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# Metal Cation Induced Modulation of the Photophysical Properties of a Platinum(II) Complex Featuring a Dipicolylanilino–Acetylide Ligand

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**Keywords:** Platinum / Luminescence / Cations / Alkyne ligands

We report the synthesis of a new, luminescent, cyclometalated platinum complex **1** incorporating a bis(2-picoly)anilino (DPA) group. The complex has the form  $\text{LPt-C}\equiv\text{C-C}_6\text{H}_4\text{-N}(\text{CH}_2\text{py})_2$ , where L is a  $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ -coordinating ligand based on phenylbipyridine. The ground-state absorption and excited-state luminescence of complex **1** are modulated by the

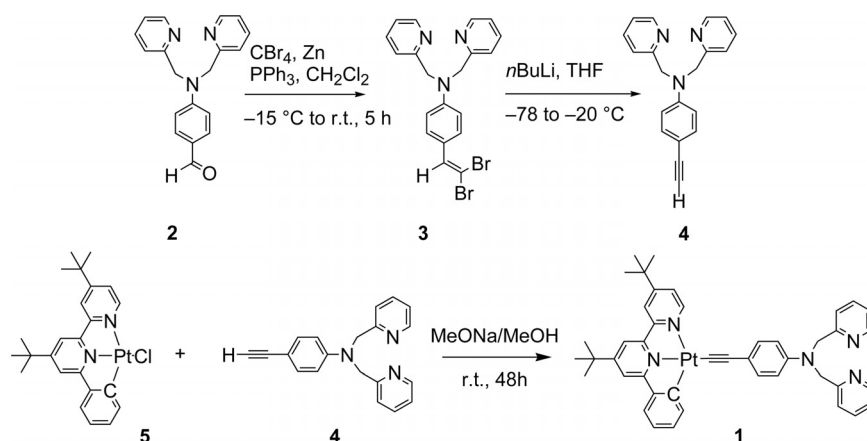
binding of selected divalent metal ions ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$ ) to the DPA unit; the extent of the observed changes are dependent upon the identity of the metal ion. In particular, binding of  $\text{Zn}^{2+}$  leads to a substantial enhancement in the emission intensity.

## Introduction

The past decade has witnessed a rapid development in new luminescent cyclometalated platinum(II) complexes for potential device applications as a result of the tunable optical properties of these complexes.<sup>[1]</sup> The interest in these cyclometalated complexes is also motivated by their potential use as molecular reporters for chemosensing applications.<sup>[2]</sup> Among platinum complexes, acetylide derivatives<sup>[3]</sup> are of interest due to the facile access of functionalized terminal

alkynes, opening a way to new systems containing a diversity of host receptors.<sup>[4]</sup>

Our group has been investigating the chemistry and excited states of acetylide–Pt complexes of the form  $\text{LPt-C}\equiv\text{C-R}$ , where L is the  $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ -coordinating ligand 6-phenyl-4,4'-bis(*tert*-butyl)-2,2'-bipyridine (*t*Bu<sub>2</sub>-phbpy). The incorporation of receptor units into the acetylide ligand allows modulation of their emissive properties by ion binding. We have shown dramatic changes in their photophysical properties, leading to unprecedented behavior. For



Scheme 1.

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example, a switch from phosphorescence to fluorescence occurs upon addition of lead(II) cations to such a complex incorporating a flavone receptor R.<sup>[5]</sup> In contrast, binding of lead(II) cations to a pyridyl-based macrocyclic receptor R induces a change in the direction of the charge transfer for the lowest-energy excited state.<sup>[6]</sup> We decided to extend this design strategy to a nitrogen-based host receptor, the

bis(2-picolyl)anilino (DPA) group. This receptor has been widely used for detection of divalent metal cations (e.g.,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ )<sup>[7]</sup> and was recently incorporated into luminescent  $\text{Re}^{[8]}$  and cationic  $\text{Ir}^{[9]}$  complexes in which a 2,2'-bipyridine ligand is connected to the receptor by either a vinyl or an ethynyl  $\pi$  linker. Herein, we report the design and synthesis of a novel platinum(II) acetylide complex  $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N}-t\text{Bu}_2\text{-phbpy})\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-N}(\text{CH}_2\text{py})_2$  (**1**; Scheme 1). The nitrogen-based receptor unit binds various metal cations in solution ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$ ), which is accompanied by distinctive changes in the optical properties, according to the identity of the metal ion.

