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Cyclometalated Pt(II) complex with bidentate Schiff-base ligand displaying unexpected cis/trans isomery: synthesis, structures and electronic properties.

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Square planar platinum complexes are an important class of compounds used in (nano)technology, optoelectronics, medicinal chemistry and catalysis. The major research interests in cyclometalated Pt(II) complexes focus on the selective modulation of their electronic properties and the control of the (cis/trans) geometry. For the first time, we unveil and demonstrate that *cis-trans* isomers of Pt(II) complex can be obtained in a derivative carring the 1-phenyl-pirazolate (H*ppz*) and 2-hydroxy-1-naphtyl-(N-phenyl)imine ligands. The two isomers display significant differences in both optical and electronic properties. While luminescence is quenched in solution, they are brightly emissive in PMMA matrix at room temperature and in 2MeTHF rigid matrix at 77 K. The phosphorescent emission of the *cis* isomer, blue-shifted compared to that of the *trans* one, results from the significantly different trans influence of the ppz ligand. Theoretical investigation highlights the almost isoenergetic potential energy of the two isomers therefore explaining their formation and evidences a large geometry distortion of their triplet state, which should be responsible of the observed luminescence efficiency.

Introduction

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Luminescent d⁶ and d⁸ metal complexes, containing π conjugated ligands with N and/or C donor atoms, have attracted widespread research interest. Their excellent properties are particularly suited for the applications in fields such as optoelectronics, chemo-/biosensors, bioimaging and medicinal chemistry.¹ In all the mentioned applications, platinum(II) derivatives have been demonstrated to be particularly advantageous. Their square planar geometry allows for the possible decoration of the metal center with mono, di or polidentated ligands² in order to control the chemical, optical and electronic properties of the complexes as well as to modulate their emission and radiative lifetimes in desired way. In this contest, whereas ligand engineering plays the most important role,^{2,3} a noticeable and niche approach to fine-tune both the optical properties of complexes as well as their reactivity / bio-activity is represented by geometry engineering.^{4,5} For example, the well-known $[Pt(NH_3)_2(Cl)_2]$ complex, and other platinum complexes having monodentate ligands, or mono-cyclometalated ones, display powerful

chemotherapeutic activity only in the *cis* form.^{6,7}

While a significant amount of literature reports on cyclometalated complexes with C^N donor atoms (e.g. 2phenylpyridine, 1-phenylpirazole or N-heterocyclic carbenes)^{8,} ^{1a,2a} complexes with bidentate ligands having O^N donor atoms, such as salicylidenimine, are less developed.⁹ Compared to the use of salicylidenimine as ancillary ligand to saturate the coordination sphere around metal centers, few papers have been reported on their application as active luminescent moieties; most of them referring to closed-shell Zn or Cu complexes and only very few on Pt complexes.^{10,11} An interesting case of bis-salicylidenimine Pt derivative was reported by Komiya et al. displaying strong solid state emission; feature that although quite rare is found with other ligands or in multinuclear systems.¹² Salicylidenimine-like ligands would offer several advantages compared to typical C^N ligands, including ease of synthesis, readily available precursors, high atom economy and broad structural variability. Such type of ligands have been applied and widely investigated in the development of efficient (metal) catalysts for enantioselective organic reactions.¹³

Herein we report the design and synthesis of prototype neutral heteroleptic Pt(II) complexes carrying a C^N ancillary ligand and an O^N bidentate one. We selected 1-phenyl-pyrazole (Hppz) and 2-phenyl-pyridine (Hppy) as the C^N ligand, since their corresponding acetylacetonate Pt(II) complexes emit in the deep blue and blue-green regions.^{14,3} The 2-hydroxy-1-naphtyl-(N-phenyl)-imine (**HNpOPh**) O^N ligand was chosen to have an emissive triplet energy level lower than the organometallic counterpart, thus driving the whole optical and electronic properties of the final complexes.

