H NOESY spectroscopy. Complex **6** provided suitable single crystals for X-ray analysis by slow diffusion of hexane into a saturated solution of the complex in dichloromethane. The crystal structure of complex **6**, as shown in Figure 3, clearly indicates that the phenoxy moiety of the ancillary ligand (O1) is coordinated *trans* to the phosphorus atom of the phosphite ligand (P1), whereas the nitrogen atom of the benzothiazole moiety (N16) is coordinated *trans* to the carbon bond of the C^P ligand (C27). From the bond lengths, the

trans effect of the cyclometalating carbon on the phosphite ligand can be inferred.[16, 17] Whereas the Pt-carbon bond is 2.007(9) Å long, reflecting the strong  $\sigma$ -donating and  $\pi$ -accepting character of the cyclometalating phenyl moiety, the Pt-nitrogen bond is longer (2.109(8) Å). The same is valid for the second pair of bonds trans to each other. The phenoxy oxygen atom as a stronger  $\sigma$  donor is closer to the metal center (2.065(7) Å) than the phosphorus atom (2.151(2) Å).

In addition, it should be noted that the two moieties of the ancillary ligand are twisted against each other by almost 31°, which breaks the conjugation of their aromatic systems. This feature, which is also re-

Figure 2. Structures of complexes 1–6.

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**Figure 3.** ORTEP representation of the crystal structure of complex **6**, with the ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

flected in the absorption spectra (see below), renders them as separate units. This coordination is also assumed to be valid for compound **5**, which only differs by one non-coordinating heteroatom, namely oxygen instead of sulfur, from complex **6**.

The structural characterization is more difficult for the compounds based on pyridine-pyrazoles and pyridine-triazoles, that is, complexes 1-4, due to the lack of single crystals suitable for X-ray diffraction. From this series, compound 2 has been chosen for the detailed structural characterization by NMR spectroscopy, because it has a bulky adamantyl substituent and the highest number of protons, which facilitates the observation of the nuclear Overhauser effect (NOE). With complex 2 we have performed a <sup>1</sup>H NOESY experiment to assess the relative spatial arrangement of the ligands by analyzing the proton couplings between the two classes of ligands attached to the Pt<sup>II</sup> centre. The assignment of the protons is shown in Figure S1 in the Supporting Information. The signals necessary for the structure determination correspond to protons 1 and 10 in the aromatic region. Proton 1 is located on the cyclometalating phenyl ring in ortho position to the coordinating carbon atom and therefore shows the typical shoulders, due to coupling with the Pt<sup>II</sup> center. The proton corresponding to signal 10 is placed ortho to the nitrogen atom on the pyridine ring of the ancillary ligand. According to this assignment, the NOESY experiment has been performed, and is shown in Figure S2 in the Supporting Information. It is worth noticing that there is no correlation between those two protons, because there is no positive signal of proton 10 when proton 1 is pulsed (bottom spectrum in the aromatic region, Figure S2 in the Supporting Information). The same is true when proton 10 is pulsed, showing no correlation with proton 1. This means that the structure shown in the inset in Figure S1 in the Supporting Information corresponds to the actual isomer. Furthermore, if the configuration was the opposite, one could have expected a correlation between one of the adamantyl signals (protons 15, 16, and 17) and one of the tert-butyl groups on the free phenoxy moieties, which is not the case. In fact, a weak correlation between the group of protons 15 and the outer tert-butyl group on the cyclometalated phenyl ring (proton 14) is observed (Figure S2, bottom, in the Supporting Information). These results therefore suggest a coordination of the pyridine trans to the cyclometalating carbon atom, and the five-membered ring trans to the phosphorus atom, respectively. This seems plausible, when considering that two negatively charged coordination sites located opposite to each other on the coordination plane would have a strongly destabilizing character, and are not favored according to the trans effect described above.<sup>[16,17]</sup> These considerations are supported by previously reported data, describing the coordination of electronwithdrawing ligands cis to the phosphor atoms of the phosphite.[8]

#### 2.3 Absorption spectroscopy and frontier orbitals

The absorption profiles of the complexes **1** and **2** are shown in Figure 4, and the spectra of complexes **3** and **4** are given in Figure 5. They all contain pyridine–pyrazole or pyridine–1,2,4-triazole ligands and show two sets of bands, one between  $\lambda =$ 



Figure 4. Room-temperature absorption spectra of the pyrazole-based complexes 1 (solid line) and 2 (dotted line) in dichloromethane. The spectrum of tris(2,4-di-*tert*-butylphenyl) phosphite is shown for comparison (not to scale, diamonds).



**Figure 5.** Room-temperature absorption spectra of the 1,2,4-triazole-based complexes **3** (solid line) and **4** (dotted line) in dichloromethane. The spectrum of tris(2,4-di-*tert*-butylphenyl) phosphite is shown for comparison (not to scale, diamonds).

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 $\lambda_{max}(em)$ , 77 K [nm]<sup>[d]</sup>

440 (1), 462 (0.63), 472 (0.77),

495 (0.44) 471 (1), 502 (0.91), 530 (0.48)

453 (0.83), 485 (1), 512 (0.63)

469 (0.94), 501 (1), 530 (0.56)

463 (0.98), 495 (1)

518 (1), 555 (0.81)

(relative intensity)

250–300 nm and another one between  $\lambda = 300-350$  nm (Figures 4 and 5).

The bands at higher energy, ( $\varepsilon \approx 14 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), can be assigned to ligand-centered (LC)  $\pi - \pi^*$  transitions involving the phenyl moieties of the phosphite ligand overlapped with transitions taking place on the five-member heterocycle of the chromophoric ligand. These assignments are corroborated by the comparison with the absorption spectrum of the free phosphite ligand, which is also shown in Figures 4-6. Furthermore, the relatively intense band ( $\varepsilon \approx 30 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in the same region for compound 4 is attributed to  $\pi$ - $\pi$ \* transitions on the tolyl substituent to the triazole ring. The bands in

2-Me-THF frozen matrices at 77 K.

 $\lambda_{max}(abs)$  [nm]

 $(\varepsilon \times 10^{-3} [m^{-1} cm^{-1}])^{[a,b]}$ 

269 (11.74), 312 (6.33), 334 (7.26)

280 (15.39), 326 (10.93)

259 (15.68), 282 (11.03, sh), 343 (8.65)

270 (30.23), 347 (7.48)

290 (17.34), 299 (15.65, sh),

393 (8.83)

267 (19.13), 293 (12.25), 413 (6.20)

Complex

1

2

3

4

5

6

422 nm.

to an intraligand charge-transfer (ILCT) mixed with a metal-toligand charge-transfer (MLCT) transition (phenoxy+Pt→benzoxazole/benzothiazole), and appears red shifted upon replacement of oxygen by sulfur. On the other hand, the bands below  $\lambda =$  350 nm are assigned to LC  $\pi \rightarrow \pi^*$  transitions on the benzazole moiety and the phenyl rings of the phosphite ligand. This assignment is confirmed by the red shift of the band at approximately  $\lambda = 300$  nm to about  $\lambda = 320$  nm by going from compound 5 to complex 6, thereby reflecting the influence of the heteroatom on the transitions in this region (Figure 6). A summary of the photophysical data in solution is reported in Tables 1 and 2.