## Results and Discussion

Free alkyne derivative  $\text{HC}\equiv\text{C-DPA}$  **4** was synthesized from bis(2-pyridylmethyl)aniline aldehyde **2**, which was prepared according to previously published procedures (Scheme 1).<sup>[7a]</sup>

Treatment of **2** with  $\text{CBr}_4$  in the presence of zinc dust and  $\text{PPh}_3$  afforded dibromide **3**, which was subsequently converted into terminal alkyne **4** in 35% yield by using  $n\text{BuLi}$  (2 equiv.) in THF at  $-78^\circ\text{C}$ . Complex **1** was then prepared by treatment of the chloridoplatinum precursor  $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N}-t\text{Bu}_2\text{-phbpy})\text{Cl}$  (**5**)<sup>[3b]</sup> with **4** in the presence of sodium methoxide in methanol at room temperature. This alternative method to the classical ligand metathesis conditions avoids the use of  $\text{Cu}^{\text{I}}$  salts, which could lead to undesirable coordination by the DPA receptor.<sup>[7g]</sup>

The electronic absorption spectrum of **1** in acetonitrile solution exhibits intense absorption bands at 250–380 nm and less intense bands at 390–560 nm (Table 1 and Figure 1). With reference to previous spectroscopic work on platinum(II) phenylbipyridyl complexes,<sup>[3b]</sup> the high-energy intense absorption bands are assigned to intraligand (IL) transitions of the phenylbipyridine and alkynyl ligands  $\{\text{IL}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N}) + \text{IL}'(-\text{C}\equiv\text{C}-\text{Ar}), \pi \rightarrow \pi^*\}$ . The broad band into the visible region at 390–560 nm seems to be composed of two main transitions at  $\lambda = 425$  and  $475$  nm. The former can be tentatively assigned to a  $[\text{d}(\text{Pt}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})]$  metal-to-ligand charge-transfer transition (MLCT), whereas the lower-energy component band is attributed to a  $[\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})]$  ligand-to-ligand charge-transfer (L'LCT) transition from the amino-substituted acetylide to the phenylbipyridine  $\pi^*$  orbitals.<sup>[3b]</sup> The tail of this superimposed MLCT/L'LCT-based absorption band extends up to 600 nm, substantially beyond that generally observed for unsubstituted platinum(II) phenylacetylide complexes ( $\lambda_{\text{onset}} = 520$  nm),<sup>[3b]</sup> showing the influence of the strongly donating DPA group.

Complex **1** shows very weak emission ( $\Phi_{\text{lum}} = 0.003$ ) centered at 550 nm upon excitation at 450 nm in acetonitrile solution at 298 K (Table 1). This behavior contrasts with that of most other cyclometalated platinum(II) acetylide complexes, which are known to be efficient <sup>3</sup>MLCT emitters, typically exhibiting quite intense luminescence in the range 550–700 nm.<sup>[3b]</sup> The incorporation of the electron-do-

Table 1. Absorption data and luminescence lifetimes for complex **1** in acetonitrile solution and in the presence of selected metal ions ( $>10$  equiv.) together with the relative emission intensity.

