A new family of luminescent compounds: platinum(II) imidoylamidinates exhibiting pH-dependent room temperature luminescence

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Received 13th February 2006, Accepted 10th April 2006
First published as an Advance Article on the web 8th May 2006
DOI: 10.1039/b602083f

The imidoylamidinate platinum(II) compounds [Pt{NH=C(R)NC(Ph)=NPh}$_2$] (R = CH$_2$Ph **2**, *p*-ClC$_6$H$_4$ **3**, Ph **4**) were prepared by the reaction of the appropriate *trans*-[PtCl$_2$(RCN)$_2$] with 4 equiv of the amidine PhC(=NH)NHPh giving **2–4** and 2 equivs of the salt PhC(=NH)NHPh·HCl. We also synthesized, by the double alkylation of **4** with MeOSO$_2$CF$_3$, complex [Pt{NH=C(Ph)N(Me)C(Ph)=NPh}$_2$][CF$_3$SO$_3$]$_2$ (**5**) which models the bis-protonated form of **4**. The complexes were characterized by ^{1}H, ^{13}C NMR, and IR spectroscopies, FAB-MS and by C, H, N elemental analysis. The X-ray crystallography of **4**·2CH$_2$Cl$_2$ enables the confirmation of the square planar coordination geometry of the metal center with almost planar imidoylamidine ligands, while in **5**·2CHCl$_3$ the planarity of the metallacycles is lost and and the central N atom is sp^3-hybridized. The imidoylamidinate complexes represent a new family of Pt(II)-based luminescent complexes and they are emissive at room temperature both in solution and in the solid state, with an emission quantum yield ranging from 3.7×10^{-4} to 6.2×10^{-2} in methanol solution; the emission intensity is pH-dependent, being quenched at low pH. UV-visible and luminescence spectroscopies indicate that the lowest excited state of these compounds is ^{3}MLCT or ^{3}IL with significant MLCT character, with emission lifetimes of a few µs. A blue shift of both the absorption and emission with increasing solvent polarity and with decreasing π-electron withdrawing properties of the ligand substituent was observed.

Introduction

Luminescent square-planar platinum(II) complexes have attracted a great deal of interest because of their useful photochemical properties, *i.e.* high efficiency and long lifetimes of the emissive states, and potential applications in many fields, such as chemosensors,[1,2] photocatalysts,[3] light-emitting diodes (LEDs),[4] and photovoltaic devices.[5,6] The most advantageous d^8-Pt(II) luminescent systems are based on [PtX$_2$(diimine)] (X = halide, cyanide, thiolate, alkyl, aryl or acetylide[5,7,8]) or terpyridine[9,10] complexes, phosphorescent Pt(II) porphyrins,[11] the series of Pt complexes with N,C,N-[12] or S,C,S-[13]pincer ligands and some other cyclometalated Pt compounds.[14]

Very recently we reported the coupling between the amidine PhC(=NH)NHPh and ligated nitriles in the platinum(II) complex [PtCl$_2$(RCN)$_2$] (R = Et, CH$_2$Ph, Ph, NEt$_2$) giving Pt-bound chelated imidoylamidines(ates) [Pt{NH=C(R)-NC(Ph)=NPh}$_2$].[15] It has been observed that the complexes with R = Ph and CH$_2$Ph exhibit luminescent properties in solution, in the solid state and on being spread onto TLC SiO$_2$ plates; the emission properties denoted that we had indeed obtained a novel type of Pt(II)-based luminescent compound.

In this work we report data on the photophysics of three platinum(II) complexes, *i.e.*, [Pt{NH=C(CH$_2$Ph)NC(Ph)=NPh}$_2$] (**2**), [Pt{NH=C(*p*-ClC$_6$H$_4$)NC(Ph)=NPh}$_2$] (**3**) and [Pt{NH=C(Ph)-NC(Ph)=NPh}$_2$] (**4**), showing pH-dependent room temperature emission in solution. The single crystal X-ray diffraction analyses of [Pt{NH=C(Ph)NC(Ph)=NPh}$_2$] (**4**) and its alkylated analogue [Pt{NH=C(Ph)N(Me)C(Ph)=NPh}$_2$][CF$_3$SO$_3$]$_2$ (**5**) along with synthetic data for **3** and **5** are also reported. The photophysical properties have been investigated with respect to the ligand π-electron withdrawing ability and solvent polarity.