Table 1. Photophysical data for solutions of compounds 1-6 in dichloromethane at room temperature and in

[a] In dichloromethane. [b] "sh" denotes a shoulder. [c]  $\lambda_{exc} = 337-431$  nm. [d] In 2-Me-THF. [e]  $\lambda_{exc} = 333-431$  nm.

lated deactivation rate constants.

Complex

 $\lambda_{max}(em)$ , RT [nm]

(relative intensity)<sup>[a-c]</sup>

n.d.

490 (0.78), 513 (1)

474 (0.8), 499 (1)

492 (0,76, sh), 516 (1)

494 (1), 515 (0.96)

546 (0.96), 564 (1)

the range  $\lambda = 330-340$  nm are assigned to  $\pi$ - $\pi$ \* transitions ( $\varepsilon$  $\approx$  11 × 10<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) on the pyridine ring. The ligand-centered nature of the transitions is confirmed by the absence of energy shifts in the excitation spectra obtained in poly(methyl methacrylate) (PMMA) or in frozen matrices (see below) as compared to fluid solution.

For compounds 5 and 6, both containing phenoxy-benzazole derivatives as chromophores, the main absorption bands  $\lambda = 300 - 400 \text{ nm}$ around are clearly red shifted upon the replacement of oxygen by sulfur (Figure 6). The change of the

heteroatom significantly affects the frontier orbitals (i.e., the HOMO-LUMO gap), as clearly mirrored in the emission spectra, as well as in the electrochemical data (see below).

We assume that the HOMO is localized on the  $Pt^{\parallel}$  center. and mixed with the electron-rich and strongly  $\sigma$ -donating phenoxy group, which is confirmed by the invariability of the HOMO values obtained by electrochemical analysis and ultraviolet photoelectron spectroscopy (UPS). On the other hand, the LUMO is stabilized upon substitution of the oxygen with sulfur. Therefore, the transition around  $\lambda = 400$  nm is assigned



Figure 6. Room-temperature absorption spectra of complexes 5 (solid line) and 6 (dotted line) in dichloromethane. The spectrum of tris(2,4-di-tert-butylphenyl) phosphite is shown for comparison (not to scale, diamonds).

$C_1 C_1 C_1 C_1 C_1 C_1 C_1 C_1 C_1 C_1 $
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 $\Phi_{\rm em}$  deaer. k<sub>nr</sub>  $[\times \, 10^{-4} \, s^{-1}]^{[f]}$  $[\times 10^{-4} s^{-1}]^{[f]}$ [%]<sup>[a-c]</sup> [µs]<sup>[a,d]</sup> [µs]<sup>[e]</sup> 1 n.d. n.d. 45.8 n.d. n.d. 2 2.8 1.88 67.5 1.49 51.7 3 0.2 0.14 702.8 37.1 1.41 4 2.5 1.49 47.1 65.4 1.68 5 2.63 68.9 1.52 36.5 4 6 5 3.86 63 1.30 24.6

 $\tau$  RT. deaer.

Table 2. Photophysical data for complexes 1-6, together with the calcu-

τ, 77 K

k.

[a] In dichloromethane. [b]  $\lambda_{exc}$  = 337–430 nm. [c] Quantum yields were measured in an integrating sphere system. [d] Monitored at  $\lambda_{em} = 484$  (2), 512 (3), 515 (4), 492 (5), and 564 nm (6), [e] Monitored at  $\lambda_{m} = 470$  (1), 454 (2), 471 (3), 501 (4), 495 (5), and 518 nm (6).

#### 2.4 Emission properties

The emission spectra of compounds 2-4 in degassed dichloromethane solutions are shown in Figure 7. Compound 1 does not show any emission in solution at room temperature, but it was possible to detect its luminescence in thin films or in frozen glassy matrices (see below). Complex 3 shows a skyblue emission with a maximum at  $\lambda = 474$  nm and a vibrational progression peaking at  $\lambda = 499$  nm. Complex **2** has a similar profile with a less pronounced shoulder at  $\lambda = 490$  nm and a second band at  $\lambda = 513$  nm. The shoulder is almost not rec-



Figure 7. Emission spectra of complexes 2 (solid line), 3 (dotted line), and 4 (dashed line) in degassed dichloromethane.  $\lambda_{exc}$  = 337 (2), 345 (3), and 348 nm (4).

ognizable in the spectrum of compound **4**, leading to a single emission peak at  $\lambda = 516$  nm. The behavior of complexes **5** and **6** is somewhat different, showing a broad, essentially unstructured emission in the green, with a maximum at  $\lambda = 494$  and at 542 nm for complexes **5** and **6**, respectively (see Figure 8). Both emission spectra show weak vibrational shoulders peaking at  $\lambda = 515$  and 564 nm for compounds **5** and **6**, respectively.



Figure 8. Emission spectra of complexes 5 (solid line) and 6 (dotted line) in degassed dichloromethane.  $\lambda_{exc}$  = 380 (5) and 430 nm (6).

The emission spectra of the diazole- and triazole-based complexes are rather structured and present characteristic vibrational progressions of triplet ligand-centered emissive states. However, the excited-state lifetimes in deareated solutions (see Table 2) are rather short and consistent with a partial metal-toligand charge-transfer (<sup>3</sup>MLCT) character, ranging from 0.14 to 3.8  $\mu s,$  and are comparable with other  $Pt^{II}$  emitters.  $^{[18,\,19]}$  Therefore, we consider that a significant mixing between these triplet states (LC and MLCT) occurs at room temperature. Indeed, a blue shift is observed for all the complexes in frozen matrices of 2-Me-THF at 77 K, (see Figures S3 and S4 in the Supporting Information), and the spectra appear even more structured. In this case, also complex 1 shows an intense emission in the deep blue region and all the complexes possess very long excited-state lifetimes in the range of several tenths of microseconds. These observations indicate that the emitting state has a predominant <sup>3</sup>LC character, and the mixing with the <sup>3</sup>MLCT state is much smaller due to the frozen matrix that prevents the stabilization of the charge-transfer state, which in turn becomes energetically inaccessible. The emission spectra of complexes 1-4 (Figure 9) as well as 5 and 6 (Figure 10) doped into



**Figure 9.** Emission spectra of complexes 1 (dotted and dashed line), 2 (dotted line), 3 (dashed line) and 4 (solid line) doped 10 wt% into PMMA.  $\lambda_{\rm exc}$  = 340 (1), 339 (2), 343 (3), and 348 nm (4).