	$\lambda_{\text{max}}$ [nm] ( $\epsilon$ , $\text{L mol}^{-1} \text{cm}^{-1}$ ) <sup>[a]</sup>	$\tau$ [ns] <sup>[b]</sup>	$I_{\text{rel}}$ <sup>[c]</sup>
<b>1</b>	295 (36900), 425 (5300), 475 (5000)	220 <sup>[d,e]</sup>	1
$\text{Zn}^{2+}$	295 (40600), 415 (6150)	(60) <sup>[f]</sup> , 460	8.1
$\text{Cd}^{2+}$	295 (40600), 415 (6200)	(50) <sup>[f]</sup> , 550	5.0
$\text{Pb}^{2+}$	295 (43000), 425 (6400)	90	1.3
$\text{Ni}^{2+}$	295 (43600), 425 (6300)	— <sup>[g]</sup>	0.5

[a] In  $\text{CH}_3\text{CN}$  at  $298 \pm 3$  K. [b] In degassed solution; estimated uncertainty in  $\tau$  is  $\pm 15\%$ . [c] Relative intensity of emission setting the value for the free complex to be 1. [d] Corresponding value in air-equilibrated solution is 70 ns. [e] The lifetime of **1** at 77 K in a solution of diethyl ether/isopentane/ethanol (2:2:1) is 12  $\mu\text{s}$ . [f] Minor short-lived component. [g] Intensity too weak for lifetime to be determined.

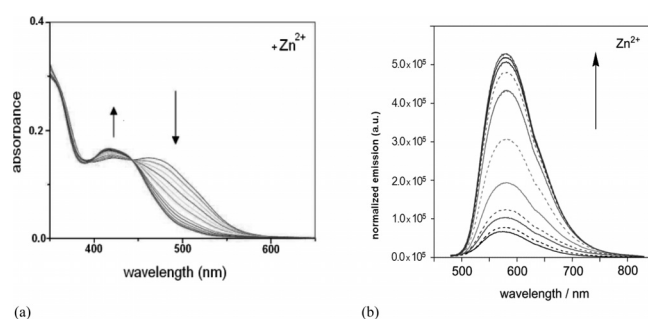


Figure 1. (a) Absorption spectral changes of **1** ( $[\mathbf{1}] = 2.95 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ , 298 K) with  $\text{Zn}(\text{ClO}_4)_2$  ( $[\text{Zn}(\text{ClO}_4)_2] = 2.30 \times 10^{-3}$  M, 1  $\mu\text{L}$  added each time) as a function of  $\text{Zn}^{2+}$  concentration (0 to 10 equiv.). (b) Variation in the emission spectrum of **1** upon addition of  $\text{Zn}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$  solvent;  $[\mathbf{1}] = 2.4 \times 10^{-5}$  M; (3 mL)  $[\text{Zn}(\text{ClO}_4)_2] = 1.2 \times 10^{-3}$  M, addition 8  $\mu\text{L}$  each time. Excitation at  $\lambda = 445$  nm (isosbestic point).

nating amino group increases the contribution of L'LCT to the excited state, which can explain the observed weak emission of **1**.<sup>[4d,10,11]</sup>

The cation-binding properties of **1** were studied by electronic absorption and luminescence spectroscopy. A range of metal ions were screened as their perchlorate salts:  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ . Addition of up to 50 equiv. of  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  to a solution of **1** in acetonitrile did not lead to any change in its absorption spectrum. However, addition of  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Pb}^{2+}$  cations resulted in significant changes in the absorption spectrum (e.g., Figure 1 shows the evolution of the spectrum upon addition of  $\text{Zn}^{2+}$ ). As these metallic salts were added to the solution, the absorption band at 475 nm strongly decreases, accompanied by a weak augmentation of the band centered at 415 nm. In all cases, well-defined isosbestic points are observed, suggestive of a ground-state equilibrium of free **1** and cation-complexed species in solution. Binding constants ( $\log K$ ) in the range from  $5.7 \pm 0.1$  ( $\text{Ni}^{2+}$ ) to  $6.7 \pm 0.3$  ( $\text{Pb}^{2+}$ ) were determined from these plots, corresponding to 1:1 stoichiometries (Table 2).