Results and discussion

Pt(II)-mediated nitrile–amidine coupling

Amidines can act as nucleophiles towards the triple CN bond in coordinated nitriles to give imidoylamidines, but the subject is still underdeveloped. Besides two collateral evidences favoring the metal-mediated nitrile–amidine coupling,[16,17] Kilner *et al.*[18] obtained the platinum(II) imidoylamidinate complexes [Pt{NH=C(Ph)NC(Ph)=NH}$_2$] by reaction of [PtCl$_2$(PhCN)$_2$] with 2 equiv of PhC(NH$_2$)=NLi. In accordance with the authors,[18] the lithiation of benzamidine was necessary to enhance the nucleophilicity of this species and to promote the reaction. The work we have recently been reported[15] and the current results on preparation of **3** (see later) demonstrate that the amidine PhC(=NH)NHPh is a sufficiently good nucleophile to react

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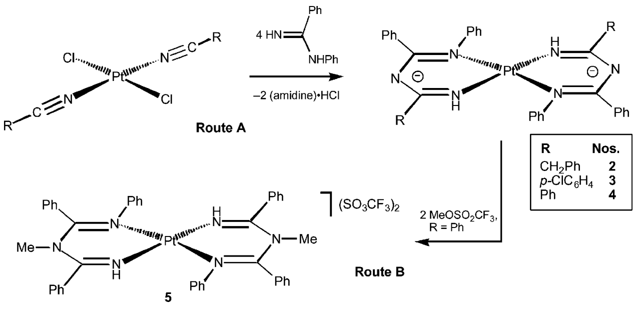
without additional activation (by, *e.g.*, lithiation), even under relatively mild conditions (40 °C), with Pt(II)-bound nitriles thus providing easy access to (imidoylamidinate)Pt(II) complexes.

We observed that for the success of the reaction another stoichiometry, as compared to that employed by Kilner and colleagues,[18] should be used. Thus, the platinum(II) compounds [Pt{NH=C(R)NC(Ph)=NPh}$_2$] (**2**,[15] **3** (this work), and **4**[15]; Scheme 1) were prepared by reaction of the appropriate *trans*-[PtCl$_2$(RCN)$_2$] (R = CH$_2$Ph,[19] Ph,[20] and *p*-ClC$_6$H$_4$ **1**; for synthesis of the latter starting material see Experimental) with 4 equiv of the amidine PhC(=NH)NHPh. The addition of the amidine to the coordinated nitriles followed by ring-closure of the newly formed imidoylamidines is accompanied by dehydrochlorination and HCl is trapped with another amidine molecule to form (Scheme 1, route A) the salt PhC(=NH)NHPh·HCl which was isolated as the other product of the reaction. We also synthesized (Scheme 1, route B), by the double alkylation of **4** with MeOSO$_2$CF$_3$, complex **5** (characterized by X-ray crystallography) which models the bis-protonated form of **4** and the latter model was needed to interpret some photophysics experiments (see later).



Scheme 1

Molecular structures of [Pt{NH=C(Ph)NC(Ph)=NPh}$_2$]·2CH$_2$Cl$_2$ (4·2CH$_2$Cl$_2$) and [Pt{NH=C(Ph)N(Me)C(Ph)=NPh}$_2$][CF$_3$SO$_3$]$_2$·2CHCl$_3$ (5·2CHCl$_3$)

Collected X-ray data for both complexes are presented in Table 1, while selected bond lengths and angles are shown in Table 2. Complex **4** has a square planar geometry. The Pt–N bonds [1.986(4) Å and 2.041(5) Å for Pt(1)–N(1) and Pt(1)–N(3), correspondingly] agree well with those found in [Pt{NH=C(Ph)NC(Ph)=NH}$_2$].[18] Atoms of the metallacycles lie in one plane with a mean deviation of 0.027 Å. The N=C bond lengths [N(1)–C(1) 1.304(8) and N(3)–C(9) 1.310(8) Å] and the N–C bond lengths [N(2)–C(9) 1.336(8) and N(2)–C(1) 1.349(8) Å] in the metallacycle have values typical for the corresponding bonds in both Pt(II) and Ni(II) imidoylamidine(ato) complexes and exhibit a similar small degree of delocalization in the ring.[16–18] The chelate angle N(1)–Pt(1)–N(3) [87.7(2)°] agrees well with that observed in [Pt{NH=C(Ph)NC(Ph)=NH}$_2$].[18]

The crystal structure of **5** contains two symmetry independent halves of **5** in the asymmetric unit. The complex **5** also has a square planar geometry (Fig. 2); the bonds Pt(1)–N(1) and Pt(1)–N(3) [1.994(6), 2.028(7) and 1.977(6), 2.033(6) Å for unit A and B, respectively] as well as the chelate angle [87.2(3) and 87.1(3)°] resemble closely those found in **4**. In **5**, the planarity of the metallacycles is lost (mean deviation from the plane 0.101 and 0.102 Å for units A and B, correspondingly) due to, at least one of these reasons, the steric strain caused by the methyl group and

Table 1 Crystal data for **4**·2(CH$_2$Cl$_2$) and **5**·2(CHCl$_3$)