**Figure 10.** Emission spectra of complexes **5** (solid line) and **6** (dotted line) doped 10 wt% into PMMA.  $\lambda_{exc}$  = 378 (**5**) and 405 nm (**6**).

PMMA films, at 10 wt% ratio, show a blue shift of about 10 nm with respect to the spectra measured in solution. The bathochromic shifts confirm the observation made for the frozen matrices, and are typical for metal complexes possessing an emissive state with charge-transfer character.<sup>[20]</sup>

The profiles of complexes **2–4** are similar to the ones observed in solution, with compound **4** exhibiting a more structured emission than in solution and an additional shoulder at  $\lambda = 494$  nm. Furthermore, the emission of complex **1** is now measurable in the rigid matrices, exhibiting a very structured profile in the deep blue region of the electromagnetic spectrum, with peaks at  $\lambda = 444$  and 472 nm. Moreover, although the emission quantum yields,  $\Phi_{em}$ , at room temperature in dichloromethane solutions are rather low and in the range of few percent (Table 2), they reach up to 38% for the blue emissive complex **1** in the solid state (Table 3).

The excitation spectra of compounds **1–4** in 2-Me-THF glasses at 77 K are shown in Figure S5 in the Supporting Information. They show two sets of bands, one below  $\lambda = 310$  nm and another one between  $\lambda = 310$  and 400 nm, and closely resemble the absorption spectra in fluid solutions (Figures 4 and 5). The largest blue shift is observed for compound **4**, from  $\lambda =$ 

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Table 3. Photophysical properties of films with complexes 1–6 doped into PMMA at 10 wt %.						
Complex	$\lambda_{\max}$ (em) PMMA 10 wt% [nm] (relative intensity) <sup>[a]</sup>	$\Phi_{ m em}$ [%] <sup>[b,c]</sup>	$ au$ RT [ $\mu$ s] <sup>[d]</sup> ([%])	k <sub>r</sub> [×10 <sup>-4</sup> s <sup>-1</sup> ] <sup>[e]</sup>	k <sub>nr</sub> [×10 <sup>-4</sup> s <sup>-1</sup> ] <sup>[e]</sup>	
1	444 (0.90), 472 (1), 495 (0.66, sh)	38	21.38 (35), 46.48 (65)	1.01	1.33	
2	479 (0.85), 509 (1), 532 (0.67)	15	17.31 (40), 50.33 (60)	0.30	1.69	
3	473 (0.71), 495 (1), 520 (0.74)	34	23.34 (44), 43.48 (56)	0.78	1.52	
4	483 (0.78, sh), 506 (1)	22	29.31 (38), 50.61 (62)	0.43	1.54	
5	497 (1)	18	3.03 (16), 41.8 (84)	0.43	1.96	
6	529 (1)	14	24.17 (20), 55.03 (80)	0.25	1.56	

[a] "Sh" denotes a shoulder. [b]  $\lambda_{exc}$  = 342–379 nm. [c] Quantum yields were measured in an integrating sphere system. [d] Monitored at  $\lambda_{em}$  = 474 (1), 494 (2), 508 (3), 513 (4), 494 (5), and 537 nm (6). [e] Rate constants were calculated by using the average excited-state lifetime for each compound.

347 nm in solution to  $\lambda =$  343 nm in the frozen glass. The same applies to the low-temperature excitation spectra of compounds 5 and 6 (Figure 6), which show better resolved vibrational progressions and overall blue shifts of the same order of magnitude as for the other compounds (2 nm).

These observations further support a mostly ligand-centered absorption and are additionally confirmed by the excitation spectra in PMMA (see Figures S7 (1-4) and S8 (5 and 6) in the Supporting Information). In the polymeric matrix, compounds 1-4 show maxima at the same wavelengths as in the low-temperature excitation spectra and the band corresponding to the tolyl moiety of compound **4** at  $\lambda = 269$  nm is clearly visible. For compounds 5 and 6, the excitation bands are less resolved, as also observed for the corresponding emission spectra in PMMA. Nevertheless, the broad excitation maxima correlate well with the absorption maxima in solution (Figure 6, Table 1).

The excited-state lifetimes show a more complex behavior in the solid state. Indeed, whereas at room temperature in fluid solution the decays are all monoexponential, the excited-state lifetimes are significantly longer and biexponential in PMMA films. One very long component (45-55 µs) with a larger contribution and a shorter component ranging from 3-30 µs are present (Table 3). This behavior is rather common for metal complexes possessing long excited-state lifetimes, because other known phenomena such as triplet-triplet annihilation and quenching due to coupling with ground states can occur.<sup>[21–23]</sup>

The long component can therefore be considered as the intrinsic lifetime in rigid matrix because it corresponds well with the excited-state lifetime at 77 K. The low emission quantum yields at room temperature in fluid solutions are related to the rates of the non-radiative deactivations, which are more than one order of magnitude higher than the rate constants of the radiative decay. Most likely, the two non-coordinated phenyl moieties on the phosphine ligand are responsible for the nonradiative decays in solution, as they provide a high density of vibrational modes supporting deactivation paths for the excited state. Consequently, the incorporation of these compounds into a matrix such as PMMA leads to a rigidochromic effect and strongly enhance the emission quantum yields, reaching up to 38% for compound 1. As can be seen from the rate constants given in Tables 3 and 4, both the radiative and non-radiative rate constants are decreased by about one order of magnitude, but the drop is larger for the non-radiative processes (Table 5). The radiative decay rate constants decrease by a factor of up to 4.5 in rigid matrices, whereas the non-radiative rate constants drop by factors of 14 to almost 368, as in the case of compound 3. Compounds 5 and **6** also show enhanced  $\Phi_{\rm em}$ values in PMMA, up to 18%, but are not affected to the same extent as the complexes bearing tailored ligands.

Table 4. Ratio between the rate constants for compounds 1-6 in dichloromethane and in PMMA.<sup>[a]</sup>

Complex	$k_{ m r, CH_2Cl_2}/k_{ m r, PMMA 10 wt\%}$	$k_{\rm nr, CH_2 Cl_2}/k_{\rm nr, PMMA 10 wt\%}$		
1	n.d.	n.d.		
2	3.73	22.58		
3	1.44	367.97		
4	3.23	35.76		
5	2.98	15.87		
6	4.48	13.98		
[a] The values represent how much the rate constants are decreased in				

the solid state in PMMA films, in comparison to the rate constants in solution.

