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Luminescent cyclometallated platinum(II) complexes with *N*-benzoyl thiourea derivatives as ancillary ligands

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ABSTRACT

A series of cyclometallated 2-phenylpyridine Pt(II) complexes having *N*-benzoyl thiourea derivatives as ancillary ligands were prepared and characterised by elemental analysis, IR and UV–Vis spectroscopy, ^{1}H and ^{13}C NMR spectroscopy as well as by X-ray diffraction on single-crystal. All complexes were obtained as a single isomer with N atom of the 2-phenylpyridine ligand and S atom of the *N*-benzoyl thiourea derivatives coordinated in *trans* positions to the platinum metal as evidenced by using X-ray crystallography and NMR spectroscopy. All Pt(II) complexes show good luminescence properties at room temperature, both in dichloromethane solution and in solid state.

1. Introduction

Cyclometallated platinum(II) complexes represent one of the most interesting and broadly studied class of complexes because of their luminescence properties [1] that find applications in optoelectronic devices [2,3], luminescent probes for biomolecules (biochemistry) [4] and chemical sensors [5]. The most useful strategy to promote luminescence in platinum(II) complexes is to employ ligands with a very strong ligand field in order to raise the d–d state, which can be achieved by using cyclometallating ligands, mostly with 2-arylpyridine or 2-thienylpyridine derivatives, resulting both homoleptic [6] or heteroleptic complexes [7].

In the case of the heteroleptic complexes, it has been clearly demonstrated the influence of the ancillary ligand on the luminescence properties of such complexes besides some advantages like: preparation, tailoring the solubility, as well as the photophysical properties. Amongst the ancillary ligands used to prepare mononuclear heteroleptic luminescent Pt(II) complexes is worth to mention: bidentate ligands such as neutral diimines (bpy) or diamines (en) [8] or bidentate anionic ligands such as acetylacetonates (acac) [9] and, more recently, 8-quinolinates [10,11], bis(pyrazolyl) borates [12] and aminoacids [4], as well as various monodentate ligands like Cl^{-}, CO [13], RS^{-} [11,14], phosphines [15]. In some cases the phenylpyridine ligand can be essentially regarded as an ancillary ligand [10]. The luminescence of Pt(II) complexes is assigned to either ligand centred (LC) or metal-to-ligand charge transfer (MLCT) states or a mixed of both. In this study we were interested to study the influence of the *N*-benzoyl thiourea derivatives on the luminescence properties of cyclometallated phenylpyridine Pt(II) complexes when they are used as ancillary ligands. These derivatives possess very strong donor groups (carbonyl and thioamide) which make them very attractive for use as ligands in coordination chemistry and they are readily available by a two-step synthesis starting from benzoylchloride and corresponding amine providing access to a whole range of these derivatives [16,17]. These ligands react with transition metals, mostly in monoanionic and bidentate form by deprotonation, forming neutral complexes with *S*, *O*-coordination [18]. In this paper a series of phenylpyridine Pt(II) cyclometallated complexes bearing *N*-benzoyl thiourea derivatives were prepared and their luminescence properties were investigated both in solid state and in dichloromethane solution.

2. Results and discussion

2.1. Synthesis

The synthesis of the new compounds described here is summarised in Scheme 1.

The preparation of mononuclear *ortho*-platinated complexes was carried out by reacting the Pt precursor [Pt(Hppy)(ppy)(Cl)] [19] with the sodium salts of the *N*-benzoyl thiourea derivatives in dichloromethane. The new mononuclear complexes were

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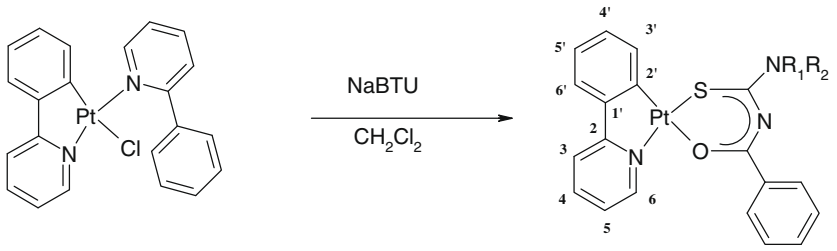

1 **2 - 13**

$R_1 = R_2 =$	*n*-Et	**2**	$R_1 = H, R_2 =$	Ph	**7**
	n-Pr	**3**		4-MeC_6H_4	**8**
	n-Bu	**4**		3-MeC_6H_4	**9**
	n-Hex	**5**		4-FC_6H_4	**10**
	n-Oct	**6**		4-ClC_6H_4	**11**
				4-BrC_6H_4	**12**
				4-$MeOC_6H_4$	**13**

Scheme 1. Synthesis of the new complexes and the *N*-benzoyl thiourea derivatives used in this study.

obtained in good yields after purification on silica. They are yellow microcrystalline solid products which are stable under atmospheric conditions. Their structure was confirmed by elemental analysis, IR spectroscopy as well as ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction.