	4·2(CH$_2$Cl$_2$)	**5**·2(CHCl$_3$)
Empirical formula	$C_{42}H_{36}Cl_4N_6Pt$	$C_{46}H_{40}Cl_6F_6N_6O_6PtS_2$
FW	961.66	1358.75
Temp./K	100(2)	120(2)
λ/Å	0.71073	0.71073
Cryst syst.	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	15.6529(9)	10.1713(7)
b/Å	6.0112(2)	14.0242(10)
c/Å	22.0709(12)	18.5465(10)
α/°	90	95.531(4)
β/°	110.086(2)	90.497(4)
γ/°	90	99.482(4)
V/Å^3	1950.40(17)	2596.4(3)
Z	2	2
ρ_{calc}/Mg m^{-3}	1.637	1.738
μ(Mo Kα)/mm^{-1}	3.910	3.166
No. of collected reflns	12271	15746
No. of unique rflns	3673	9361
$R_{Int.}$	0.0699	0.0452
$R1^a$ ($I \geq 2\,\sigma$)	0.0352	0.0482
$wR2^b$ ($I \geq 2\,\sigma$)	0.0794	0.1161

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for **4**·2(CH$_2$Cl$_2$) and **5**·2(CHCl$_3$)

		5·2(CHCl$_3$)	
	4·2(CH$_2$Cl$_2$)	A	B
Pt(1)–N(1)	1.986(4)	1.994(6)	1.977(6)
Pt(1)–N(3)	2.041(5)	2.028(7)	2.033(6)
N(1)–C(1)	1.304(8)	1.283(10)	1.305(10)
C(1)–N(2)	1.349(8)	1.389(10)	1.374(10)
N(2)–C(8)		1.452(10)	1.500(10)
N(2)–C(9)	1.336(8)	1.379(11)	1.385(10)
C(9)–N(3)	1.310(8)	1.318(10)	1.288(10)
N(1)–Pt(1)–N(3)	87.7(2)	87.2(3)	87.1(3)
C(1)–N(2)–C(9)	122.9(5)	124.7(6)	124.9(6)

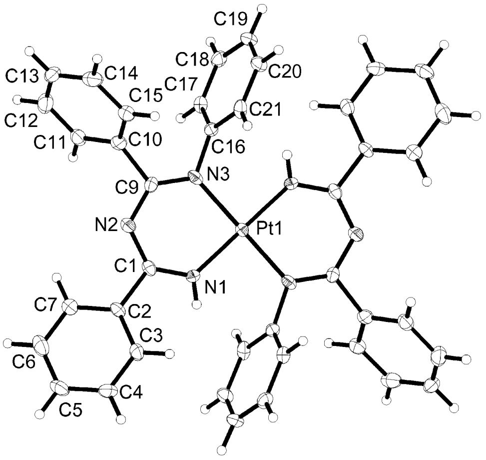


Fig. 1 X-Ray molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability.

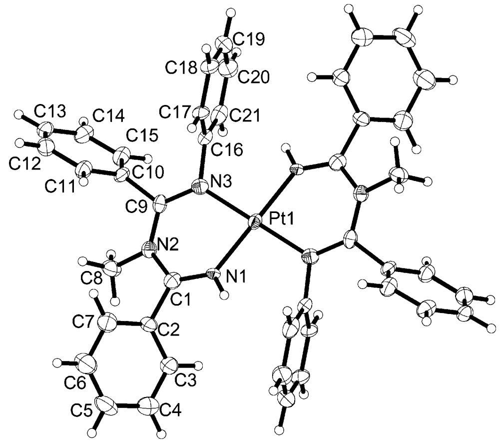


Fig. 2 X-Ray structure of $\mathbf{5}^{2+}$; the counterions were omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

N(2) and Pt(1) are bent away from the plane defined by N(1)–C(1)–C(9)–N(3) [Pt(1), N(2) distances from the plane 0.317, 0.179(7) and 0.305, 0.192(7) Å. Angles between the lines defined by bonds Pt(1)–N(1#1) and N(2)–C(8) and the plane N(1)–C(1)–C(9)–N(3) are 80.9(3), 72.7(5) and 81.2(3), 73.6(5) for units A and B, respectively (#1 for A is $-x$, $-y$, $-1-z$ and for B $-x$, $-y$, $-z$)]. Moreover, C(1)–N(2) and N(2)–C(9) distances in **5** have more of a single bond character as compared to **4** and this, along with the angles around the N(2) atom, implies that the N atom is sp^3-hybridized.

CCDC reference numbers 297957 and 297958.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602083f

Absorption spectra of the (imidoylamidine)Pt(II) complexes

The UV-visible absorption spectra of compounds **2–4** in CH_2Cl_2 solutions are shown in Fig. 3.

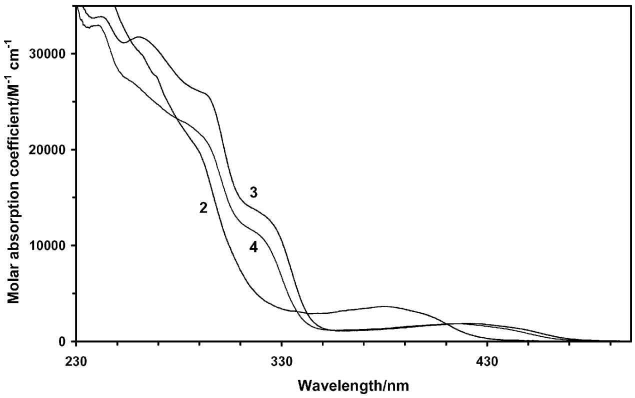


Fig. 3 Absorption spectra of **2**, **3** and **4** solutions in CH_2Cl_2.