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Electronic Supplementary Information (ESI) available: materials and methods; synthetic procedures and characterizations; extended electrochemistry and photophysics characterizations; theoretical calculations. Crystallographic information can be obtained via CCDC.com website (deposition numbers 1538320-1538321). See DOI: 10.1039/X0xX00000x

The unexpected and worth standing result, representing an unique case so far,¹⁵ is that the new ppz Pt(II) complex (**Pt-1**) can be isolated in both its *cis* and *trans* forms, as defined in Fig. 1. For comparative purposes, complex **Pt-2**,¹⁶ bearing 2-phenylpyridine (ppy) as C^N ligand, was also synthesized, in



Scheme 1. Synthetic route to complexes **Pt-1** and **Pt-2**, isolated yields are indicated. i) Hppz or Hppy, 2-ethoxyethanol/H₂O, 80°C, argon; ii) 2-Ethoxyethanol, Na₂CO₃, T, argon.

Results and discussion

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Synthetic procedures. The synthesis of the Pt(II) complexes **Pt-1** and **Pt-2** is depicted in Scheme 1. The reaction of the μ -dichloro-bridged dimer **1**,¹⁷ with the **HNpOPh** ligand, at 80 °C in 2-ethoxyethanol and in the presence of Na₂CO₃, led to the formation of a mixture of two Pt compounds having the same molecular weight (HPLC-MS analysis Fig. S14-15). The two products, hypothesized to be the cis/trans isomers of **Pt-1**, were separated by column chromatography and completely characterized. The *cis/trans* configuration of complexes **Pt-1** was ascertained by ¹H-NMR studies and lately confirmed by single crystal X-ray diffraction investigations (see below). The reaction temperature was found to play a crucial role on the isomeric ratio of **Pt-1** (Scheme 1). At 100 °C a cis/trans ratio of 75:25 (determined via HPLC) was obtained whereas at 140°C the ratio inverts to 35:65.

For comparative purposes, the ppy derivative **Pt-2** was synthesised by the reaction of **2** with **HNpOPh** at 120°C, according to the report of Liu *et al.*¹⁶ In this case, the complex **Pt-2**, was isolated as *trans* isomer only in 43% yield, comparable to that obtained in the synthesis of **Pt-1**.

A preliminary study on the thermal stability of the kinetic isomer *cis*-**Pt1** was conducted heating at 130-140°C, under Argon, a 1-1.5 mg/mL solution of the isomer in ethoxyethanole. HPLC analysis evidenced that in the first hours *trans*-**Pt1** forms while, on prolonged heating (over five hours) a black precipitate forms. Contrarily the *trans* isomer results in no isomerization but eventually formation of analogue black precipitate. Further studies are ongoing to elucidate mechanisms and degradations.¹⁸



Figure 1. a) ¹H NMR spectra of the HNpOPh ligand, b) *cis*-**Pt-1**; c) *trans*-**Pt-1**. Significative protons of the ppz ligand (H₃, H₄, H₅, H₅) are numbered; and the structures are reported as inset.

NMR analysis. The ¹H NMR spectra of *cis* and *trans*-Pt-1 and of the HNpOPh ligand are reported in Fig. 1. The well-resolved spectra easily allow recognizing, in both isomers, the diagnostic protons H₃ (pyrazoyl ring, characterized by small $J_{H_{-}}^{3}$ _H about 2.5 – 3.0 Hz) and $H_{5'}$ (phenyl ring).¹⁴ These proton resonances undergo the largest shift on going from one isomer to the other, indicating a strong relationship with the geometry of the molecule. H₃ resonance shifts by almost 3 ppm, i.e. from 5.45 ppm in cis-Pt-1 to 8.15 ppm in trans-Pt-1 (Fig. 1b and c). Such shift originates from the shielding exerted on H₃ by the ring-current of the phenyl ring of the O^N ligand and this is possible only in the cis isomer (see Fig. 2). An analogous effect shields and shifts proton H₅, to 5.8 ppm in trans-Pt-1 compared to 7.91 ppm in cis-Pt-1. Therefore, the cis/trans configuration of Pt-1 complex (drawings in Fig. 1) can be safely inferred.