### 2.5 Electrochemical characterization

The electrochemical analysis was carried out by cyclic voltammetry (CV) in DMF or dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate (see the Experimental Section). CV plots are given in the Supporting Information, Figures S9-S14. Most of the redox processes appeared to be irreversible at low scan rates (i.e., 0.1 or 0.2 V s<sup>-1</sup>). Therefore, the CVs were carried out by varying the scan rate in the range between  $0.1-5 \text{ V s}^{-1}$ . The electrochemical measurements indicated that the oxidation processes are irreversible between +1.25 and +1.52 V, which can be attributed to the oxidation of the metal core (Table 5).  $^{[19,24,25]}$  Such irreversibility is typical of  $\mathsf{Pt}^{II}$  complexes due to solvent coordination to the metal center upon oxidation, followed by a rearrangement of the ligands,<sup>[26]</sup> which might also account for the lower current involved in the oxidation wave as compared to the reduction process. Complexes 1 and 4 showed reversibility in the reduction for scan rates above 0.5 and 2 V s<sup>-1</sup>, respectively, whereas complexes 3 and 6 gave irreversible reductions between -1.7 and -1.9 V. The reduction of compounds 2 and 5 fall outside of the electrochemical window of the solvent/electrolyte, suggesting more negative reduction potentials (higher lying LUMOs).<sup>[27]</sup> In general, the reduction occurs on the ligands, as already reported for other transition-metal complexes.<sup>[18, 24, 28]</sup> In addition, the reduction wave observed for complex 6 appears negatively shifted (-1.82 V), as compared to an Ir<sup>III</sup> complex carrying the same triazole-based ligand, suggesting a lower electron affinity upon coordination to  $Pt^{II}$ .<sup>[15]</sup>

On the basis of the above-mentioned findings, it was possible to estimate the formal potentials  $E^{\circ}$  for compounds 1 and



Table 5.         Frontier orbitals obtained from CV and UPS measurements.					
Complex	E <sub>p,red</sub> [V] (LUMO [eV])	E <sub>p,ox</sub> [V] (HOMO [eV])	HOMO [eV] <sup>[e]</sup>	LUMO [eV] <sup>[f]</sup>	$\Delta_{\rm HOMO-LUMO} \\ [eV]^{[h]}$
1	-1.70 <sup>[a,c]</sup>	$+1.46^{\scriptscriptstyle[a,d]}$	-5.95	-3.06	2.89
	(-2.64)	(-5.80)			(3.16)
2	n.d.	$+1.42^{[b,d]}$	-5.89	-3.17	2.72
		(-5.79)			(n.d.)
3	$-1.89^{[b,d]}$	$+1.52^{[b,d]}$	n.d.	-3.04 <sup>[g]</sup>	2.82
	(-2.65)	(-5.86)			(3.25)
4	-1.59 <sup>[b,c]</sup>	$+1.51^{[b,d]}$	-5.86	-3.14	2.72
	(-2.75)	(-5.90)			(3.15)
5	n.d.	$+1.33^{[b,d]}$	-5.84	-3.06	2.78
		(-5.67)			(n.d.)
6	$-1.90^{[b,d]}$	$+ 1.28^{[b,d]}$	-5.84	-3.34	2.50
	(-2.63)	(-5.60)			(2.97)

[a] 1 mm solutions in DMF/0.1 m tetrabutylammonium hexafluorophosphate (TBAH). [b] 1 mm solutions in dichloromethane/0.1 m TBAH. Glassy carbon was employed as the working electrode, a platinum ring as the counter electrode, and a silver wire as the reference electrode. The scan rate was varied in the range  $0.1-5 \text{ V s}^{-1}$ . [c] The formal potentials ( $E^{\circ}$ ) were calculated as the average value between the cathodic and anodic peak potentials (see text for compounds 1 and 4). [d] Irreversible at all scan rates, that is, in the range  $0.1-5 \text{ V s}^{-1}$ . [e] HOMO levels of drop-casted neat films were measured by UPS. [f] LUMO values estimated from the energy of the emission onset in the 77 K measurements in 2-Me-THF. [g] Calculated by using the HOMO value from the electrochemical measurements. [h] Values in parentheses are calculated from the onset potential (except for the oxidation of compounds 1 and 4, where  $E^{0}$  was used), based on the value of -4.8 eV for ferrocene with respect to the zero vacuum level, as the potential values are referenced against ferrocene.<sup>[29]</sup>

**4**, whereas for the other compounds only the peak potential,  $E_{pr}$ , could be measured (see Table 5). Differential pulse voltammetry (DPV) was also carried out under the same conditions used for the CV to assess the redox potentials. However, it failed to provide reliable  $E^{\circ}$  values, due to the limitation of this technique when irreversible processes take place. However, approximate HOMO–LUMO band gaps can be estimated from the onset potentials of the faradic current rise in the CV plots, the corresponding values are reported in parentheses in Table 5.

Due to the irreversibility of the oxidation processes, another approach was selected to estimate the energy level of the frontier orbitals. The HOMO energy was measured by using ultraviolet photoelectron spectroscopy (UPS), and the LUMO energy was calculated by addition of the HOMO–LUMO gap, which was derived from on the onset of the emission measured at 77 K. The calculated LUMOs are summarized in Table 5, and are in good agreement with the HOMO–LUMO band gaps obtained by CV. The gaps lie in the range between -3.04 and -3.34 eV, suggesting for complexes 2 and 5 a LUMO energy in close proximity to the reduction potentials of the other complexes reported herein.

## 2.6 OLED devices

In order to test the suitability of this family of compounds for OLED preparation, initial tests with compound **1** have been performed. Two device architectures have been studied, as



Table 6. Setups of the tested devices with compound 1.				
Device I Device II				
ITO	ITO			
NPB (15 nm)	MoO <sub>3</sub> (5 nm)			
CzSi+10 wt% <b>1</b> (25 nm)	NPB (10 nm)			
BAlq (10 nm)	CzSi+10 wt % 1 (20 nm)			
ZrQ <sub>4</sub> (30 nm)	BAlq₃ (10 nm)			
LiF (0.5 nm)	ZrQ <sub>4</sub> (15 nm)			
Al (150 nm)	LiF (0.5 nm)			
	Al (150 nm)			

summarized in Table 6. Both consist of a an indium tin oxide (ITO) anode on a glass substrate, a hole transporting layer of N,N'-bis(1-naphthalenyl)-N,N'-bisphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), followed by the emissive layer of complex 1 doped at 10 wt% into the host material CzSi (CzSi = 9-(4-(*tert*-butyl)phenyl)-3,6-bis(triphenylsilyl)-9*H*-carbazole). Furthermore, zirconium quinolate (ZrQ<sub>4</sub>) was used as the electron transporter and bis(2-methyl-8-quinolinolato-N1,O8)-(1,1'-biphenyl-4-olato)aluminum (BAlq) as the hole blocker. The structures of these materials are depicted in Figure S17 in the Supporting Information. In setup II, molybdenum oxide (MoO<sub>3</sub>), which supports the hole injection, is introduced between NPB and the anode to confine more charge carriers within the emissive layer.