The coordination of the *N*-benzoyl thiourea ancillary ligands in monoanionic deprotonated form to the Pt centre can be easily seen in the IR spectra. Thus, the N–H stretching frequency located around 3250 cm^{-1} and the strong absorption band located in the 1650–1690 cm^{-1} range assigned to ν(C=O) frequency in the IR spectra of free *N*-benzoyl thiourea derivatives disappear in the IR spectra of all complexes as a result of coordination.

The ^{1}H NMR spectroscopy indicated that all Pt(II) complexes were obtained as single isomer (only one set of signals) which was tentatively assigned as the isomer having N atom of the 2-phenylpyridine ligand and S atom of the *N*-benzoyl thiourea derivatives coordinated in *trans* positions to the platinum metal, though it is possible that complexes exist as a mixture of two isomers. This supposition is further supported by the single-crystal X-ray diffraction studies. The existence of only one isomer in solution was reported for other heteroleptic Pt(II) complexes bearing 2-phenylpyridine ligand [10,11].

The complexes can be divided in two groups according to their characteristic signals presented in the ^{1}H NMR spectra. Thus, one of the most important features of the ^{1}H NMR spectra is the signal assigned to the hydrogen H-6 which appears at 9.28–9.29 ppm in compounds **2–6** and slightly shielded at 9.15–9.24 ppm in compounds **7–13**. Also, the signal assigned to H-6 is accompanied by the ^{195}Pt satellites with a coupling constant $^3J_{Pt-H}$ = 33.0 Hz, similar to other cyclometallated 2-phenylpyridine Pt(II) complexes, thus indicating the binding of Pt to the deprotonated phenylpyridine ligand. The splitting pattern of the H-3, H-4 and H-5 protons signals from the pyridine ring is typical for such complexes. The protons H-4′ and H-5′ from the phenyl ring of the 2-phenylpyridine ligand appear shielded at around 7.10 ppm. Moreover, the presence of the ^{195}Pt satellites was evidenced in the ^{13}C NMR spectra accompanying the signals attributed to the carbon atoms of the 2-phenylpyridine ligand.

In the case of Pt complexes bearing *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives, complexes **2–6**, due to the hindered rotation about the C–NR_1R_2 bond, the alkyl groups are magnetically non-equivalent and therefore they can be seen in the ^{1}H and ^{13}C NMR spectra as two distinct sets of signals.

2.2. Description of the structures

Single crystals of complexes **2** and **8** suitable for X-ray diffraction were obtained by cooling a solution of these compounds in a mixture of dichloromethane and ethanol (ca. 1/1 v/v) at −25 °C. The crystallographic data for these two complexes are collected in Table 1 and selected bonds and angles are presented in Table 2.

The molecular structure of compound **2** is shown in Fig. 1. Complex **2** crystallised in the monoclinic crystal system, space group $P2_1/n$, with four discrete molecules in the unit cell. The platinum atom is surrounded by one sulfur atom and one oxygen atom of the *N*-benzoyl thiourea ligand, one aromatic carbon atom (metallated phenyl ring) and one nitrogen atom (pyridine ring) in an approximately square-planar arrangement with the sulfur atom located *trans* to the nitrogen atom of the pyridine ring. Both the metallated phenyl ring and the pyridine ring of the cyclometallated ligand are almost coplanar with respect to the five-membered chelate ring, the angle between the phenyl and the pyridyl rings of the cyclometallated phenylpyridine ligand is 3.5°, whilst the phenyl ring of the benzoyl group from the *N*,*N*-diethyl-*N*′-benzoyl thiourea ligand is twisted with 29.8° with respect to the core plane.

The shortest Pt–Pt distance between two neighbouring molecules is 8.217 Å, precluding any Pt–Pt interactions. The Pt–C and Pt–N bond lengths are comparable with the values reported for similar *ortho*-platinated complexes with phenylpyridine ligand [13,19,20]. The Pt–S bond length, 2.239 Å, is comparable with the two values found for the simple *cis* complex of Pt(II) with *N*,*N*-diethyl-*N*′-benzoyl thiourea which are 2.231 and 2.233 Å, respectively [21] and similar to that found in *cis*-bis(*N*,*N*-di(*n*-butyl)-*N*′-benzoylthioureato)platinum(II), 2.230(2)–2.233(2) Å [22], the two examples available for comparison. On the other hand the relatively long Pt–O bond length (2.076 Å) in complex **2** compare to *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)platinum(II) (2.018 and 2.023 Å) [21] is a consequence of the *trans* influence of the coordinated carbon atom of cyclometallated 2-phenylpyridine ligand.