NMR analysis also provides important information relative to the Pt - O^N ligand interactions. The coordination of the imine N atom, results in a shift towards lower frequencies of the imine proton from 9.36 ppm in the **HNpOPh** (Fig. 1a) to 9.11 ppm in *cis*-**Pt-1** and 8.88 ppm in *trans*-**Pt-1**. We attribute this progressive shielding to a partial loss of sp² character reflecting the strength of back-donation from the Pt centre to the coordinated group.¹⁹ The different chemical shift between the two isomers is ascribed to the different trans-influence of the two coordinated atoms of the ppz ligand.

In *trans*-**Pt-1** the imine nitrogen atom has the pyrazole nitrogen in trans arrangement; the latter atom has a smaller trans-influence with respect to the coordinated carbon atom (formally negatively charged), hence the trans-bond is less weakened (Fig. 1c).^{19,20} In the *cis* isomer instead, the trans correlation of *carbon-Pt-imine group* weakens and lengthens the Pt-N(imine) bond resulting in an intermediate H-shielding (9.1 ppm, Fig. 1b).

Similarly, the stronger Pt-ligand interaction in *trans*-**Pt-1** is also supported observing the more intense and resolved Pt-H long-range coupling on the 8.88 ppm peak compared to the weaker, Pt-H coupling, shoulder in *cis*-**Pt-1** (*i.e.* peak at 9.1ppm).

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X-Ray analysis. Single crystals of the two Pt isomers were grown from slow diffusion of hexane into dichloromethane solutions. The X-ray analysis (see SI) confirms the assignment of cis/trans configuration to complex Pt-1. Their molecular structures are reported in Fig. 2 (left and right, respectively), where for the trans isomer, which contains two molecules (A and B) in the asymmetric unit, only molecule A is reported. The two independent molecules of trans-Pt-1 differ essentially by the inclinations of the phenyl ring with respect to the chelated N^O ligand. The complexes are characterized by an almost perfectly square-planar coordinated Pt ion with fivemembered and six-membered metallacycles, due to the C^N and the O^N ligands, respectively. They evident differences in bond lengths (see Table 1) are imputable to the stronger transinfluence of C18 with respect to N2. In particular, the Pt-O1 bond length was found significantly longer in the trans isomer, as also in the Pt-2 complex,¹⁶ while the Pt-N1 one was found longer in the cis isomer. Correspondingly, the N1-C11 imine bond was shorter in the latter isomer, owing to the reduced back-donation from the metal centre to the O^N ligand (vide supra).

The skeleton of the *cis* isomer significantly deviates from planarity, unlike that of the *trans* isomer, as can be clearly seen in Fig. 3. This was due to a distortion of the sixmembered ring, with the Pt ion significantly out of the least square plane through the non-metal atoms of this ring (0.647(1) Å), while in *trans*-Pt-1 this distance was as low as 0.243(1) and 0.188(1) Å for molecules A and B, respectively. Such different conformation should be related to crystal packing effects because: (i) a distortion comparable with that of cis-Pt-1 was observed also in Pt-2¹⁶ whose molecular geometry is quite similar to that of trans-Pt-1 (Table 1); and (ii), DFT optimized geometries provide more comparable distortion of the six-membered ring (see later).