The electroluminescence (EL) spectra of these devices, recorded upon application of a voltage of 14 V, are shown in Figure 11. The emission maximum is almost unchanged as



Figure 11. EL-spectra of complex 1 in different device setups at 14 V. Setup I (solid line), setup II (dotted line).

compared with the one in a rigid matrix of PMMA (CIE coordinates x=0.173, y=0.212), but the vibrational progression is less structured than in PMMA films. The devices have turn-on voltages around 4.5 V, which is in the range of previously published Pt<sup>II</sup>-based OLEDs (Figure 12).<sup>[8,30-32]</sup> It is clear that the introduction of the blocking layer in setup II leads to higher luminance values than in setup I at the same voltages (Figure 12), which is caused by the higher number of charge recombination on the emissive layer, as described above.

The current efficiency,  $\eta_{cr}$  and the power efficiency,  $\eta_{pr}$  (Figure 13 as well as Figures S15 and S16 in the Supporting Information) suggest that there is still room for improvement in the device architecture. The maximum current efficiency lies

**KK** These are not the final page numbers!



Figure 12. Luminance versus voltage curves for devices I (solid line) and II (dotted line).



**Figure 13.** Current efficiencies  $\eta_c$  of devices I (solid line) and II (dotted line).

between 1.00 and 1.50 cd A<sup>-1</sup>, just above 100 cd m<sup>-2</sup> (Figure 13). At the same time, the power efficiency stays below 0.5 Lm W<sup>-1</sup> in the device without a blocking layer (Figure S15 in the Supporting Information). The low efficiencies are possibly due to a mismatch of the frontier orbitals of the host and the emitter, that is, differences between the HOMO and the LUMO levels of the dopant and the host. Consequently, less excitons are formed on the dopant, leading to lower luminances and efficiencies. The current density versus voltage plot is shown in Figure S16 in the Supporting Information. Optimized devices usually show current efficiencies around 5 Lm W<sup>-1</sup> at 1000 cd m<sup>-2</sup> and current efficiencies around 10 cd A<sup>-1.[33,34]</sup>

The low efficiencies of the devices have to be overcome by developing suitable matrix materials for these blue Pt<sup>II</sup> emitters. Indeed, the matrices used in these tests are optimized for Ir<sup>III</sup> emitters, which possess different HOMO–LUMO levels even when the emission energies are similar. Therefore, the injected charges only recombine inefficiently and accumulate in the emissive layer (EML). This is not only a problem for the efficiencies, but also for the device lifetime, because a high charge-carrier density can lead to side reactions and a subsequent decomposition of the charge-transporting materials. Improvements of the device architecture would involve matrix materials with HOMO and LUMO levels that match the values reported in Table 5. This would increase the number of charge recombination on the emissive dopant and consequently enhance the efficiencies.

## 3. Conclusion

A new class of Pt<sup>II</sup> emitters carrying a phosphite ligand has been investigated. This chelate is known for its use in homogeneous catalysis providing high solubility and inhibiting aggregation. Moreover, it is spectroscopically transparent and the photophysics of the complexes are dominated by the luminophoric ligand coordinated to the  $Pt^{II}$  ion. Different chromophores have been used, following a simple synthetic strategy, leading to emitters reaching the blue region of the electromagnetic spectrum with good emission quantum yields. With the bluest emitter, device preparation has been performed, proving the suitability of the compounds for their use in OLED devices. Although tailored ligands have to be employed to achieve a high-energy emission, commercially available ligands can be used for the fast and large scale preparation of green emitters.

## **Experimental Section**

## Photophysics

Absorption spectra were measured on a Varian Cary5000 doublebeam UV/Vis/NIR spectrometer and baseline corrected. Steadystate emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon-arc lamp, double-grating excitation and emission monochromators (2.1 nm mm<sup>-1</sup> dispersion, 1200 grooves mm<sup>-1</sup>), and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. Emission and excitation spectra were corrected for the source intensity (lamp and grating) by standard correction curves. Time-resolved measurements were performed by using the timecorrelated single-photon counting (TCSPC) and the multichannel scaling (MCS) single-photon-counting option on the HORIBA Jobin–Yvon IBH FL-322 Fluorolog 3. NanoLED ( $\lambda = 402 \text{ nm}$ , FHWM <750 ps) with repetition rates between 10 kHz and 1 MHz (TCSPC) or a pulsed xenon lamp (MCS) were used to excite the sample. The excitation sources were mounted directly on the sample chamber at 90° to a double-grating emission monochromator (2.1 nm mm<sup>-1</sup> dispersion, 1200 grooves mm<sup>-1</sup>) and collected by a TBX-4-X singlephoton-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected by using an IBH Data Station Hub photon-counting module, and data analysis was performed by using the commercially available DAS6 software (HORIBA JobinYvon IBH). The quality of the fit was assessed by minimizing the reduced chi squared function ( $\chi^2$ ) and visual inspection of the weighted residuals.

Luminescence 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, C7473 photonic multichannel analyzer, integrating sphere, and employing the U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan).

All solvents were of spectrometric grade. Degassed samples were prepared by bubbling with a solvent-saturated stream of argon for 30 min.  $^{[35,36]}$ 

## UV photoelectron spectroscopy

UPS was measured on a Riken Keiki AC-2 system by using the lowenergy electron counter method, with a deuterium lamp as light source and a grating type monochromator as spectrometer.

#### Electrochemistry

The electrochemical characterization (cyclic and differential pulse voltammetry) for the metal complexes 2–6 herein reported has

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been performed in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate, whereas for complex 1 the characterization has been carried out in *N*,*N*-dimethylformamide/0.1 M TBAH. The concentrations of the samples were 1 mm. Glassy carbon was employed as the working electrode, a platinum wire as counter electrode, and a silver wire as quasi-reference electrode (QRE). Dichloromethane 99.8% extra dry over molecular sieves and DMF 99.8% extra dry (Acros Organics) were used as received without any further purification. TBAH (electrochemical grade,  $\geq$  99%, Fluka) was used as supporting electrolyte, which was re-crystallized from a 1:1 ethanol/water solution and dried at 60 °C under vacuum.