Table 2. Calculated stability constants ( $\log K_s$ )<sup>[a]</sup> for complexation of metallic salts ( $\text{ClO}_4^-$  salts) with **1** in acetonitrile solution at 298 K.

Metal cation	$\log K_s$ absorption	$\log K_s$ emission <sup>[b]</sup> { $\lambda_{\text{exc}}$ , nm}
$\text{Zn}^{2+}$	6.7 ( $\pm 0.5$ )	2.5 ( $\pm 0.6$ ) {470}
$\text{Pb}^{2+}$	6.7 ( $\pm 0.3$ )	3.5 ( $\pm 0.6$ ) {445}
$\text{Ni}^{2+}$	5.7 ( $\pm 0.1$ )	n.d.
$\text{Cd}^{2+}$	6.5 ( $\pm 0.4$ )	2.8 ( $\pm 0.3$ ) {440}

[a] Complexation ratio of 1:1. [b] Measured in degassed MeCN.

These absorption spectral changes are consistent with coordination of the metal ions at the DPA unit. They can be explained by the weakening of the L'LCT contribution due to complexation of the metal cation at the amino group, whereas the MLCT band appears to be weakly affected, and a small  $\approx 10$ -nm blueshift is observed. In line with this explanation, a comparable shift in the absorption spectrum to higher energy was observed upon addition of trifluoroacetic acid to a solution of **1** in  $\text{CH}_3\text{CN}$ , reflecting the protonation of the anilino nitrogen atom.

Upon addition of  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$  cations in  $\text{CH}_3\text{CN}$  at 298 K, the luminescence intensity of **1** gradually increases upon excitation at the isosbestic wavelength. Figure 1b illustrates the changes in emission intensity of complex **1** in acetonitrile upon addition of  $\text{Zn}^{2+}$  ions. After the addition of 10 equiv. of  $\text{Zn}^{2+}$ , the emission intensity of **1** exhibited an eightfold enhancement ( $I/I_0$ ). This is indicative of the formation of a new emissive metal-cation-complexed species **1**- $\text{Zn}^{2+}$ . A longer component is observed in the decay kinetics of the zinc-complexed compound compared to **1**. This observation suggests that the enhancement in emission intensity in the presence of zinc is due to a reduction in the nonradiative decay pathways. Such an effect would indeed be expected to result from an increase in the energy of the deactivating  $^3\text{L'LCT}$  state, in line with that observed in the UV/Vis data under these conditions, as its ability to act as a deactivating pathway for the excited state becomes reduced.

Binding constants ( $\log K_s$ ; Table 2) corresponding to 1:1 stoichiometries with  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were determined from the emission data (Table 1). The significantly lower affinity of **1** for these cations in the excited state compared to the ground state, by four orders of magnitude, can be attributed to a strong decrease in electron density in the DPA unit in the excited state, through the anilino nitrogen atom. This is consistent with the involvement of the low-lying excited L'LCT state.

Similar behavior of **1** was observed in the presence of 10 equiv. of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  but with a 5.0- and 1.3-fold enhancement, respectively (Figures 2b and 3b). In contrast, addition of  $\text{Ni}^{2+}$  gives rise to a decrease in the initial luminescence intensity of **1** (Figure 4). We can consider different types of coordination: bidentate in which the two pyridyl groups are involved or terdentate including the tertiary amine. The differences in the enhancement in the luminescence intensity could reflect the differences in the binding mode of these metal cations with the DPA unit. For electronic reasons, a strong interaction of the metal cation with the tertiary amine in the excited state would induce a high

enhancement in the luminescence,<sup>[4d,12]</sup> as is the case for  $\text{Zn}^{2+}$ , whereas the interaction with the pyridine groups may be predominant for the softer metal ions. The decrease in luminescence observed with  $\text{Ni}^{2+}$  may arise from an electron-transfer quenching pathway, as the DPA unit is clearly not able to induce the square-planar conformation that would be required for electron spin pairing. It is also probable that the  $\text{Ni}^{2+}$ -based d-d states will be sufficiently low in energy to quench the emission through energy transfer.