The absorption data (wavelengths of maxima and respective molar absorption coefficients) is summarised in Table 3. All complexes exhibit high-energy absorption bands in the region 220–280 nm, assignable as $^1(\pi-\pi^*)$ IL (intraligand) transitions based on energy, intensity and similarity with the absorption spectrum of the free amidine PhC(=NH)NHPh. The lowest-energy absorption bands at 380–430 nm are intrinsic of the d^8 platinum complexes, as the absorption of the free amidine is significant only below 370 nm.

Table 3 Wavelengths of the absorption maxima, corresponding molar absorption coefficients, emission quantum yields and lifetimes for complexes **2–4**

	λ_{max}/nm (ε/M^{-1} cm^{-1})		λ_{em}/nm, RT		Φ_L/× 10^{-2}		τ/μs	
	MeOH	CH_2Cl_2	MeOH	CH_2Cl_2	MeOH air-saturated (degassed)	air-saturated CH_2Cl_2	degassed MeOH	MCH : toluene (7 : 2), 110 K
2	231 (32 000) 268 (sh) (19 200) 299 (sh) (6 800) 375 (2600)	233 (55 800) 266 (sh) (28 400) 290 (sh) (19 700) 380 (3700)	463	477	0.013 (0.037)	< 1 × 10^{-3}	1.6	3.2
3	226 276 (sh) 396 (sh) 400	242 (33 900) 261 (31 800) 294 (25 600) 322(sh) (13 100) 420 (1900)	502 537 578	516 550	3.0 (5.8)	3.5 × 10^{-3}	—	2.7
4	229 256 282 315 407	241 (33 000) 256 (27 200) 293 (sh) (21 000) 320 (sh) (10 900) 415 (1800)	512 549 596 (sh)	532 567	3.3 (6.2)	4.0 × 10^{-3}	1.8 (75%) 0.6 (25%)	2.8

We assign these bands as of MLCT character based on their low energy, ligand dependence and intensity ($\varepsilon > 1000$ M^{-1} cm^{-1}), and by analogy with the published data.[21–25]

Two further features of the absorption spectra deserve mention: (i) All complexes display a significant solvatochromic shift. In accordance with their CT character,[26] absorption bands red shift when going from MeOH to CH_2Cl_2 solution ($\Delta\lambda = 6$ nm for **2**, 20 nm for **3** and 9 nm for **4**); (ii) The lowest energy absorption band is red-shifted for **3** and **4** in comparison with **2**, see Fig. 3. This difference is understandable taking into account that the aromatic part of the R group can participate in π-conjugation in **3** and **4** but not in **2**. The λ_{max} variation with the change of the substituent is consistent with a ligand based LUMO, in agreement with the assignment of this band as of CT origin.

Emission spectra of the (imidoylamidine)Pt(II) complexes

All compounds are emissive in methanol solution at 298 K (Fig. 4) with a luminescence quantum yield that increases on going from complex **2** to complexes **3** and **4**.

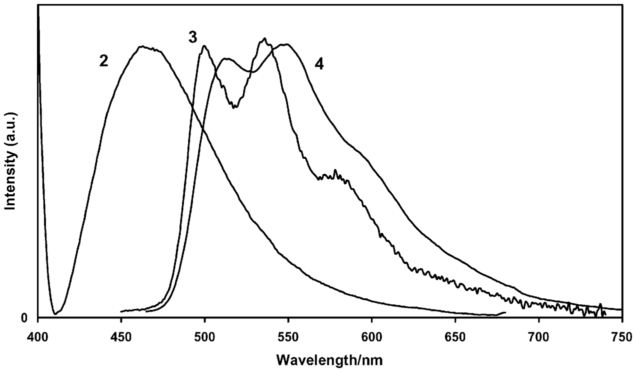


Fig. 4 Emission spectra of compounds **2–4** in degassed MeOH solution at room temperature. The excitation wavelengths were 370 nm, 395 nm and 400 nm, respectively.

Excitation of complex **2** resulted in a broad and structureless emission band with a maximum at 463 nm and a quantum efficiency of 1.3×10^{-4} and 3.7×10^{-4} in air-saturated and degassed solutions, respectively. Excitation of compounds **3** and **4**, on the other hand, resulted in a strong, structured emission with maxima at 502 nm, 537 nm and 578 nm for complex **3** and 512 nm and 549 nm, with a shoulder at 596 nm for complex **4**. The quantum yields of the emission in air-saturated and degassed MeOH solutions are respectively 3.0×10^{-2} and 5.8×10^{-2} for complex **3**, and 3.3×10^{-2} and 6.2×10^{-2} for complex **4**. Using an average lifetime of 2 μs at room temperature in methanol solution, and a concentration of O_2 in air-equilibrated MeOH at 298 K of 1.0×10^{-2} M,[27] bimolecular quenching rate constants for compounds **2–4** of 9×10^7, 4×10^7 and 6×10^7 M^{-1} s^{-1}, respectively, are obtained. These rate constants, whilst large, are well below diffusion control (*ca.* 10^9 M^{-1} s^{-1} for triplet state quenching by O_2).[27]