The structures are characterized by the presence of intramolecular C–H··· π hydrogen bond between the phenyl ring and the adjacent C–H bond of the C^N ligand as confirmed by a QTAIM topological analysis of the electron density.²¹

 $\label{eq:table_table_table} \begin{array}{l} \textbf{Table 1} - \text{Selected bond lengths and intermolecular distances (Å) from X-ray crystal structures (first line) and B3LYP/TZVP calculations when available (second line, italic). \end{array}$

	cis-Pt-1	trans-Pt-1		Pt-2 ^a	
		Molecule A	Molecule B		
Pt-N1	2.084 (2)	2.008 (2)	2.000 (2)	2.005 (4)	
	2.135	2.039		2.061	
Pt-N2	2.000 (2)	1.983 (2)	1.983 (2)	2.009 (4)	
	2.028	2.0	2.010		
Pt-O1	1.998 (2)	2.048 (2)	2.048 (2)	2.065 (4)	
	2.007	2.0	192	2.119	
Pt-C18	1.988 (2)	2.003 (3)	2.008 (3)	1.980 (5)	
	2.008	2.026		2.016	
N1-C11	1.301 (2)	1.313 (4)	1.319 (3)	1.303 (6)	
	1.304	1.312		1.318	
Pt…Pt	4.1096 (5)	6.0323 (3)	6.0323 (3)	7.026	
ata taken from	ref. 16				

The crystal structure of *cis*-**Pt-1** also shows a dense network of π - π stacking interactions and for the closest centrosymmetric

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dimer, a relatively short Pt…Pt separation distance, 4,1096(5) Å, was observed. The crystal structure 10f10170779121235 governed as well by π - π stacking interactions; however, different from the previous case, the Pt ions are far away from each other, thus excluding any metal-metal interaction in *trans*-Pt-1.



Figure 2 – Ortep plots of complexes cis-Pt-1 (left) and trans-Pt-1 (molecule A, right) with ellipsoids at 50% probability level.



Figure 3 – Partial molecular structures of cis-**Pt-1** (left) and trans-**Pt-1** (right) with short Pt…Pt (long dashes lines), C…C (dashes lines) and C–H…C(N) (dots lines) intermolecular contacts.

Electrochemical and optical properties.

The redox properties of the three platinum complexes have been investigated by cyclic voltammetry on glassy carbon, in dichloromethane solution with 0.1 M TBAPF_6 supporting electrolyte. (Fig. 4, S14-21 and Table 2).

The first oxidation peak potentials, E_{pla} , are nearly the same for the three complexes (0.65-0.69 V vs Fc⁺|Fc irrespectively from the C^N ligand and the configuration) and significantly more positive than in Pt(ppz)acac (0.35 V vs Fc⁺|Fc).¹⁴ On the other hand, the E_{pla} for the HNpOPh ligand (Fig. S14-15) is more positive (about 0.76 V vs Fc⁺|Fc) than our complex ones. These observations are consistent with an electron poorer Pt redox centre by interaction via π -back donation with the electronenriched O^N ligand. The oxidation peaks appear chemically irreversible at low scan rates, pointing to a chemical follow-up of the oxidation product on the experiment timescale. However, a portion of return peak gradually appears with increasing scan rate (Fig. S16, 18 and 20) in the sequence *trans*-Pt-1 > Pt-2 > *cis*-Pt-1, accounting for a decreasing order of stability of the electron transfer product.

Trans-**Pt-1** results in the most stable oxidation product and it has E_{pla} practically constant with scan rate implying an

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electrochemically reversible electron transfer. This also allows to assess, considering the half-peak width, that the first oxidation process is a monoelectronic one. Instead, *cis*-**Pt-1** features the most reactive electron transfer product and, unlike the two *trans* complexes, has a neat second oxidation peak before the background.

The reduction peak potentials E_{plc} are nearly the same for the three complexes, at -2.21 -2.25 V vs Fc⁺|Fc, about 0.15 V less negative than in the case of Pt(ppy)acac or dpm (about -2.4 V vs Fc⁺|Fc in DMF)²² and surely less negative also respect to Pt(ppz)acac (see SI section 4).^{14,23} This should point to a significant involvement of the O^N ligand, providing a lower energy LUMO, as pointed out by the theoretical computations. However, it must be noticed that the reduction peak potential of the free O^N ligand (about -2.13 V vs Fc⁺|Fc) undergoes a slight, but significant, negative shift upon Pt coordination. This shift could account for a combination of the back donation from Pt (resulting in a negative shift) with increased effective conjugation in the LUMO (resulting in a positive shift) as accounted by DFT calculations.