For the electrochemical experiments, a CHI750C Electrochemical Workstation (CH Instruments, Inc., Austin, TX, USA) was used. The electrochemical experiments were performed in a glass cell under an Ar atmosphere. To minimize the ohmic drop between the working and the reference electrodes, the feedback correction was employed. The electrochemical experiments were performed by using a homemade 3 mm diameter glassy carbon disk electrode (from a glassy carbon rod, Tokai Inc.). The working electrodes were stored in ethanol and were polished before experiments with a 0.05 µm diamond suspension (Metadi Supreme Diamond Suspension, Buehler) and ultrasonically rinsed with ethanol for 5 min. The electrode was electrochemically activated in the background solution by means of several voltammetric cycles at 0.5 V s<sup>-1</sup> between the anodic and cathodic solvent/electrolyte discharges, until the same quality features were obtained. The reference electrode was a silver quasi-reference electrode (Aq-QRE), which was separated from the catholyte by a glass frit (vycor). The reference electrode was calibrated at the end of each experiment against the ferrocene/ferricenium couple, whose formal potential is 0.464 V against the KCl saturated calomel electrode (SCE); in the following, all potential values will be reported against SCE. A platinum ring or coil served as the counter electrode.

#### **Device preparation**

All layers were prepared by thermal evaporation in a high-vacuum system with a pressure of less than  $10^{-4}$  Pa without breaking the vacuum. ITO-coated glass plates with a surface resistivity of 15  $\Omega$  were used as substrates. They were ultrasonically cleaned and treated with oxygen plasma for work function tuning and chemical cleaning. During the evaporation, the deposition rates were monitored by controllers, which were calibrated by using a Dektak 6M profiler. The deposition rate was 0.1 mms<sup>-1</sup> and the layer thickness was checked by quartz balances. The *J*-*V*-*L* characteristics were measured by using a Keithley238 (high-current source measure unit) and a Keithley2000 (multimeter) with a calibrated silicon photodiode under nitrogen. Spectra were recorded on a tec5 spectrometer unit LOE-USB. The luminance values were measured at normal incidence, and the total flux was estimated by assuming a Lambertian distribution.

#### Synthesis and characterization

All reagents were of analytical grade and used as received. Column chromatography was performed with silica gel 60 (particle size 63–200 µm, 230–400 mesh, Merck). NMR spectra were recorded on an ARX300 or an AMX400 from Bruker Analytische Messtechnik (Karlsruhe, Germany). The <sup>1</sup>H NMR chemical shifts ( $\delta$ ) of the signals are given in [ppm] and referenced to residual protons in the deuterated solvents: [D<sub>1</sub>]chloroform<sub>1</sub> ( $\delta$ =7.26 ppm), [D<sub>6</sub>]dimethyl sulfoxide ( $\delta$ =2.50 ppm), or [D<sub>2</sub>]methylene chloride ( $\delta$ =5.32 ppm). The signal splittings are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All coupling constants (J) are

given in Hertz (Hz). Mass spectrometry was performed in the Department of Chemistry, University of Münster. Electrospray ionization (ESI) mass spectra were recorded on a BrukerDaltonics (Bremen, Germany) MicroTof with loop injection. Elemental analysis was recorded at the University of Münster (Germany).

**4,4,4-Trifluoro-1-(pyridin-2-yl)butane-1,3-dione (PL1)**: The synthesis of this precursor has already been published and it has been prepared according to a literature procedure.<sup>[37]</sup> 2-Cyanopyridine (10.5 g, 101 mmol) and hydrazine monohydrate (5.5 g, 110 mmol) were stirred in ethanol (30 mL) overnight. Then, water (30 mL) was added to the reaction mixture and all solvents were removed under reduced pressure to yield an orange solid, which was washed with cold petrol ether. The solid was re-crystallized from toluene and used without further purification (7 g, 51%).

**3-(Trifluoromethyl)-5-(2-pyridyl)pyrazole** (HL1): The ligand (fppzH) was prepared according to a literature procedure.<sup>[38, 39]</sup>

2-(3-(Adamantan-1-yl)-1 H-pyrazol-5-yl)pyridine (HL2): Sodium methoxide (544 mg, 10.07 mmol) was suspended in dry tetrahydrofuran (10 mL). A solution of adamatyl methylketone (1 g, 5.05 mmol) in dry THF (10 mL) was added. The mixture was heated to reflux for one hour. Then a solution of methyl picolinate (690 mg, 5.04 mmol) in dry THF (12 mL) was added slowly. The resulting colored solution was heated to reflux overnight under nitrogen. After that the reaction mixture was allowed to cool to room temperature. All solvent was removed under reduced pressure and the mixture was extracted between water and dichloromethante at pH 5. The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to yield a brownish oil 1-((3r,5r,7r)-adamantan-1-yl)-3-(pyridin-2-yl)propane-1,3-dione (PL2) (1.2 g, 4.24 mmol, 84%) as a precursor for the next step. This was then heated to reflux with hydrazine monohydrade (2.12 g, 42.4 mmol) in ethanol (10 mL) overnight. The solvent was removed under reduced pressure and the resulting solid was extracted between water and ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The resulting solid was re-crystallized from hexane to yield an off-white solid (0.5 g, 42%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.56$  (ddd, J = 4.9, 1.7, 0.9 Hz, 1 H), 8.23 (s, 1 H), 8.19 (dt, J=8.0, 1.0 Hz, 1 H), 7.76 (td, J=7.8, 1.8 Hz, 1 H), 7.20 (ddd, J = 7.5, 4.9, 1.2 Hz, 1 H), 2.29 (s, 9 H), 2.04 (d, J =14.1 Hz, 1 H), 1.88–1.71 ppm (m, 6 H); MS (ESI+, MeOH): m/z calcd for C<sub>18</sub>H<sub>22</sub>N<sub>3</sub>: 280.1808 [M+H]<sup>+</sup>; found: 280.1814; m/z calcd for C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>Na: 302.1628 [*M*+Na]<sup>+</sup>; found: 302.1629.

**2-(3-(Adamantan-1-yl)-1***H***-1,2,4-triazol-5-yl)pyridine (HL3)**: This ligand was prepared according to the literature procedure by using adamantanecarbonyl chloride<sup>[37]</sup> (1.3 g, 91%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.69 (d, *J* = 4.0 Hz, 1 H), 8.20 (d, *J* = 7.9 Hz, 1 H), 7.81 (t, *J* = 7.0 Hz, 1 H), 7.41–7.29 (m, 1 H), 2.12 (s, 9 H), 1.81 ppm (s, 6 H); MS (ESI<sup>+</sup>, MeOH): *m/z* calcd for C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>: 281.1761 [*M*+H]<sup>+</sup>; found: 281.1762; *m/z* calcd for C<sub>18</sub>H<sub>22</sub>N<sub>3</sub>Na: 303.1580 [*M*+Na]<sup>+</sup>; found: 303.1580.