Table 1
Crystallographic data for compounds **2** and **8**.

Compound	**2**	**8**
Empirical formula	$C_{23}H_{23}N_3OPtS$	$C_{26}H_{21}N_3OPtS$
Formula weight (g mol^{-1})	584.59	618.61
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions		
a (Å)	14.9455(12)	27.8193(15)
b (Å)	9.7791(6)	9.9384(9)
c (Å)	15.5698(12)	16.3976(13)
α (°)	90.00	90.00
β (°)	108.498(6)	96.833(4)
γ (°)	90.00	90.00
V (Å^3)	2158.0(3)	4501.4(6)
Z	4	8
D_{calc} (Mg m^{-3})	1.799	1.826
μ (mm^{-1})	6.618	6.351
F(0 0 0)	1136	2400
Colour	yellow	yellow
Crystal size (mm^3)	0.50 × 0.25 × 0.15	0.50 × 0.40 × 0.25
θ Range (°)	2.65–33.47	2.46–33.56
Reflections collected	21 684	38 811
Independent reflections (R_{int})	7710 (0.0757)	8682 (0.0658)
Data/restraints/parameters	7710/0/264	8682/0/294
Goodness-of-fit on F^2	0.995	1.098
Final R indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.0553, wR_2 = 0.0692	R_1 = 0.0528, wR_2 = 0.1048
R indices (all data)	R_1 = 0.1172, wR_2 = 0.0800	R_1 = 0.0792, wR_2 = 0.1141
Largest difference in peak and hole (e Å^{-3})	1.400 and −2.913	3.383 and −1.700

Table 2
Selected bond lengths and angles for compounds **2** and **8**.

	2	**8**
Pt–C	1.973(5)	1.979(6)
Pt–N	2.045(5)	2.035(5)
Pt–O	2.076(3)	2.075(4)
Pt–S	2.2389(15)	2.2447(14)
N(R2)–C(S)	1.341(7)	1.347(8)
N–C(S)	1.336(7)	1.333(7)
N–C(O)	1.325(7)	1.325(7)
C–O	1.268(6)	1.262(7)
C–S	1.738(6)	1.728(6)
C(O)–C(Ph)	1.489(7)	1.485(8)
C–Pt–N	80.8(2)	81.1(2)
N–Pt–O	91.75(16)	91.05(17)
O–Pt–S	93.22(11)	92.93(11)
S–Pt–C	93.22(11)	94.93(17)

Compound **8** (Fig. 2) crystallised in the monoclinic crystal system, group *C2/c*, with the same square–planar arrangement around the platinum atom bound to the phenylpyridine ligand in an *ortho*-metallated fashion and chelated to *N*-benzoyl thiourea derivative and the same coordinated atoms (one aromatic C atom (metallated ring), one N atom (pyridine ring), one O atom (carbonyl group) and one S atom (thiocarbonyl group)) as found for compound **2**; indeed bond lengths and angles for the central core are all very similar to those found in complex **2**. The same orientation with respect to the core plane was found for the two rings of the phenylpyridine ligand, which are almost coplanar with the five-membered chelate ring, the angle between the phenyl and the pyridyl rings of the cyclometallated phenylpyridine ligand is 3.5°, the same value as found for complex **2**. The phenyl ring of the benzoyl group from the *N*-benzoyl thiourea ligand is also twisted in respect to the core plane by 27.5°, a smaller value compare to that found for complex **2**. An interesting feature of the structure of this complex is the orientation adopted by the *p*-tolyl ring of the *N*-benzoyl thiourea ligand with a twist of 65.1° with respect to the core plane, leading to the formation of weak intermolecular NH···Pt interactions [23] (H···Pt 2.74 Å; N-H···Pt 156.8°) compared to those found in the salt $(N^nPr_4)_2[PtCl_4]\cdot[PtCl_2(NH_2Me)_2]$ (Fig. 3). In this example the neutron diffraction studies [24] revealed the presence of short intermolecular N–H···Pt interactions [H···Pt 2.262(11) Å] as well as a weaker C–H···Pt interaction [H···Pt 2.768(9) Å; C–H···Pt l64.4(7) Å]. Also, intermolecular aromatic π–π interactions are present that contribute to the crystalline packing of compound **8**. In this case, the shortest Pt–Pt distance between two neighbouring molecules is 4.18 Å.