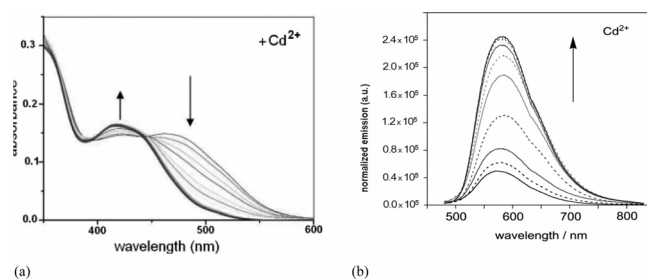


Figure 2. (a) Absorption spectral changes of **1** ( $[\text{I}] = 2.95 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ , 298 K) with  $\text{Cd}(\text{ClO}_4)_2$  ( $[\text{Cd}(\text{ClO}_4)_2] = 2.30 \times 10^{-3}$  M, 1  $\mu\text{L}$  added each time) as a function of  $\text{Cd}^{2+}$  concentration (0 to 10 equiv.). (b) Variation in the emission spectrum of **1** upon addition of  $\text{Cd}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$  solvent;  $[\text{I}] = 3.25 \times 10^{-4}$  M; (3 mL)  $[\text{Cd}(\text{ClO}_4)_2] = 1.1 \times 10^{-3}$  M, addition 6  $\mu\text{L}$  each time. Excitation at  $\lambda = 440$  nm (isosbestic point).

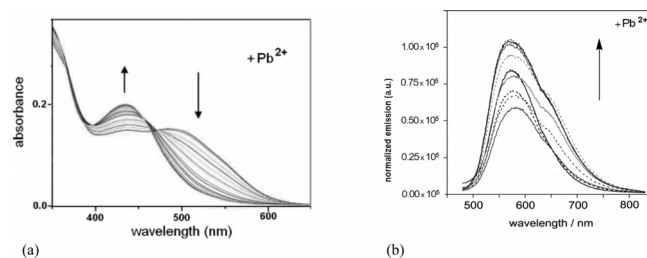


Figure 3. (a) Absorption spectral changes of **1** ( $[\text{I}] = 2.95 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ , 298 K) with  $\text{Pb}(\text{ClO}_4)_2$  ( $[\text{Pb}(\text{ClO}_4)_2] = 2.3 \times 10^{-3}$  M, 1  $\mu\text{L}$  added each time) as a function of  $\text{Pb}^{2+}$  concentration (0 to 10 equiv.). (b) Variation in the emission spectrum of **1** upon addition of  $\text{Pb}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$  solvent;  $[\text{I}] = 3.25 \times 10^{-4}$  M; (3 mL)  $[\text{Pb}(\text{ClO}_4)_2] = 1.4 \times 10^{-3}$  M, addition 6  $\mu\text{L}$  each time. Excitation at  $\lambda = 470$  nm (isosbestic point).