**2-(3-(***p***-Tolyl)-1***H***-1,2,4-triazol-5-yl)pyridine (HL4):** This ligand has already been published and has been prepared according to a literature procedure.<sup>[37]</sup> <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta$ =8.72 (d, *J*=4.5 Hz, 1H), 8.16 (d, *J*=7.9 Hz, 1H), 8.03 (s, d, *J*=8 Hz, 2H), 7.98 (d, *J*=8.2 Hz, 1H), 7.58–7.47 (m, 1H), 7.32 (d, *J*=8.0 Hz, 2H), 2.37 ppm (s, 3H); MS (ESI<sup>+</sup>, MeOH): *m/z* calcd for C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>: 237.1135 [*M*+H]<sup>+</sup>;

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found: 237.1127; *m/z* calcd for  $C_{14}H_{12}N_4Na$ : 259.0954 [*M*+Na]<sup>+</sup>; found: 259.0947

**2-(Benzo[d]oxazol-2-yl)phenol (HL5)**: This ligand was purchased from Sigma–Aldrich and used without further purification.

**2-(Benzo[d]thiazol-2-yl)phenol (HL6)**: This ligand was purchased from Sigma–Aldrich and used without further purification.

 $[\{Pt-(\mu-CI)\{\kappa^2-P,C-P(OC_6H_2-2,4-tBu_2)(OC_6H_3-2,4-tBu_2)_2\}\}_2] \qquad (P1): Tris(2,4-di-tert-butylphenyl) phosphite (934 mg, 1.44 mmol) and potassium tetrachloroplatinate (600 mg, 1.44 mmol) were combined in 2-methoxyethanol (48 mL) and heated to 140 °C under nitrogen overnight. The clear solution was cooled to room temperature and the solvent was removed under reduced pressure. The off-white residue was dissolved in dichloromethane and filtered through a pad of celite. The filtered solution was then concentrated under reduced pressure and the product was precipitated from dichloromethane with ethanol to yield a white solid. The supernatant was removed and the solid dried under vacuum (1.27 g 50%).<sup>[11,40]</sup>$ 

General synthetic route for the preparation of the complexes 1– 6: [{Pt-{ $\mu$ -Cl}{ $\kappa^2$ -P,C-P(OC<sub>6</sub>H<sub>2</sub>-2,4-tBu<sub>2</sub>)(OC<sub>6</sub>H<sub>3</sub>-2,4-tBu<sub>2</sub>)<sub>2</sub>]} (P1) (1 equiv) together with the ancillary ligand (2 equiv) were heated to 50 °C in a 1:1 mixture of dichloromethane and methanol overnight. The solvents were removed under reduced pressure and the crude reaction mixture was purified through column chromatography on silica, using a 6:4 mixture of dichloromethane and cyclohexane as eluent. The fractions containing the product were collected, the solvent was removed under reduced pressure, and the resulting solid was re-crystallized from hexane.

**[Pt(phos)(py-pyr-CF<sub>3</sub>)] (1):** Pt<sup>II</sup> precursor **P1** (0.1 g, 0.06 mmol) and **HL1** (0.013 g, 0.06 mmol) were used for this reaction. A slightly yellow solid (43 mg, 81%) was obtained. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.41–9.14 (m, 1H), 8.87 (d, *J* = 5.5 Hz, 1H), 7.83 (td, *J* = 7.8, 1.4 Hz, 1H), 7.73–7.57 (m, 3H), 7.36–7.31 (m, 2H), 7.09 (t, *J* = 2.2 Hz, 1H), 7.02 (ddd, *J* = 5.6, 4.7, 1.3 Hz, 1H), 6.99–6.90 (m, 2H), 6.87 (d, *J* = 9.7 Hz, 1H), 1.52 (s, 18H), 1.44 (s, 9H), 1.19 (s, 18H), 1.07 ppm (s, 9H); MS (ESI<sup>+</sup>, MeOH/CHCl<sub>3</sub>): *m/z* calcd for C<sub>51</sub>H<sub>67</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>PPt: 1053.46165 [*M*+H]<sup>+</sup>; found: 1053.46165; *m/z* calcd for C<sub>51</sub>H<sub>66</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>PPtNa: 1075.44306 [*M*+Na]<sup>+</sup>; found: 1075.44930.

[Pt(phos)(py-pyr-ada)] (2): Pt<sup>II</sup> precursor P1 (0.754 g, 0.43 mmol) and HL2 (0.24 g, 0.86 mmol) were used for this reaction. An offwhite solid (450 mg, 68%) was obtained. <sup>1</sup>H NMR (400 MHz,  $CD_2CI_2$ ):  $\delta = 9.56-9.32$  (m, 1 H), 8.83 (d, J = 5.6 Hz, 1 H), 7.79 (td, J =8.0, 1.5 Hz, 1 H), 7.68 (dd, J=8.6, 1.8 Hz, 2 H), 7.61 (d, J=7.7 Hz, 1 H), 7.38 (dt, J=17.7, 8.9 Hz, 2 H), 7.11 (t, J=2.2 Hz, 1 H), 7.02 (dd, J = 8.6, 2.5 Hz, 2 H), 6.96 (ddd, J = 7.3, 5.7, 1.3 Hz, 1 H), 6.49 (d, J =1.5 Hz, 1 H), 2.13 (d, J=2.5 Hz, 6 H), 2.09 (s, 3 H), 1.83 (t, J=2.8 Hz, 6H), 1.55 (s, 18H), 1.48 (s, 9H), 1.21 (s, 18H), 1.10 ppm (d, J= 7.8 Hz, 9 H); MS (ESI<sup>+</sup>, MeOH): m/z calcd for  $C_{60}H_{83}N_3O_3PPt$ : [*M*+H]<sup>+</sup>; found: 1119.5801; *m*/*z* calcd 1119.5819 for C<sub>60</sub>H<sub>82</sub>N<sub>3</sub>NaO<sub>3</sub>PPt: 1141.5638 [*M*+Na]<sup>+</sup>; found: 1141.5602; elemental analysis calcd (%) for C<sub>46</sub>H<sub>61</sub>N<sub>3</sub>O<sub>2</sub>PPt: C 64.38, H 7.38, N 3.75; found: C 64.57, H 7.55, N 3.57.

[Pt(phos)(py-1,2,4-triaz-ada)] (3): Pt<sup>II</sup> precursor P1 and HL3 were used for this reaction. Column chromatography was performed with dichloromethane/methanol (97:3) as eluent. An off-white solid (0.73 g, 81.3%) was obtained. <sup>1</sup>H NMR (300 MHz,  $CD_2CI_2$ ):  $\delta$  = 9.42–9.16 (m, 1 H), 8.86 (d, *J*=5.7 Hz, 1 H), 8.06 (d, *J*=7.6 Hz, 1 H), 7.95

(td, J=7.8, 1.5 Hz, 1 H), 7.64 (dd, J=8.6, 1.9 Hz, 2 H), 7.45–7.33 (m, 2 H), 7.23–7.15 (m, 1 H), 7.13 (t, J=2.2 Hz, 1 H), 7.01 (dd, J=8.6, 2.5 Hz, 2 H), 2.18 (d, J=2.8 Hz, 6 H), 2.10 (s, 3 H), 1.84 (s, 6 H), 1.54 (s, 18 H), 1.46 (s, 9 H), 1.21 (s, 18 H), 1.11 ppm (s, 9 H); MS (ESI<sup>+</sup>, MeOH): m/z calcd for  $C_{59}H_{82}N_4O_3PPt$ : 1120.5771 [M+H]<sup>+</sup>; found: 1120.5751; elemental analysis calcd (%) for  $C_{45}H_{60}N_4O_2PPt$ : C 63.25, H 7.29, N 5.00; found: C 62.73, H 7.40, N 4.86.