Figure 5 – Molar absorptivity spectra of the $\ensuremath{\mathsf{Pt}}(\ensuremath{\mathsf{II}})$ complexes in DCM solution

The electronic absorption spectra of the complexes, recorded in dichloromethane, are reported in Fig. 5 and Table 2 (the UV features and solvatochromism of **HNpOPh**^{24,25} are reported in Fig. S22). Below 280 nm (ϵ > 2⁻¹⁰⁴ M⁻¹ cm⁻¹) the strong

absorptions are attributable to $\pi - \pi^*$ transitions, rule of the cyclometalated ligands (*i.e.* ppy/ppz and NpOPH)³³The intense absorption at 330-340 nm is a distinctive feature of the ppz derivatives *cis/trans*-**Pt-1** compared to **Pt-2**.

Lastly, the broad and only partially resolved bands between 400-480 nm observed in **Pt-2** and cis/trans-**Pt-1** (Fig. 5) originate from the presence of the O^N ligand, since the parent complexes Pt(ppy)dpm and Pt(ppz)acac have no significant absorption in this spectral region (Fig. 6 left).^{14,22}

We would attribute the 400-480 nm bands, in the three Pt complexes, predominantly to metal-to-ligand charge transfer transitions (1,3 MLCT) involving the Pt center and the O^N ligand (see DFT and section 5 SI).

Above 420 nm the UV spectra closely match in the complexes adopting the same geometry, (*trans*-)**Pt-2** and *trans*-**Pt-1** (Fig. 3b) while, albeit maintaining similar shape, an hypsochromic shift of about 20 nm is observed in the *cis*-**Pt-1** complex.



Figure 6 – Normalised absorption (left panel DCM, RT) and emission (right panel, 77K) spectra of Pt(ppy)dpm and Pt-2

The three complexes are non-luminescent in degassed diluted solutions, but become brightly emissive both at 77K in glassy 2MeTHF (Fig. 7) as well as in doped PMMA matrix (Fig. S24).



Figure 7. Excitation and emission spectra of all the Pt(II) complexes at 77K in rigid 2MeTHF matrix.

At 77K, the emission maxima for the three complexes range from 575 to 620 nm; luminescence are characterized by a broad and featureless structure, a large Stokes-shift and their excitation spectra match the absorption ones while gaining structured vibronic progression (spaced by 1500-1600cm⁻¹) at low energy, Fig. 7. The identical emission profiles in **Pt-2** and *trans*-**Pt-1** appear as the smear of the first two vibronic modes, one as a high energy shoulder at ca. 605 nm and one with $\lambda_{em,max} = 618-620$ nm.

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Table 2. Summary of the electrochemical and optical properties of the studied complexes. Reported emission data refers either to the 2MeTHF frozem matrix at 77K (upright numbers) or to the PMMA doped thin film at room temperature (*italicized numbers*)

	Electrochemistry					Absorption		Emission		
	E _{p,la} [V]	Е _{р,іс} [∨]	Е_{НОМО} [eV]	Е_{LUMO} [eV]	E g ^{EC} [eV]	$λ_{abs}$ [nm] (ε [x 10 ⁴ M ⁻¹ cm ⁻¹])	Е g ^{ОРТ} [eV]	λ _{em,max} [nm] (FWHM [cm ⁻¹]) 77K ^{a)} / <i>PMMA</i> ^{b)}	τ [μs], (%) 77κ <i>/ ΡΜΜΑ</i>	Ф _L РММА
cis- Pt-1	0.65	-2.25	-5.45	-2.55	2.90	333 (2.10), 438 (0.47)	2.84	575 (3200) <i>592 (3470)</i>	7.08 0.63 (25.1), 3.09 (74.9)	0.030
trans- Pt-1	0.69	-2.21	-5.49	-2.59	2.90	340 (2.77), 456 (0.72)	2.74	617, 605 [°] (4160) <i>605 (3880)</i>	2.13 (38.7), 6.04 (62.4) <i>0.32 (31.3), 2.05 (68.7)</i>	0.005
Pt-2	0.66	-2.22	-5.46	-2.58	2.88	322 (1.17), 369 (1.18), 400 (0.61), 457 (0.47)	2.71	620, 605 [°] (4015) <i>615 (4330)</i>	1.21 (30.7), 4.42 (69.3) 0.15 (26.5), 1.14 (73.5)	0.005

