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Synthesis, photophysical characterization and DFT studies on fluorine-free deep-blue emitting Pt(II) complexes

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Abstract: Herein we show that cyclometalated, square planar Pt(II) complexes can be tuned to achieve deepblue phosphorescent emitters. For this purpose, the introduction of an electron-donating moiety on two different bidentate N^N and N^O fluorine-free luminophores, namely 2-(1*H*-tetrazol-5-yl)pyridine and picolinic acid, was carried out. The remaining two coordination sites of the Pt(II) metal center were filled by a sterically demanding cyclometallating unit, namely a tertiary phosphite C^P ligand. This ancillary ligand avoids aggregation and provides high solubility in organic solvents. Based on this approach, we were able to blue-shift the emission of the complexes down to 411 nm, and to achieve a maximal photoluminescence quantum yield of 56% in the solid state.

Keywords: deep-blue; density functional theory; phosphite; photophysics; platinum.

Dedicated to: Professor Wolfgang Jeitschko on the occasion of his 80th birthday.

1 Introduction

Triplet emitters have found application as dopants in optoelectronic devices, such as organic light-emitting diodes [1-3] (OLEDs) and light-emitting electrochemical cells (LEECs) [4-10]. Besides Ir(III) [11-13], Rh(III) [14], Re(I) [15] and Cu(I) [16-20] complexes, coordination compounds featuring Pt(II) [21-34] and Au(III) [35-40] cations have been described. The latter possess a d^8 electronic configuration and mostly a square-planar coordination environment. Bidentate [41-52], tridentate [53-55] as well as tetradentate [56-60] ligands have been employed, yielding highly luminescent coordination compounds. We have recently shown, that the frontier molecular orbitals of neutral Pt(II) complexes bearing dianionic tridentate N^N^N ligands can be correlated with occupied and unoccupied states measured by a combination of scanning tunneling microscopy (STM) and spectroscopy (STS) techniques, and that they can also be independently tuned by introducing electron donating and withdrawing moieties. We found that the highest occupied molecular orbital (HOMO) appears mainly associated with the triazolate unit of the chelating luminophore, whereas the lowest unoccupied molecular orbital (LUMO) is predominately linked to the central pyridine ring. This behavior also correlates with the photophysical properties, which showed a structured emission band indicating metal-perturbed ligand-centered triplet states (3MP-LC) [61-63]. However, the search for stable, deep-blue emitting species with high photoluminescence quantum yields (Φ_i) is still a subject of intensive research [50]. In order to achieve strongly luminescent, blue emitting compounds, good Σ donors with large ligand field splittings are required to destabilize the otherwise thermally accessible, non-radiative metalcentered states.

Mydlak et al. have shown an interesting concept in which tris(2,4-di-*tert*-butylphenyl) phosphite acted as a bidentate ancillary ligand precursor, and either a N^N pyrdine-triazole/pyrazole or a phenoxy-benzo(thi/ox)azolebased chelators acted as the luminophoric unit (Fig. 1) [51].

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The enhanced ligand field splitting provided by the ancillary ligand, which coordinates to the metal ion with one electron-poor phosphorus on the one hand and a cyclometalating carbon atom on the other hand, yielded a set of emissive compounds with relatively high $\Phi_{\rm L}$ in poly(methyl metacrylate) films (PMMA) ($\lambda = 444$ nm, $\Phi_{\rm L} = 0.38$). If compared with tridentate luminophores, bidentate ligands generally show a smaller π -conjugated system offering a wider HOMO-LUMO gap that enables the fabrication of deep-blue emitting species. However, deviation from the preferred square-planar geometry in the excited state



Fig. 1: Selected structures of the Pt(II) complexes from Mydlak et al. [51].

can cause a fast radiationless deactivation to the ground state. In the case of blue triplet emitters with high-energy excited states, thermally accessible metal-centered (MC) states efficiently funnel the energy to the ground state by vibronic coupling at conical intersections [64, 65], due to the dissociative character associated with the population of unoccupied $d_{x^2-y^2}$ orbitals overlapping with the ligands.