In contrast to methanol solutions, the emission is considerably suppressed in CH_2Cl_2 solution. Although a weak emission was observed for complexes **3** and **4** with a quantum yield in air-saturated CH_2Cl_2 of 3.5×10^{-5} and 4.0×10^{-5}, respectively, complex **2** is essentially non-emissive in fluid CH_2Cl_2 at 298 K ($\Phi_L < 1 \times 10^{-5}$). This quenching by the chlorinated solvent is attributable in both cases to the formation of a weakly emissive (**3** and **4**) or essentially non-emissive (**2**) exciplex by means of an excited-state charge-transfer interaction.[28]

At 77 K, the emission intensity increases and a blue shift of 7–8 nm is observed. For complex **4** the two vibronic components at 504 nm and 544 nm are well defined, the shoulder at 592 nm is also better resolved. A small change in the relative intensities of the vibronic components is also seen, *i.e.* the peak at 504 nm is resolved better and is slightly more intense. Fig. 5 shows the emission spectra of compound **3** in EtOH : MeOH (4 : 1) solution at 293 K and 77 K.

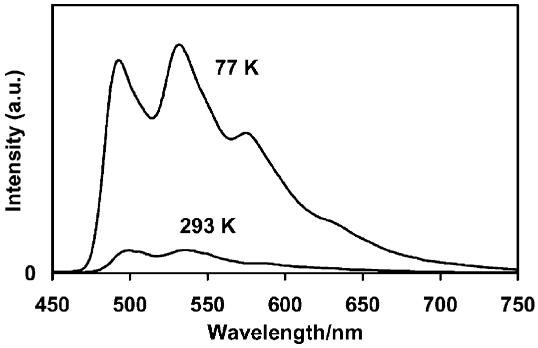


Fig. 5 Emission spectra of complex **3** in EtOH : MeOH (4 : 1) at 293 K and 77 K.

In addition to the higher vibronic resolution, a blue shift is also apparent, changing the maximum emission wavelengths from 500, 537, 581 nm at 293 K to 493, 532, 575, 634 (sh) nm in this solvent mixture at 77 K.

In the solid state all complexes showed strong emission with emission maxima occurring at approximately the same emission wavelengths as in the methanol solutions, and with lifetimes in the range of 1.6 to 1.8 μs.

Lifetime measurements were also carried out at room temperature and in low temperature methylcyclohexane : toluene (7 : 2) glass (110 K) and are presented in Table 3. The luminescence decays for all complexes at 110 K were well fitted with mono-exponential functions with lifetimes in the range of 2 to 3 μs (Fig. 6).

For complexes **3** and **4**, a lifetime of 2 μs and a luminescence quantum yield of 6×10^{-2} (room temperature data) imply a radiative lifetime of 30 μs, compatible with an IL spin-forbidden transition (phosphorescence). For complex **2**, the radiative lifetime is even higher, 5 ms, characteristic again of a spin-forbidden transition, in this case mainly of the MLCT type.

Room temperature luminescence decays of in MeOH solutions are shorter and bi-exponential, with lifetimes of 1.8 μs (75%) and 600 ns (25%) for complex **4**. In CH_2Cl_2 solutions, the luminescence decays are even more complex and considerably faster than in MeOH, in agreement with a solvent quenching effect.

Solvent and ligand dependence of the emission

The emission of the complexes studied shifts with ligand modification and solvent polarity. The emission maxima shift to lower energy as the ligand becomes a stronger π-electron-acceptor. This shift is parallel to that observed in the absorption spectra but

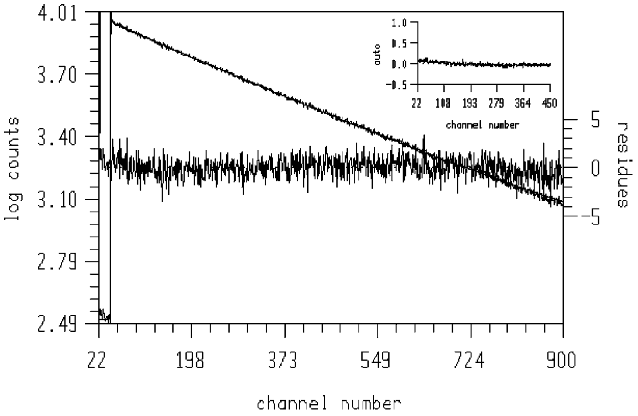


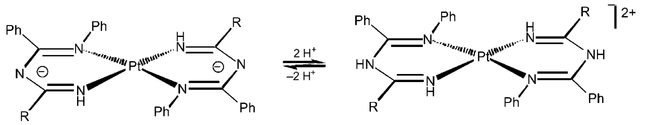
Fig. 6 Luminescence decay of complex **4** in methylcyclohexane : toluene (7 : 2) glass at 100 K. Excitation and emission wavelengths were 415 nm and 501 nm, respectively. The timescale was 7.46 ns per channel. The decay is well fitted (reduced $\chi^2 = 1.09$) by an exponential function with a lifetime of 2.8 μs.