HOMO and LUMO values are calculated from CV data: E_{HOMO} (eV) = -1e x [$E_{p,la}$ /V ($Fc^+|Fc$) + 4.8 V ($Fc^+|Fc$ vs zero)]; E_{LUMO} (eV) = -1e x [$E_{p,lc}$ /V ($Fc^+|Fc$) + 4.8 V ($Fc^+|Fc$ vs zero)]; c) high energy shoulder, a)77K data are taken from frozen 2MeTHF diluted solution; b) PMMA data are taken from a 4% w/w dopped PMMA film on quartz recorded at room temperature under N₂

The Huang-Rhys parameter (S_{HR}, *i.e.* the ratio of the height of the first two vibronic peaks) greater than 1 points to a large structural distortion between the ground and excited state geometries. The emission of the *cis*-**Pt-1** is located, in agreement with the hypsochromic shift of the UV spectra, at $\lambda_{\text{em.max}} = 575$ nm with FWHM of 3200 cm⁻¹ (Fig. 7).

The photoluminescence of **Pt-2** (λ_{max} = 620 nm) differs completely from that of the parent Pt(ppy)dpm (λ_{max} = 475 nm, Fig. 6 right) and, given the decay lifetime in the microsecond regime, we attribute the phosphorescence to a triplet state localized onto the O^N ligand. Likewise, analogues origin has the luminescence of *cis* and *trans*-**Pt-1**, since the reference complex Pt(ppz)acac shows no emission¹⁴ and *trans*-**Pt-1** emission perfectly matches that of **Pt-2**.

Excited state lifetimes (Table 2) evidence a mono-exponential decay in the case of *cis*-**Pt-1** (7.08 μ s) whereas in **Pt-2** and *trans*-**Pt-1** a bi-exponential decay is found with a faster component around 1-2 μ s (contributing to the decay for ca. 30-38%) and a slower one at 4.5-6 μ s. The microsecond decay regime is in agreement with a highly perturbed ³LC/MLCT emissive state.

In 4% doped PMMA thin film on quartz (at room temperature and under N₂) a quantum efficiency (Φ_L) of 0.5% is measured for **Pt-2** and *trans*-**Pt-1** whereas. Interestingly, *cis*-**Pt-1** displays higher Φ_L = 3%. All complexes show a bi-exponential decay overall shorter compared to 77K data (Table 2) suggesting that non-radiative processes, including the coupling of the excited state to the ground state vibrational modes are enhanced at higher temperature. Interestingly, both at 77K and in PMMA at room temperature the lifetime of the *cis*- isomer is constantly longer than that of the two *trans* ones. Altogether, the photophysical behavior of complexes (*i.e.* weak spectral overlap, featureless and broad emission, large S_{HR} parameter, enhanced luminescence in rigid environment) are consistent with a strongly distorted excited emitting state.¹⁵

Theoretical studies.

DFT and TDDFT calculations were employed to shed light on the stereochemical outcome of the reaction, leading to the formation of *cis/trans*-**Pt-1**, as well as to elucidate the molecular electronic properties.