Herein we present a straightforward strategy towards square-planar Pt(II) complexes (C1-C4) which carry a bulky ancillary unit based on the ligand precursor tris(2,4di-*tert*-butylphenyl) phosphite (\mathbf{L}_{anc}) and either picolinic acid (L1), 4-methoxypicolinic acid (L2), 2-(1H-tetrazol-5-yl) pyridine (L3) or 5-(3-methoxyphenyl)-1H-tetrazole (L4) as luminophoric ligand precursors (Scheme 1). \mathbf{L}_{anc} offers a good solubility in a variety of organic solvents as the sterical demand of the two remaining phenoxy moieties avoids intermolecular aggregation and suppresses quenching pathways. Cyclometallation provides a strong σ -donating character, and the phosphite unit contributes with a strong π -accepting capacity, which both enhance the ligand field splitting as required to suppress the thermal population of metal-centered excited states. The emission properties of the complexes were tuned on the luminophore: To blueshift the luminescence by enhancing the gap between



Scheme 1: Synthetic route towards complexes C1–C4.

the frontier orbitals, two strategies were pursued. On the one hand, the introduction of a π electron-donating OCH₃ substituent on the central pyridine should destabilize the LUMO of the corresponding complex (**C1** vs. **C2**, **C3** vs. **C4**). On the other hand, substituting the five-membered tetrazole ring of the chromphoric ligand by an electron-poor and less delocalized carboxylic group (**C3** vs. **C1**, **C4** vs. **C2**) should stabilize the HOMO and further shift the emission to shorter wavelengths, while keeping the basicity of the anionic coordination site unaffected.

2 Results and discussion

2.1 Synthesis and characterization

The ligand precursors **L1**, **L2** and **L3** are commercially available; the synthesis of **L4** and of the intermediate **E1** were carried out by adapting known procedures (Schemes 1 and 2) [66–68]. Compound **L4** was prepared by heating 4-methoxypyridine-2-carbonitrile and sodium azide in a mixture of *n*-butyl alcohol and acetic acid. After addition of water, the product precipitated as a white powder and no further purification was necessary.

The binuclear Pt(II) complex **E1** was synthesized by refluxing tris(2,4-di-*tert*-butylphenyl) phosphite and potassium tetrachloroplatinate (II) in 2-methoxyethanol, followed by a two-step purification procedure. Compound **E1** is a mixture of *cis* and *trans* isomers (only the *trans* isomer is shown in Scheme 2 for clarity). The general synthesis of the complexes **C1–C4** is described in Scheme 1. The corresponding chromophoric ligand precursors **L1– L4** were reacted overnight with the binuclear complex **E1** at 50°C in a 1:1 mixture of dichloromethane (DCM) and methanol. The crude product was then purified by column chromatography on silica gel with dichloromethanemethanol as eluent to give the desired pure compound.

2.2 Molecular structures in the crystal

To verify the structure of the two classes of complexes, the coordination geometries were studied by X-ray diffraction. C2 and C3 were dissolved in dichloromethanemethanol (1:1) and the solvent was slowly evaporated at -18°C, yielding crystals suitable for X-ray diffractometric analysis. The relevant crystal data can be found in Table 1. Figures 2 and 3 clearly indicate that the nitrogen atom of the pyridine from the luminophore [N1 (C2) or N5 (C3)] is coordinated *trans* to the cyclometallating carbon (C36) of the ancillary ligand, whereas the anionic moiety of the luminophore [O4 (C2); N1 (C3)] is coordinated *trans* to the phosphorus of the ancillary ligand (P1). The bite angle of the bidentate luminophoric and ancillary ligands cause a distorted square-planar coordination geometry for the structures of both complexes [C2: O4-Pt1-N1 78.8(1)°, C36-Pt1-P1 80.7(1)°; C3: N1-Pt1-N5 77.6(2)°, C36-Pt1-P1 81.2(2)°]. The Pt-C bond lengths [C2: 2.003(4) Å; C3: 2.015(7) Å] are significantly shorter than the Pt–N bonds [C2: 2.102(3) Å; C3: 2.134(6) Å], indicating a strong trans effect of the cyclometallating, in-plane coordinated phenyl ring due to its strong σ donor character. The same is valid for the second pair of coordinative bonds trans to each other. The carboxylic acid oxygen atom as well as the nitrogen atom of the tetrazole are much closer to the metallic center [C2: 2.070(3) Å; C3: 2.084(6) Å] than the phosphorus atom [C2: 2.142(1) Å; C3: 2.165(2) Å]. The observed metal-ligand bonds and angles are in good agreement with those described for related complexes [51].