greater than that for the ~400 nm absorption band. The phenyl substituent, attached directly to the chelate cycle in complex **4** increases the ligand π-electron-withdrawing ability and emission occurs at 512 nm, while the maxima occur at 463 nm for complex **2** and at 502 nm for complex **3** (all wavelengths refer to MeOH solutions). The emission band position was found to depend also on solvent polarity. A red shift of about 20 nm was observed in CH_2Cl_2 solutions compared to the methanol solutions. Although the greatest effect of solvent polarity on the absorption spectra was observed for complex **3** (the absorption maxima in MeOH, EtOH : MeOH (4 : 1) and CH_2Cl_2 solutions were observed at 400 nm, 412 nm and 420 nm), the greatest dependence of emission on solvent was observed for compound **4**. The emission maxima for the latter in CH_2Cl_2 occurs at 532 nm whereas in MeOH solution it is observed at 512 nm. For complex **3** the first emission maximum also red shifts parallel to the absorption shift from 502 nm in MeOH to 516 nm in CH_2Cl_2 solution.

pH-Dependence of the luminescence

Another interesting aspect of the photophysics of the complexes under study is the emission dependence on the pH of the solution. In acidic media, we observed the complete quenching of the emission. The emission is reversible upon neutralization and, in basic solutions (NaOH in methanol), the complex characteristic emission bands at about 500 nm appear in the spectra. The same observation holds for the absorption spectra, *i.e.* the CT bands are not visible in acid solutions; instead, very weak absorption bands, which are blue shifted in respect to the CT bands can be distinguished. Quenching of the emission upon protonation could be due to an enhanced non-radiative deactivation *via* short lived d–d states as a result of increased energy of the emissive CT excited states.

We believe that the pH-dependence of the emission is due to the acid–base properties of the central nitrogen atom which, similarly to analogous nickel(II) complexes,[16,29] can be protonated (Scheme 2).



Scheme 2

In order to obtain additional data favoring the relevance of the quenching with the protonation of the N atoms, we synthesized (Scheme 1, route B), by the double alkylation of **4**, complex **5** which models the bis-protonated form and it was observed that the dicationic complex **5** does not exhibit emission neither in the solid state nor in solution. Based on the crystallographic data (see above), we believe that alkylation and, apparently, protonation might change hybridization of the N atom from sp^2 to sp^3 and these structural changes could affect the electronic distribution in the complex and, consequently, the luminescence. The correlations between acid–base properties of these (imidoylamidine)Pt(II) complexes and the pH-dependence of the emission will be subject to further studies.

Nature of the excited state in the (imidoylamidine)Pt(II) complexes

The low energy (~550 nm), long radiative lifetime and the broad and structureless emission of complex **2** indicate a ^{3}MLCT excited state. For complexes **3** and **4**, the structured and red-shifted emission and the much higher emission quantum yields indicate a mainly IL CT $^3(\pi\text{–}\pi^*)$ excited state, with some MLCT contribution.[25] As mentioned above, the difference between **2**, **3** and **4** is understandable taking into account that only for the latter can the aromatic part of the R group participate in π-conjugation, resulting in a lowered LUMO energy of the ligand. The dependence of λ_{em} with the substituent and solvent polarity (a 50 nm shift when changing the substituent from CH_2Ph to Ph and a 20 nm shift when going from MeOH to CH_2Cl_2) also agrees with the assignments made.

Final remarks

We have shown that neutral (imidoylamidinate)Pt(II) complexes constitute a new family of room temperature luminescent square-planar compounds. They are planar chelates simply derived from nucleophilic addition, under mild conditions, of PhC(=NH)NHPh to each of the nitrile ligands activated by coordination at $[PtCl_2(RCN)_2]$, with ring closure, in the presence of an excess of the amidine to trap the HCl formed upon dehydrochlorination. The generality of this simple route to the synthesis of other metal chelates with imidoylamidinate ligands is anticipated. It does not require the previous synthesis of imidoylamidinate salts to be used as reagents, in contrast to some fluoroalkyl imidoylamidinate complexes of various metals with bis(perfluoroalkyl)triazapentadienyl ligands, typically $N(Ph)=C(C_3F_7)NC(C_3F_7)=N(Ph)^-$,[30–32] for which no luminescent behaviour has been quoted.

π-Conjugation effects appear to play a relevant role in the luminescent behaviour which is strong only when the R group of the organonitrile is capable of π-conjugation. It is barely or not detected for R groups such as an alkyl or an amide in the (imidoylamidinate)Pt(II) chelates related to **2–4** but derived from amidine coupling to, *e.g.*, acetonitrile or organocyanamide (Et_2NCN) ligands. Moreover, an increase of the π-electron withdrawing character of R significantly increases the luminescence quantum efficiency and leads to a shift of the emission to lower energy. The emission is also dependent on pH, being quenched in acidic media probably due to ligand protonation.