The geometry optimizations of the two isomers, led to almost isoenergetic systems, with the *trans* form of **Pt-1** more stable than the *cis* one only by 1.0 kcal/mol. Thermal analysis provided even closer free energies for the formation of the two isomers at both the experimentally studied reaction temperatures (100 and 140°C). Thus, a lower activation barrier for the formation of the cis complex can explain the prevalence of the cis form at lower temperature. Worth noting, calculations performed on **Pt-2** complex for both the *trans* and the hypothetical *cis* isomer provided a significantly greater stability for the *trans* one (3.9 kcal/mol) which, indeed, is the only one formed in the reaction.

Fig. 8 collects the HOMO and LUMO plots and the triplet spin density of *trans*-**Pt-1** complex. Frontier orbital plots fully support the above discussions. In fact, in all cases (see Fig. 8 and S25) the HOMOs mostly involve the Pt $d_{x2-\gamma2}$ orbital together with the naphtyl moiety of the O^N ligand and partially extend also on the phenyl ring of the C^N ligand. LUMOs are almost exclusively located onto the O^N ligand with no or minor contribution from the pyrazole or pyridine ring respectively.

TDDFT spectrum nicely correlates to the UV-vis one (Fig. S27); the lowest energy excitation, in all the complexes, are ascribed to a HOMO to LUMO transition, hence confirming their MLCT character. Higher energy excitations are essentially of HOMO

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to LUMO+1 character, which appears to be more of interligand type (see Fig. S25 and Table S1).



Figure 8. DFT calculations of *trans*-**Pt-1**: a) HOMO, b) LUMO and c) triplet spin density plots; d) superimposed ground state geometry (yellow structure) and the excited triplet one (pink) evidencing the significant distortion between the two structures (see also Fig. S26).

Significant distortion is evident comparing the relaxed singlet and triplet structures (Fig. 8d and S26). This observation justify the absence of luminescence in fluid matrix at room temperature. To be noted that almost negligible distortion occurs at the square planar platinum center, while the naphtyl moiety bends over 20 degrees in the excited triplet state. Analogues behaviour is seen in **Pt-2**, while an even larger bent can be observed for *cis*-**Pt-1** (Fig. S26). Instead, the increased luminescence efficiency observed for *cis*-**Pt-1** with respect to *trans*-**Pt-1** can be justified in terms of the smaller ground state dihedral angle (17° *vs* 21° respectively; Fig. S26), between the least-squares plane through the Pt-ppz system and that of the NpOPh one (defined through its N-C-C-C-O chelated atoms). In fact, coordination environment might alter Pt *d*-splitting and non-radiative deactivation rates.²

Conclusions

In conclusion, we prepared and fully characterized the *cis* and *trans* isomers of **Pt-1**, bearing an ancillary *ppz* cyclometalated ligand and the *NpOPh* (O^N) one. We showed that the stereoselectivity on the cis/trans ratio can be obtained controlling the reaction conditions. To the best of our knowledge this is the first report on the formation of *cis*/trans isomers in neutral bis-cyclometaled Pt(II) complexes; the *cis* isomer is made thermodynamically accessible due to the trans influence exerted by the ppz ligand.

NMR provides important inside about *trans influence* and *Pt-ligand* interactions. Likewise the results from the combined electrochemical, photophysical and DFT/TDDFT studies demonstrated that most of the electronic properties of the complexes are determined by the O^N ligand. In fact the first monoelectronic oxidation involves the Pt center plus O^N ligand, while the first reduction, partially reversible, involves the O^N ligand. Large excited state distortion quenches the emission of the complexes but they become highly luminescent in rigid matrix and the emissions are assigned to the perturbed ³LC states centered on the NpOPh ligand. Complexes adopting *trans* configuration show similar absorption, emission and excited state features scarcely

influenced by the C^N ligand. On the other hand trithencis isomer absorption and emission are over all the complex has a higher luminescence efficiency.

This research is in progress with more structural variability on the O^N ligand (preliminary results are consistent with the findings herein described) and further expanding its scopes, addressing the issues of isomerization reaction mechanism and, more interesting, on the solid state photoluminescent emission observed in this compound class.

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Notes and references

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