2.3 Photophysical characterization

The absorption spectra of **C1–C4** are shown in Fig. 4. Each complex shows two absorption bands, one centered at 225 nm and another band in the range between 320 and



Scheme 2: Preparation of the binuclear Pt(II) complex E1.

	C2	С3
Formula	$C_{49}H_{68}NO_6PPt \cdot 2 CH_3OH$	C ₄₈ H ₆₆ N ₅ O ₃ PPt
Formula weight <i>M</i> ,	1057.19	987.12
Crystal size, mm ³	$0.22 \times 0.16 \times 0.10$	$\textbf{0.15} \times \textbf{0.15} \times \textbf{0.04}$
Temperature, K	223(2)	223(2)
Wavelength/λ, Å	MoK _a /0.71073	MoK _a /0.71073
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /n	Pī
a, Å	12.8655(1)	13.3179(2)
<i>b</i> , Å	25.1730(3)	15.2625(2)
<i>c</i> , Å	16.4476(2)	15.2754(2)
α , deg	90	65.387(1)
eta, deg	92.542(1)	69.850(1)
γ , deg	90	75.049(1)
Volume, ų	5321.5(1)	2626.1(1)
Z	4	2
D _{calcd.} , g cm ⁻³	1.32	1.25
μ (Mo K_{α}), mm ⁻¹	2.7	2.7
F(000), e	2184	1012
Refl. collected	35383	24211
Refl. unique/R _{int}	10436/0.044	9058/0.053
hkl range	±16, -29:31, ±20	-14:15, -16:18, +18
$R1 / wR2 [l > 2 \sigma(l)]$	0.0351/0.0739	0.0524/0.1213
R1/wR2 (all data)	0.0441/0.0793	0.0609/0.1266
Goodness of fit (F ²)	1.067	1.038
$\Delta\! \rho_{\rm max/min}$, e Å-3	0.80/-0.72	0.85/-0.95





Fig. 2: Molecular structure of compound **C2** in the crystal. Displacement ellipsoids are drawn at the 30% probability level, H atoms were omitted for clarity.



Fig. 3: Molecular structure of compound **C3** in the crystal. Displacement ellipsoids are drawn at the 30% probability level, H atoms were omitted for clarity.



Fig. 4: Absorption spectra of complexes C1–C4 in dichloromethane at r. t.

350 nm. Additionally, all complexes show a shoulder around 275 nm.

The bands at high energies and the shoulder at 275 nm can be attributed to ligand-centered (LC) π - π * transitions of the phosphite ligand, whereas the band at 320–350 nm can be assigned to π - π * transitions arising from the chromophoric ligand. The latter is significantly red-shifted upon replacement of the carboxylic moiety

by a tetrazole, as the size of the chromophoric system is increased. Notably, introduction of a OCH₃ substituent on the chromophoric ligand does not significantly change the absorption spectrum of **C2** as compared to **C1** which lets us assume that the OCH₃ group does not significantly affect the frontier orbital gaps for the N[^]O luminophore. In contrast, the absorption of **C4** compared to **C3** is significantly blue shifted, which points to a shift in the HOMO-LUMO gap upon introduction of the OCH₃ moiety.

Emission at room temperature in degassed dichloromethane was not measureable for the complexes, pointing towards fast radiationless deactivation processes such as coupling with solvent molecules or thermal population of dark states. Emission spectra of C1-C4 in frozen glassy matrices of dichloromethane-methanol (1:1) at 77 K are shown in Fig. 5 along with the calculated vibrationally resolved emission spectra. In Table 2, the key photophysical properties of all complexes are shown. The measured spectra show broad, unstructured emission profiles, which can be attributed to excited states with charge-transfer character, whereas the microsecondrange lifetimes are indicative of a clear ³MP-LC character. The emission band of C1, which possesses an electronpoor carboxylate group on the small pyridine-based chromophoric ligand, appears blue-shifted as compared to that of C3 carrying a tetrazolate ring with extended delocalization. However, upon introduction of the OCH, substituent on C1 to yield C2, no significant shift is observed (Table 2). In contrast, introduction of the OCH, substituent to **C3** yielding **C4**, leads to the bluest emission of all complexes, with a maximum peaking at 411 nm. This shows again that the influence of the OCH₃ groups is solely found in complexes with extended luminophores. On the other hand, the introduction of the OCH₃ substituent decreases Φ_L , which can be related to the blue-shift that brings the emissive state energetically closer to dark metal-centered states, which in turn become thermally more accessible.