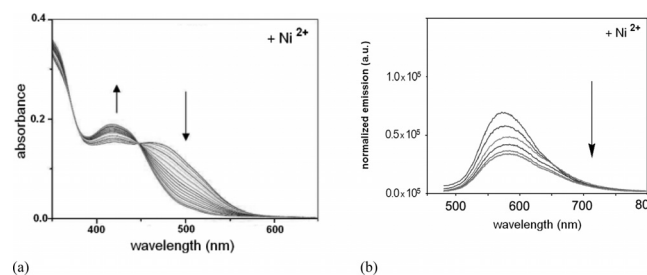


Figure 4. (a) Absorption spectral changes of **1** ( $[\text{I}] = 2.95 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ , 298 K) with  $\text{Ni}(\text{ClO}_4)_2$  ( $[\text{Ni}(\text{ClO}_4)_2] = 2.30 \times 10^{-3}$  M, 1  $\mu\text{L}$  added each time) as a function of  $\text{Ni}^{2+}$  concentration (0 to 10 equiv.). (b) Variation in the emission spectrum of **1** upon addition of  $\text{Ni}(\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$  solvent;  $[\text{I}] = 3.25 \times 10^{-4}$  M; (3 mL)  $[\text{Ni}(\text{ClO}_4)_2] = 1.2 \times 10^{-3}$  M, addition 8  $\mu\text{L}$  each time. Excitation at  $\lambda = 445$  nm (isosbestic point).



## Conclusions

In the present study, we have synthesized an original cyclometalated platinum complex bearing an acetylide ligand substituted with a bis(2-picolyl)amino group. This nitrogen-based receptor acts as a strong ligand for  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  ions. The observed photophysical changes in **1** upon ion binding reflect the differences in the binding modes of these metal cations with the DPA unit. The design concept employed suggests that novel future strategies for sensing of important metal ions based on perturbations in the phosphorescence of third-row transition-metal complexes could realistically be established. For example, it can be envisaged that the significantly longer lifetimes of complexes such as those reported here, compared to the fluorescence of biomolecules in cells and tissues, could allow time-gated procedures to be used to detect zinc ions, in which interference from background emission is eliminated.<sup>[13]</sup>

## Experimental Section

**General Procedure:** All manipulations were performed by using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. Compound **2** was synthesized following the reported procedure<sup>[9b]</sup> and NMR spectra were recorded with Bruker DPX-200, AV 300, or AV 500 MHz spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are given vs.  $\text{SiMe}_4$  and were determined by reference to residual  $^1\text{H}$  and  $^{13}\text{C}$  solvent signals. Assignments of carbon atoms were based on HMBC, HMQC, and COSY experiments. Elemental analyses and high-resolution mass spectra were performed with a MS-MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. UV/Vis absorption spectra were recorded by using a UVIKON 9413 or Biotek Instruments XS spectrophotometer by using quartz cuvettes of 1-cm pathlength. Steady-state luminescence spectra were measured in degassed solution by using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. Luminescence quantum yields were determined by using the method of continuous dilution, using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  as the standard ( $\Phi = 0.028$  in air-equilibrated aqueous solution) and correcting for the refractive index. Emission lifetimes were measured by time-correlated single-photon counting (TCSPC) following excitation at 374.0 nm with an EPL-375 pulsed diode laser. The emitted light was detected at 90° by using a Peltier cooled R928 PMT after passage through a monochromator. The stoichiometry and complexation constants were determined by global analysis of the evolution of all absorption and fluorescence spectra by using Specfit Global analysis system V3.0 for 32-bit Windows system.<sup>[14]</sup>

**CAUTION!** Perchlorate salts are potentially explosive and should be handled with care.

**Synthesis of 3:** Zinc dust (237 mg, 3.63 mmol) and  $\text{CBr}_4$  (1.204 g, 3.63 mmol) were placed in a Schlenk tube and  $\text{CH}_2\text{Cl}_2$  (5 mL) was added slowly. The mixture was stirred at  $-15^\circ\text{C}$  for 15 min. Then,  $\text{PPh}_3$  (950 mg, 3.63 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added, and stirring was continued for 30 min at  $-15^\circ\text{C}$ . A solution of 4-{bis[(pyridin-2-yl)methyl]amino}benzaldehyde (**2**; 500 mg, 1.65 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was then added, and stirring was continued for 3 h at room temperature. Afterwards, the reaction mixture was treated with  $\text{HCl}$  (1N, 5 mL), and the aqueous phase was treated with saturated  $\text{K}_2\text{CO}_3$ . Compound **3** was extracted with