Hence, this study presents a type of complexes whose luminescence properties can be easily tuned by changing the electronic properties of the R group of the parent organonitrile and the pH of the solution. It is expected that a further tuning can be achieved by playing with the nature of the organic group of the amidine applied to their synthesis, *e.g.*, by using a substituted phenylamidine such as ArC(=NH)NHAr (Ar = substituted phenyl). Hence, they provide an opportunity to investigate and establish "structure–basicity–luminescence" relationships. The luminescence properties of complexes **3** and **4**, namely an intense emission in the visible, a relatively long lifetime, and pH and O_2 sensitivity, render these platinum complexes potential candidates for sensing applications.

Experimental

Materials and syntheses

For synthetic needs commercially available solvents were used after distillation, while for the spectroscopic measurements solvents of spectroscopic grade were used. $MeOSO_2CF_3$ was purchased from Aldrich, whereas PhC(=NH)NHPh,[33] *trans*-[$PtCl_2(RCN)_2$] (R = CH_2Ph,[19] Ph[20]), [Pt{NH=C(CH_2Ph)NC(Ph)=*N*Ph}$_2$] (**2**)[15] and [Pt{NH=C(Ph)NC(Ph)=NPh}$_2$] (**4**)[15] were prepared according to the published methods.

***trans*-[$PtCl_2$(*p*-$ClC_6H_4CN)_2$] (1).** The compound was prepared by a modified procedure described in the literature.[34] [$PtCl_2(MeCN)_2$] (300 mg, 0.86 mmol) and *p*-ClC_6H_4CN (400 mg, 2.91 mmol) were suspended in 2 mL of toluene and the reaction mixture was refluxed with stirring for 6 h, whereupon Et_2O (10 mL) was added to form a greenish–yellow powder which was filtered off, washed with Et_2O (four 5 mL portions) and dried in air. Yield 380 mg, 82%. Anal. Calcd for $C_{14}H_8N_2PtCl_4$: C, 31.17; H, 1.50; N, 5.20. Found: C, 31.30; H, 1.52; N, 5.20%. FAB$^+$–MS, *m*/*z*: 539 [M]$^+$. IR spectrum in KBr, selected bands, cm^{-1}: 2291 m–s ν(C≡N), 1582 m–s ν(C=C from Ar), 1095 s ν(C–Cl). ^{1}H NMR in $CDCl_3$, δ: 7.75 (d, 2*H*) and 7.56 (d, 2*H*)(*p*-ClC_6H_4). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 142.62 (C–Cl), 134.87 and 130.14 (*m*- and *p*-C_6H_4), 116.04 (C≡N).

Reaction of *trans*-[$PtCl_2$(*p*-$ClC_6H_4CN)_2$] with the Amidine. *trans*-[$PtCl_2$(*p*-$ClC_6H_4CN)_2$] (28.7 mg, 0.053 mmol) and PhC(=NH)NHPh (42 mg, 0.212 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and left at 40 °C. Yellow needles appeared on the top of the vial after 6 h, whereupon they were filtered off and then mechanically separated from the colourless crystals of PhC(=NH)NHPh·HCl. Yield: is 32 mg, 70%.

[Pt{NH=C(*p*-ClC_6H_4)NC(Ph)=NPh}$_2$] (3). Anal. Calcd for $C_{40}H_{30}N_6PtCl_2 \cdot 0.2CH_2Cl_2$: C, 55.07; H, 3.50; N, 9.59. Found: C, 55.18; H, 3.32; N, 9.49%. FAB$^+$–MS, *m*/*z*: 859 [M]$^+$. IR spectrum in KBr, selected bands, cm^{-1}: 33310 m–s ν(N–H), 1537 s ν(C=N and C=C from Ar), 1420 s ν(C=C from Ar), 695 m δ(C–H). ^{1}H NMR in $CDCl_3$, δ: 7.33 (m, 4*H*) and 7.13 (m, 10*H*) (Ph), 6.29 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 160.50 and 154.93 (two C=N), 146.18, 136.03, 129.19, 128.47, 128.83, 127.82, 127.54, 127.33 and 125.96 (carbons in Ph and *p*-ClC_6H_4).

Methylation of 4. Complex **4** (40 mg, 0.051 mmol) was suspended in dry THF (1 mL) and $MeOSO_2CF_3$ (0.106 mmol) was added dropwise to the suspension and left to stand on stirring for 2 h at the room temperature. The almost colorless suspension was then concentrated under vacuum to give an oily residue which was washed twice with Et_2O (two 1-mL portions), then dissolved in $CHCl_3/Et_2O$ (1 : 1, 2 mL) and the solution was left to stand in a vial at room temperature for evaporation. After evaporation, almost colorless crystals were formed on the top of the vial (yield is 13.6 mg, 23%) along with some amount of oily residue on the bottom. The crystals were collected for X-ray analysis and the oily residue was dried under vacuum to give a pale-yellow powder (yield is 30.8 mg, 52%).