All the complexes are weakly emissive in doped PMMA, as neat films and as powders, with the notable exception of **C3** which shows an impressively high Φ_L in the amorphous solid state (CIE coordinates: 0.196, 0.251; Fig. 6). It is clear that the luminophore needs to have a significant delocalization, as provided by the tetrazolate unit, and that shorter emission wavelengths are associated with highly energetic excited states that favor the thermal population of dark metal-centered states.

2.4 Density functional theory studies

We have determined the character of the vertical $T_1 \rightarrow S_0$ transition by analyzing the eigenvector of the T_1 de-excitation at the TDDFT optimized T_1 geometry. For all complexes, the transition has an almost pure HOMO–LUMO character, with a weight of at least 81% in all cases, independently of the different ligands and their substituent. Figure 7 also shows that the shape of the HOMO and LUMO orbitals is practically invariant for **C1–C4**.



Fig. 5: Normalized emission spectra at 77 K (solid line) and vibrationally resolved calculated emission spectra of complexes C1–C4 at 77 K (dashed line).

	C1	C2	С3	C4
λ_{abs} , nm	227, 323	226, 321	226, 353	227, 335
$\lambda_{em, 77K}$, nm	427	427	441	411
$\tau_{77K}^{a} \pm 0.5, \mu s$	15.2	15.1	13.1	11.8
$\Phi_{\rm L,neat} \pm 0.02$	< 0.01	< 0.01	0.04	0.01
$\Phi_{\text{L,PMMA}} \pm 0.02$	< 0.01	< 0.01	0.10	0.03
$\Phi_{\rm L,powder} \pm 0.02$	0.03	< 0.01	0.56	0.03

Table 2: Photophysical data of C1–C4.

^aIntensity-weighted average lifetimes.



Fig. 6: Normalized emission spectrum of compound C3 (powder, at room temperature).

The HOMO is associated with the cyclometallating phenyl group and the Pt(II) center, whereas the LUMO is mainly related to the luminophoric ligand. These findings are in agreement with the spectroscopically observed charge-transfer character of the emissive state (vide supra), which can now be confidently ascribed to an inter-ligand charge-transfer excitation mixed with a metal-to-ligand charge-transfer portion that explains the observed phosphorescence. Moreover, the calculations also show that the HOMO energy is only marginally affected by the changes on the luminophoric ligand, whereas the LUMO is destabilized upon replacement of tetrazolate moieties by carboxylate donors and upon insertion of OCH, groups, which in turn widens the HOMO-LUMO gap. The calculated blueshift is larger for tetrazolate-bearing ligands, as already observed in the absorption and emission spectra (vide supra). Actually, no spectroscopic shift is experimentally observed when OCH, units are inserted on picolinate chelators, which points toward the fact that the emissive states cannot be simply described as monoelectronic excitations, even though the calculated trends are in good agreement with the experimental results. Finally, the lack of vibrational progression in the emission spectra at 77 K can be ascribed to the frozen solvent matrix, as opposed to the calculated spectra showing defined vibrational shoulders.



Fig. 7: Visualization of the calculated HOMO and LUMO orbitals of complexes C1–C4 together with the respective orbital energies and HOMO-LUMO gaps.

3 Conclusion

We have reported the synthesis, structural and photophysical characterization of Pt(II) complexes bearing fluorine-free bidentate luminophores and cyclometallating ancillary ligands. The complexes exhibit deep-blue phosphorescence, which can be assigned to mixed ³LC/³MLCT states. We found that the electronic molecular set-screws that enable the tuning of the excited state energies are located on different submolecular units: Variations in the substitution pattern of the luminophoric ligand mainly affect the LUMO, whereas the HOMO could be further adjusted if the ancillary ligand is varied. For instance, introduction of electron withdrawing moieties could stabilize the HOMO, shifting the emission into the near UV. However, further blue-shifts would be associated with fast radiationless deactivation processes that diminish the quantum yields, due to thermal population of dark metalcentered states. Our findings provide useful criteria for the design and realization of fluorine-free phosphorescent dopants for electroluminescent devices with improved stability, and could also be relevant for photocatalysis and light-harvesting units in general.