dichloromethane ( $3 \times 50$  mL). The extracts were filtered and evaporated under reduced pressure. Chromatography ( $\text{Et}_2\text{O}/\text{MeOH}$ , 95:5) gave **3** (480 mg, 65% yield) as a white powder.  $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{N}_3$  (458.95); calcd. C 52.31, H 3.73, N 9.15; found C 52.65, H 3.76, N 9.15. HRMS: calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_3^{79}\text{Br} [\text{M}]^+$  378.06058; found 378.0615.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.61 (d,  $^3J$  = 4.0 Hz, 2 H), 7.66 (ddd,  $^3J$  = 6.0, 4.0 Hz,  $^4J$  = 1.0 Hz, 1 H), 7.45 (d,  $J$  = 8.0 Hz, 2 H), 7.25 (m, 5 H,  $\text{H}_{\text{arom}}$  and  $\text{CH}=\text{C}$ ), 4.86 (s, 4 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.6, 150.2, 148.7, 137.3, 136.7, 130.3, 124.4, 122.6, 121.2, 112.4, 85.2, 57.6 ppm.

**Synthesis of 4:** To a solution of **3** (1 g, 2.2 mmol) in dry THF (10 mL) at  $-78^\circ\text{C}$  was dropwise added  $n\text{BuLi}$  (1.6 M in hexane, 3 mL, 4.8 mmol). After stirring for 3 h at  $-10^\circ\text{C}$ , the mixture was hydrolyzed with brine (50 mL) and warmed to room temperature, before being extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. The residue was then purified by column chromatography ( $\text{SiO}_2$ ;  $\text{MeOH}/n\text{-pentane}/\text{Et}_2\text{O}$ , 1:19:80) to give **4** (220 mg, 35% yield) as a white powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.62 (d,  $^3J$  = 4.0 Hz, 2 H), 7.65 (ddd,  $^3J$  = 7.8, 7.7 Hz,  $^4J$  = 1.6 Hz, 1 H), 7.24 (m, 6 H), 6.65 (d,  $J$  = 9.0 Hz, 2 H), 4.86 (s, 4 H), 2.96 (s, 1 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.6, 150.3, 148.8, 137.3, 133.9, 122.6, 121.1, 112.6, 110.5, 75.6, 57.6 ppm. HRMS: calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_3 [\text{M}]^+$  299.14225; found 299.1402.