[Pt{NH=C(Ph)N(Me)C(Ph)=NPh}$_2$][CF_3SO_3]$_2$ (5). Anal. Calcd for $C_{44}H_{38}N_6F_6S_2O_6Pt \cdot 2/3CHCl_3$: C, 44.72; H, 3.25; N, 7.01. Found: C, 44.60; H, 3.28; N, 6.85%. FAB$^+$–MS, *m*/*z*: 821 [M − H]$^+$. ^{1}H NMR in $CDCl_3$, δ: 7.52, 7.33 and 7.15 (m's, 15*H*, Ph), 6.65 (s, br, 1*H*, NH), 3.81 (s, 3*H*, Me). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 165.97 and 156.12 (two C=N), 143.91, 132.52, 129.80, 128.97, 128.81, 128.09, 127.54, and 126.55 (carbons in Ph's), 42.47 (Me).

Physical measurements

C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28 × 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a JASCO FT/IR-430 instrument in KBr pellets (separate experiments show that the spectra of all the compounds are similar in KBr and Nujol. Hence, only the spectra in KBr which are better resolved and not overlapped with Nujol bands are given). ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

Absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR spectrophotometer using 1.0 cm path length cells. All spectra were run against solvent as a blank. The emission spectra were obtained on a SPEX Fluorolog F112A fluorimeter and corrected for instrumental response. Fluid solution samples were degassed by freeze–pump–thaw cycles at least four times. Emission spectra at low temperature were obtained in EtOH : MeOH (4 : 1) (at 77 K) or methylcyclohexane : toluene (7 : 2) (at 110 K) solvent mixtures using an Oxford DN 1704 cryostat. Excitation wavelengths for quantum yield determinations were 330 nm in the case of complex **4**, 360 nm for complex **2** and 407 nm for complex **3**. A Corion WG-360-S 650F cut-off filter was used in the emission when performing luminescence measurements with λ_{ex} < 360 nm. 9-Bromoanthracene in MeOH ($\phi_F = 0.020$[27]) was used as a standard for the quantum yield determinations in the case of complexes **2** and **4**. For determination of the emission quantum yields of complex **3**, a tetracene solution in MeOH was used ($\Phi_F = 0.16$ in polar solvents[27]). Time resolved picosecond luminescence measurements were performed using the single-photon timing method with laser excitation. The set-up consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (Rhodamine 6G or DCM) laser, delivering fundamental or frequency-doubled 5 ps pulses at a repetition rate of 3.4 MHz, or alternatively, of a Spectra-Physics Millenia Xs Nd:YVO$_4$ diode pumped laser, pumping a pulse picked Spectra-Physics Tsunami titanium-sapphire laser, delivering 100 fs frequency-doubled pulses at a repetition rate of 4 MHz. Intensity decay measurements were made by alternate collection of impulse and decay, with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from excitation wavelength with a scattering suspension (1 cm cell). For the decays, a cut-off filter was used, effectively removing all excitation light. The emission signal passed through a depolarizer, a Jobin-Yvon HR320 monochromator with a grating of 100 lines nm^{-1}, and was recorded on a Hamamatsu 2809U-01 microchannel plate photomultiplier as a detector. The instrument response function had an effective FWHM of 35 ps.[35]

Crystal structure determinations of 4·2CH$_2$Cl$_2$ and 5·2CHCl$_3$

Crystals of both complexes were obtained directly from the reaction mixtures. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The single crystals were mounted in inert oil within the cold gas stream of the diffractometer. The Denzo-Scalepack[36] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS program.[37] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.14 (**4**)[38] or Denzo-Scalepack (**5**) was applied to data ($T_{\min}/T_{\max}$ values were 0.2427/0.8262 and 0.5504/0.8506 for **4** and **5**, respectively). The structure was refined with SHELXL-97[39] and WinGX graphical user interface.[40] In **4**, the NH hydrogens were located from the difference Fourier map and refined isotropically. Other hydrogens were placed in idealized position and constrained to ride on their parent atom. In **4**, the Pt atom lies on an inversion centre and has planar coordination geometry while in **5** the asymmetric unit has two independent half molecules with the Pt atoms on inversion centres. Again, molecules have planar coordination geometry. The crystallographic data are summarised in Table 1 and selected bond lengths and angles in Table 2.

Acknowledgements

This work was supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, through the POCI 2010 programme (FEDER funded) and by a HRM Marie Curie Research Training Network (AQUACHEM project MRTN-CT-2003-503864). G. S. and N. A. B. are grateful to FCT (grants SFRH/BPD/5728/2001 and SFRH/BPD/11448/2002, respectively) and V. Yu. K. for a grant for Cientista Convidado/Professor at the Instituto Superior Técnico. N. A. B. and V. Yu. K. thank the Russian Fund for Basic Research for grants 05-03-32140 and 06-03-32065 and the Scientific Council of the President of the Russian Federation (grant MK-1040.2005.3). N. A. B., M. H., and V. Yu. K. express their gratitude to the Academy of Finland for financial support.

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