4 Experimental section

4.1 Synthesis and characterization

As starting materials tris(2,4-di-tert-butylphenyl) phosphite (98%; Sigma-Aldrich, Munich, Germany), K_PtCl (99.95%; ChemPur, Karlsruhe, Germany), and 4-methoxypyridine-2-carbonitrile (98%; abcr. Karlsruhe, Germany) were used as received. The luminophoric ligand precursors L1 (2-picolinic acid, 99%; Sigma-Aldrich, Munich, Germany), L2 (4-methoxy-pyridine-2-carboxylic acid Sigma-Aldrich, Munich, Germany) and L3 (5-(2-pyridyl)-1H-tetrazole, 98%; Alfa Aesar, Karlsruhe, Germany), were commercially available. Column chromatography was performed with silica gel 60 (particle size 35-70 µm, 230-400 mesh, Merck). NMR and mass spectra were measured at the Department of Organic Chemistry, University of Münster. NMR spectra were recorded on an Avance 400 Spectrometer from Bruker Analytische Messtechnik (Karlsruhe, Germany) for ligand precursor L4 and on an DD2 600 spectrometer from Agilent for the Pt(II) complexes. The ¹H NMR chemical shifts (δ) of the signals are given in parts per million (ppm) and referenced to residual protons in the deuterated solvents [D₄]DMSO (2.50 ppm) and [D₅]DCM (5.32 ppm). The ¹⁹⁵Pt NMR chemical shifts are referenced to Na₂PtCl₆, whereas the ³¹P NMR chemical shifts are referenced to phosphoric acid as an external standard. The signal multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (*J*) are given in Hertz. High resolution mass spectrometry (HRMS) was performed via electrospray ionization (ESI) on a Bruker Daltonics MicroTof spectrometer with loop injection.

4.2 Synthesis of 4-methoxy-2-(1*H*-tetrazol-5-yl)pyridine (L4)

4-Methoxypicolinonitrile (776 mg, 5.79 mmol) and NaN (526 mg, 8.11 mmol) were suspended in *n*-butanol (14 mL) and acetic acid (1.37 mL, 23.15 mmol) was added dropwise. The mixture was stirred for 2 h at 80°C. After the mixture had cooled down, the same amount of acetic acid was added, followed by stirring at 80°C overnight. After cooling down, water was added and a white precipitate was formed, which was filtered off, washed with water and dried. The compound was again dissolved in ethyl acetate and absorbed onto silica gel by removing the solvent under reduced pressure. This was loaded onto a column packed with silica gel to perform a column chromatography separation with hexane-ethyl acetate as eluent to get the pure compound L4 as a white solid (748 mg, 73%). – ¹H NMR (400 MHz, [D] DMSO): $\delta = 8.59$ (d, I = 5.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.21 (dd, J = 5.9, 1.6 Hz, 1H), 3.96 (s, 3H). - ¹³C NMR (101 MHz, [D_c]DMSO): δ = 166.58, 154.79, 151.08, 145.21, 112.21, 108.42, 55.99. - HRMS ((+)-ESI; MeOH): m/z = 178.07185 (calcd. 178.07234 for C₂H₀N₂O, [M+H]⁺), 201.05717 (calcd. 201.05644 for C₂H₂N₂ONa, [M+Na]⁺).

4.3 Synthesis of [{Pt-(μ -Cl){ κ^2 -P,C-P(OC₆H₂-2,4-'Bu₂)(OC₆H₃-2,4-'Bu₂)₂] (E1)

Tris(2,4-di-*tert*-butylphenyl) phosphite (934 mg, 1.44 mmol) and K₂PtCl₄ (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%). – HRMS ((+)-ESI; MeOH): m/z = 1791.72042 (calcd. 1791.72005 for C₈₀H_{1/2}Cl₂KO₆P,Pt₂, [M+K]+).

4.4 General synthetic procedure for the preparation of complexes C1–C4

The corresponding ligand precursors L1–L4 (0.228 mmol) and NaOMe (0.228 mmol) were dissolved in dichloromethane-methanol (1:1, 25 mL) and stirred for 30 min. Next, the reaction mixture was degassed intensely before the Pt precursor E1 (0.114 mmol) was added. After the reaction mixture was stirred at 50°C for 12 h in a nitrogen atmosphere, it was cooled down. A small amount of silica gel was added into the reaction vessel and the crude product was absorbed onto silica gel by removing the solvent under reduced pressure. This was loaded onto a column packed with silica gel, and a column chromatographic separation was performed using dichloromethane-methanol as the eluent to give the final product C1–C4 as white solid.