**Synthesis of 1:** In a Schlenk tube, 4-ethynyl[bis(2-pyridinylmethyl)amino]benzene (**4**; 50 mg, 0.17 mmol) was added to a solution of  $\text{NaOMe}$  obtained from  $\text{NaH}$  (93 mg, 2.50 mmol) in anhydrous  $\text{MeOH}$  (10 mL) at  $0^\circ\text{C}$ . The solution was degassed by a freeze-pump-thaw cycle, then  $[\text{Pt}(\text{tBu}_2\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}]$  (115 mg, 0.20 mmol) was added, and the solution was stirred at room temperature for 48 h. Brine (20 mL) was added, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  mL). The organic layer was dried with  $\text{MgSO}_4$ , and the solvents were removed under vacuum. Column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95:5) yielded **1** as a red oily solid (42 mg, 25% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.15 (d,  $^3J$  = 5.7 Hz, 1 H,  $\text{H}^{6\text{py}}$ ), 8.61 (m, 2 H,  $\text{H}^6$ ), 8.04 (dd,  $^3J$  = 7.5 Hz,  $^4J$  = 1.1 Hz, 1 H,  $\text{H}^{6\text{ph}}$ ), 7.82 (d,  $^4J$  = 1.7 Hz, 1 H,  $\text{H}^{3\text{py}}$ ), 7.65 (ddd,  $^3J$  = 7.7 Hz,  $^4J$  = 1.8 Hz, 2 H,  $\text{H}^4$ ), 7.59 (d,  $^4J$  = 1.3 Hz, 1 H,  $\text{H}^{3\text{py}*}$ ), 7.57 (d,  $^4J$  = 1.3 Hz, 1 H,  $\text{H}^{5\text{py}*}$ ), 7.54 (dd,  $^3J$  = 5.7 Hz,  $^4J$  = 1.9 Hz, 1 H,  $\text{H}^{5\text{py}}$ ), 7.41 (m, 3 H,  $\text{H}^{\text{meta}}$  and  $\text{H}^{3\text{ph}}$ ), 7.31 (m, 2 H,  $\text{H}^3$ ), 7.19 (m, 2 H,  $\text{H}^5$ ), 7.16 (ddd,  $^3J$  = 7.4 Hz,  $^4J$  = 1.4 Hz, 1 H,  $\text{H}^{4\text{ph}}$ ), 7.06 (ddd,  $^3J$  = 7.4 Hz,  $^4J$  = 1.3 Hz, 1 H,  $\text{H}^{5\text{ph}}$ ), 6.66 (m, 2 H,  $\text{H}^{\text{ortho}}$ ), 4.85 (s, 2 H,  $\text{CH}_2$ ), 1.46 (s, 9 H,  $\text{tBupy}$ ), 1.44 (s, 9 H,  $\text{tBupy*}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.3 ( $\text{C}^{6\text{py}*}$ ), 163.3 ( $\text{C}^{4\text{py}}$ ), 163.1 ( $\text{C}^{4\text{py}*}$ ), 159.1 ( $\text{C}^2$ ), 158.1 ( $\text{C}^{2\text{py}}$ ), 154.4 ( $\text{C}^{2\text{py}*}$ ), 151.6 ( $\text{C}^{6\text{py}}$ ), 149.6 ( $\text{C}^6$ ), 147.1 ( $\text{C}^{2\text{ph}}$ ), 145.7 ( $\text{C}^{\text{ipso}}$ ), 142.7 ( $\text{C}^{1\text{ph}}$ ), 138.7 ( $\text{C}^{6\text{ph}}$ ), 136.8 ( $\text{C}^4$ ), 132.8 ( $\text{C}^{\text{para}}$  and  $\text{C}^{4\text{ph}}$ ), 124.4 ( $\text{C}^{5\text{py}}$ ), 124.0 ( $\text{C}^{3\text{ph}}$ ), 123.3 ( $\text{C}^{5\text{ph}}$ ), 122.0 ( $\text{C}^5$ ), 121.0 ( $\text{C}^3$ ), 119.0 ( $\text{C}^{3\text{py}}$ ), 115.4 ( $\text{C}^{3\text{py}*}$ ), 114.3 ( $\text{C}^{5\text{py}*}$ ), 112.3 ( $\text{C}^{\text{ortho}}$ ), 112.3 ( $\text{C}^{\text{B}}$ ), 106.2 ( $\text{C}^{\text{a}}$ ), 57.3 ( $\text{CH}_2$ ), 36.0, 35.7, 30.6, 30.4 ( $\text{tBupy}$ ) ppm.  $\text{C}_{44}\text{H}_{43}\text{N}_5\text{Pt} \cdot \text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$  (896.90) calcd. C 59.56, H 5.17, N 7.80; found C 59.64, H 4.961, N 7.85. HRMS: calcd. for  $\text{C}_{44}\text{H}_{43}\text{N}_5\text{PtNa} [\text{M} + \text{Na}]^+$  858.130430; found 858.3026.

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- [10] Alternatively, a second explanation can be proposed for the lack of luminescence of **1**, as already reported for related complexes bearing an amino substituent: this behavior can result from an efficient photoinduced electron transfer (PET) quenching of the MLCT/LCT excited state by the lone pair electrons of the nitrogen atom of the DPA.<sup>[11]</sup> In such a case, the increase in the luminescence intensity could be explained by the coordination of M<sup>2+</sup>, which involves the lone pair and thus inhibits the PET process.
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