**[Pt(phos)(py-1,2,4-triaz-tol)] (4):** Pt<sup>II</sup> precursor **P1** (0.100 g, 0.057 mmol) and **HL4** (0.027 g, 0.114 mmol) were used for this reaction A yellowish solid (72 mg, 58%) was obtained. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.38 (t, *J* = 2.0 Hz, 1H), 8.91 (d, *J* = 5.6 Hz, 1H), 8.20 (t, *J* = 7.8 Hz, 3H), 8.01 (td, *J* = 7.8, 1.5 Hz, 1H), 7.68 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.41 (dd, *J* = 2.4, 1.5 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.27-7.21 (m, 1H), 7.17 (t, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.5 Hz, 2H), 1.56 (s, 18H), 1.53 (s, 10H), 1.27 (s, 5H), 1.21 (s, 20H), 1.13 (s, 10H), 1.01–0.76 ppm (m, 5H); MS (ESI<sup>+</sup>, MeOH/CHCl<sub>3</sub>): *m/z* calcd for C<sub>56</sub>H<sub>74</sub>N<sub>4</sub>O<sub>3</sub>PPt: 1076.51412 [*M*+H]<sup>+</sup>; found: 1076.51437.

**[Pt(phos)(phenoxy-benzoxazole)]** (5): Pt<sup>III</sup> precursor P1 (0.5 g, 0.29 mmol) and HL5 (0.12 g, 0.57 mmol) were used for this reaction A white solid (80 mg, 13%) was obtained. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.39–8.31 (m, 1H), 8.28 (t, *J* = 2.5 Hz, 1H), 7.96 (dt, *J* = 8.1, 2.0 Hz, 3 H), 7.63–7.54 (m, 1H), 7.48–7.40 (m, 1H), 7.40–7.25 (m, 4H), 7.17 (dd, *J* = 8.6, 0.9 Hz, 1H), 7.10 (t, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.5 Hz, 2 H), 6.73 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 1.45 (s, 9 H), 1.43 (s, 18 H), 1.20 (s, 18 H), 1.05 ppm (s, 9 H); MS (ESI<sup>+</sup>, MeOH): *m/z* calcd for C<sub>55</sub>H<sub>71</sub>NNa<sub>5</sub>PPt: 1051.4717 [*M*+H]<sup>+</sup>; found: 1051.4664; *m/z* calcd for C<sub>55</sub>H<sub>70</sub>NNaO<sub>5</sub>PPt: 1073.4536 [*M*+Na]<sup>+</sup>: found: 1073.4499; elemental analysis calcd (%) for C<sub>55</sub>H<sub>70</sub>NO<sub>5</sub>PPt: C 62.84, H 6.71, N 1.33; found: C 62.7, H 6.71, N 1.21.

[Pt(phos)(phenoxy-benzothiazole)] (6): Pt<sup>II</sup> precursor P1 (1 g, 0.57 mmol) and HL6 (0.24 g, 1.04 mmol) were used for this reaction. A yellow solid (314 mg, 26%) was obtained. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.42 (dt, *J* = 7.1, 3.1 Hz, 1H), 8.15–7.95 (m, 1H), 7.83–7.77 (m, 1H), 7.48 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.42–7.33 (m, 2H), 7.33–7.19 (m, 5H), 7.07 (t, *J* = 2.3 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.62–6.55 (m, 1H), 1.44 (s, 9H), 1.23 (s, 36H), 1.01 ppm (s, 9H); MS (ESI<sup>+</sup>, MeOH): *m/z* calcd for C<sub>55</sub>H<sub>70</sub>NNaO<sub>4</sub>PPtS: 1089.4308 [*M*+Na]<sup>+</sup>; found: 1089.4301; elemental analysis calcd (%) for C<sub>55</sub>H<sub>70</sub>NO<sub>4</sub>PPtS: C 61.90, H 6.61, N 1.31; found: C 62.47, H 6.73, N 1.19.

## X-ray diffraction

Data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT;<sup>[41]</sup> data reduction, Denzo-SMN;<sup>[42]</sup> absorption correction, Denzo;<sup>[43]</sup> structure solution, SHELXS-97;<sup>[44]</sup> structure refinement, SHELXL-97;<sup>[45]</sup> and graphics, XP.<sup>[46]</sup>

X-ray crystal structure analysis of complex **6**: Formula  $C_{55}H_{70}NO_4PPtS$ ; M = 1067.24; yellow crystal;  $0.33 \times 0.13 \times 0.10$  mm<sup>3</sup>; a = 10.7222(1), b = 19.0007(3), c = 25.4732(4) Å;  $\beta = 101.569(1)^{\circ}$ ; V = 5084.20(12) Å<sup>3</sup>;  $\rho_{calcd} = 1.394$  gcm<sup>-3</sup>;  $\mu = 2.877$  mm<sup>-1</sup>; empirical absorption correction ( $0.450 \le T \le 0.761$ ); Z = 4; monoclinic; space group  $P2_1/c$  (No. 14);  $\lambda = 0.71073$  Å; T = 223(2) K;  $\omega$  and  $\phi$  scans; 26796 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm I$ ); [(sin  $\theta)/\lambda$ ] = 0.60 Å<sup>-1</sup>; 8374 independent ( $R_{int} = 0.052$ ) and 7708 observed reflections [ $I > 2\sigma(I)$ ]; 586 refined parameters; R = 0.073;  $wR^2 = 0.211$ ; max. (min.)

Chem. Eur. J. 2015, 21, 1–13

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residual electron density 3.88  $(-3.25) e Å^{-3}$ ; hydrogen atoms calculated and refined as riding atoms.

CCDC 928013 contains the supplementary crystallographic data for the structure **6**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif.

## Acknowledgements

We thank the German Federal Ministry for Education and Research (BMBF) for funding, Project 13N10529 (So-Light).

**Keywords:** electrochemistry • light-emitting diodes phosphites • photophysics • platinum

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Received: October 27, 2014 Published online on ■■ ■, 0000



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# Electroluminescent Devices

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Sterically Hindered Luminescent Pt<sup>II</sup>– Phosphite Complexes for Electroluminescent Devices