4.4.1 C1

Yield: 31%. – ¹H NMR (600 MHz, $[D_2]DCM$): δ = 8.68 (d, J = 5.3 Hz, 1H), 8.16–8.12 (m, 1H), 8.07 (td, J = 7.7, 1.5 Hz, 1H), 7.77 (t, J = 2.3 Hz, 1H), 7.60 (dd, J = 8.6, 1.6 Hz, 2H), 7.48 (ddd, J = 7.5, 5.4, 1.5 Hz, 1H), 7.44–7.39 (m, 2H), 7.14 (t, J = 2.2 Hz, 1H), 7.04 (dd, J = 8.6, 2.5 Hz, 2H), 1.53 (s, 18H), 1.39 (s, 9H), 1.23 (s, 18H), 1.11 (s, 9H). – ³¹P NMR (243 MHz, $[D_2]DCM$): δ = 90.24 (d, J = 6926.8 Hz). – ¹⁹⁵Pt NMR (128 MHz, $[D_2]DCM$): δ = -4152.40 (d, J = 6937.4 Hz). – HRMS ((+)-ESI; MeOH): m/z = 963.44227 (calcd. 963.44034 for $C_{48}H_{67}NO_5PPt$, $[M+H]^+$), 985.42408 (calcd. 985.42228 for $C_{48}H_{66}NO_5PPtNa$, $[M+Na]^+$).

4.4.2 C2

Yield: 35%. – ¹H NMR (600 MHz, [D₂]DCM): δ = 8.45 (d, *J* = 6.3 Hz, 1H), 7.77 (t, *J* = 2.1 Hz, 1H), 7.65 (d, *J* = 2.9 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.42 (s, 2H), 7.14 (t, *J* = 2.0 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.4 Hz, 2H), 6.93 (dd, *J* = 6.2, 2.9 Hz, 1H), 3.96 (s, 3H), 1.54 (s, 18H), 1.40 (s, 9H), 1.25 (s, 18H), 1.12 (s, 9H). – ³¹P NMR (243 MHz, [D₂]DCM): δ = 90.16 (d, *J* = 6963.3 Hz). – ¹⁹⁵Pt NMR (128 MHz, [D₂]DCM): δ = -4167.59 (d, *J* = 6973.4 Hz). – HRMS ((+)-ESI; MeOH): *m*/*z* = 993.45150 (calcd. 993.45091 for C₄₉H₆₉NO₆PPt, [M+H]⁺), 1015.43322 (calcd. 1015.4330 for C₄₉H₆₈NO₅PPtNa, [M+Na]⁺).

4.4.3 C3

Yield: 29%. – ¹H NMR (600 MHz, $[D_2]DCM$): δ = 9.03 (t, *J* = 1.8 Hz, 1H), 8.99 (d, *J* = 5.5 Hz, 1H), 8.36–8.32 (m, 1H), 8.11

(td, *J* = 7.8, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.43– 7.40 (m, 2H), 7.39 (ddd, *J* = 7.1, 5.6, 1.4 Hz, 1H), 7.19 (t, *J* = 2.1 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.5 Hz, 2H), 1.55 (s, 18H), 1.46 (d, *J* = 0.5 Hz, 9H), 1.22 (d, *J* = 0.6 Hz, 19H), 1.12 (s, 9H). $-^{31}$ P NMR (243 MHz, [D₂]DCM): δ = 96.88 (d, *J* = 6581.5 Hz). $-^{195}$ Pt NMR (128 MHz, [D₂]DCM): δ = -4270.80 (d, *J* = 6570.1 Hz). - HRMS ((+)-ESI; MeOH): *m/z* = 987.46676 (calcd. 987.46275 for C₄₈H₆₆N₅O₃PPt, [M+H]⁺), 1009.44891 (calcd. 1009.44470 for C₄₈H₆₆N₅O₃PPtNa, [M+Na]⁺).

4.4.4 C4

Yield: 28%. – ¹H NMR (600 MHz, $[D_2]DCM$): δ = 9.01 (t, 1H), 8.73 (d, *J* = 6.4 Hz, 1H), 7.82 (d, *J* = 2.8 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.41 (dd, *J* = 2.4, 1.3 Hz, 2H), 7.17 (t, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.5 Hz, 2H), 6.83 (dd, *J* = 6.5, 2.9 Hz, 1H), 4.00 (s, 3H), 1.54 (s, 18H), 1.46 (s, 9H), 1.22 (s, 18H), 1.12 (s, 9H). – ³¹P NMR (243 MHz, $[D_2]$ DCM): δ = 97.02 (d, *J* = 6600.3 Hz). – ¹⁹⁵Pt NMR (128 MHz, $[D_2]DCM$): δ = -4278.58 (d, *J* = 6607.6 Hz). – HRMS ((+)-ESI; MeOH): *m*/*z* = 1017.47675 (calcd. 1017.47333 for C₄₉H₆₉N₅O₄PPt, $[M+H]^+$), 1039.45838 (calcd. 1039.45527 for C₄₉H₆₈N₅O₄PPtNa, $[M+Na]^+$).

4.5 X-ray diffractometry

The crystallographic data of **C2** and **C3** (Table 1) were collected on a rotating anode Nonius κ -CCD diffractometer with Montel mirror-monochromatized MoK_a radiation ($\lambda = 0.71073$ Å) by using an ω - φ scan method at 223(2) K. Programs used: data collection Collect [69]; data reduction DENZO-SMN [70]; absorption corrections were applied using multi-scan techniques, DENZO [71]; the structures were solved by Direct Methods and refined by full-matrix least-squares techniques using the program SHELXL-97 [72]; graphics were done with XP [73]. The non-hydrogen atoms of the compounds were refined anisotropically. The hydrogen atoms attached to carbon atoms were generated geometrically.

Exceptions and special features: Compound **C2** contains in the asymmetric unit tree *tert*-butyl groups and two methanol molecules disordered over two positions. For compound **C3** four *tert*-butyl groups were found to be disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. A badly disordered (probably) methanol molecule was found in the asymmetrical unit and could not be satisfactorily refined. The routine SQUEEZE in PLATON [74] was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters do not include the squeezed solvent molecule.

CCDC 1435528 (**C2**) and 1435529 (**C3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4.6 Photophysical characterization

Absorption spectra were measured on a Varian Cary 5000 double-beam UV/Vis-NIR spectrometer and baseline-corrected. Steady-state excitation and emission spectra were recorded on a FluoTime300 spectrometer from PicoQuant equipped with a 300 W ozone-free Xe lamp (250-900 nm), a 10 W Xe flash lamp (250-900 nm, pulse width $< 10 \ \mu s$) with repetition rates of 0.1– 300 Hz, an excitation monochromator (Czerny-Turner 2.7 nm mm⁻¹ dispersion, 1200 grooves mm⁻¹, blazed at 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm mm¹ dispersion and 1200 grooves mm⁻¹, or blazed at 1250 nm with 5.4 nm mm⁻¹ dispersion and 600 grooves mm⁻¹), Glan-Thompson polarizers for excitation (Xe lamps) and emission, a Peltier-thermostatized sample holder from Quantum Northwest (-40 to 105°C), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 300–720 nm). Steady-state and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps). Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. Lifetime analysis was performed using the commercial FluoFit software. The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals and their autocorrelation. 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 multi-channel analyzer, integrating sphere and employing U6039-05 $\Phi_{\rm r}$ measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade.

4.7 Density functional theory

The DFT calculations were performed with the GAUSSIAN 09 package [75] using the PBE0 hybrid exchange-correlation functional [76]. The SDD basis set [77] was employed for all elements with the exception of phosphorus, which was described by the 6-31G* basis set. Vibrationally resolved emission spectra at 77 K were calculated with the Franck-Condon method [78]. For this purpose, the S_o ground state and T₁ excited state geometries were optimized using standard Kohn-Sham DFT with multiplicity 0 and 1, respectively. To plot the emission spectrum, each vibronic line was represented by a Gaussian with half width at half maximum of 300 cm⁻¹. To determine the character of the $T_1 \rightarrow S_0$ transition, TDDFT calculations were carried out at the TDDFT-optimized T₁ geometry. The molecular orbitals at the T₁ geometry were visualized using the VMD program [79]

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