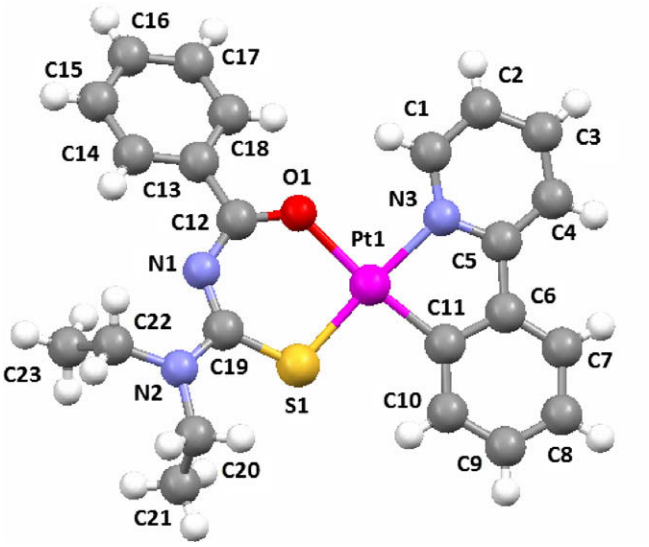

Fig. 1. The molecular structure of compound **2**.

For both complexes discussed above, the bond lengths of the thiocarbonyl [C–S 1.738(6) Å for complex **2** and 1.728(6) Å for complex **8**] and carbonyl [C–O 1.268(6) Å for complex **2** and 1.262(7) Å for complex **8**] bonds are longer than the average values of C=S and C=O bonds, whilst the C–N bonds in the chelate ring are all shorter than the average for C–N single bonds. The latter observation indicates extensive delocalization of electrons within the chelate ring of these two complexes as a consequence of the coordination of the ligands to platinum centre in the deprotonated form which leads to the partial double-bond character of the C–N bonds [21,22].

2.3. Absorption and emission properties

The UV–Vis absorption spectra of compounds **2**–**13** were recorded in solution (about 0.02 mM in dichloromethane) and several examples are shown in Fig. 4. The absorption and emission data are collected in Table 3.

In order to have a better appreciation of the shape of the spectra and their peak positions, the normalised spectra to the 258 nm maximum were obtained (Figs. S1–S4). Complexes **2**–**6** have only two well-resolved absorption maxima (at 279 nm, with a slight bathochromic shift for compound **4**, and at 375 nm with a slight bathochromic shift for compounds **2** and **4** compared to the same series), whilst compounds **7**–**13** exhibit besides the 282 nm (hypsochromically shifted for compound **12**) and 375 nm peaks, another maximum at 258 nm (hypsochromically shifted for compound **12**). It is worth to note that for compounds **2**–**6**, an equivalent of the 258 nm peak can be observed in a shoulder (254–260 nm), which could not be resolved by the measurements in dichloromethane solution even using the most favourable

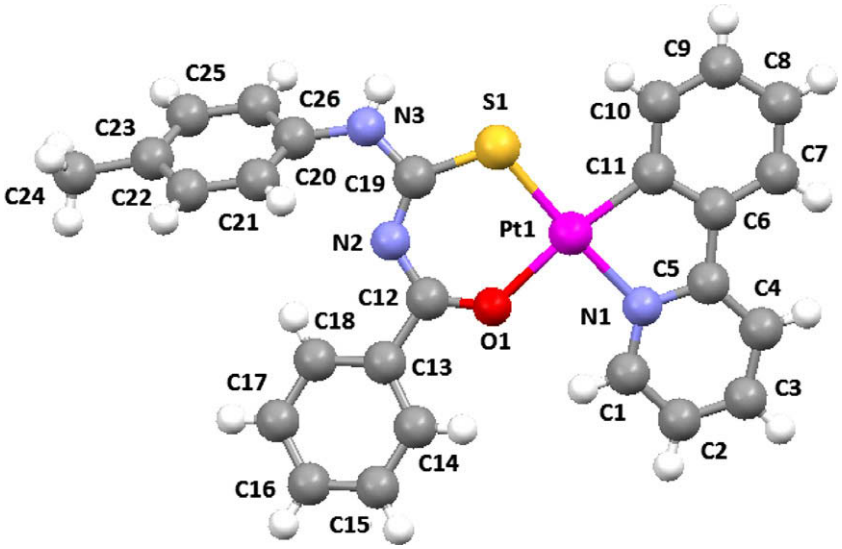

Fig. 2. The molecular structure of compound **8**.

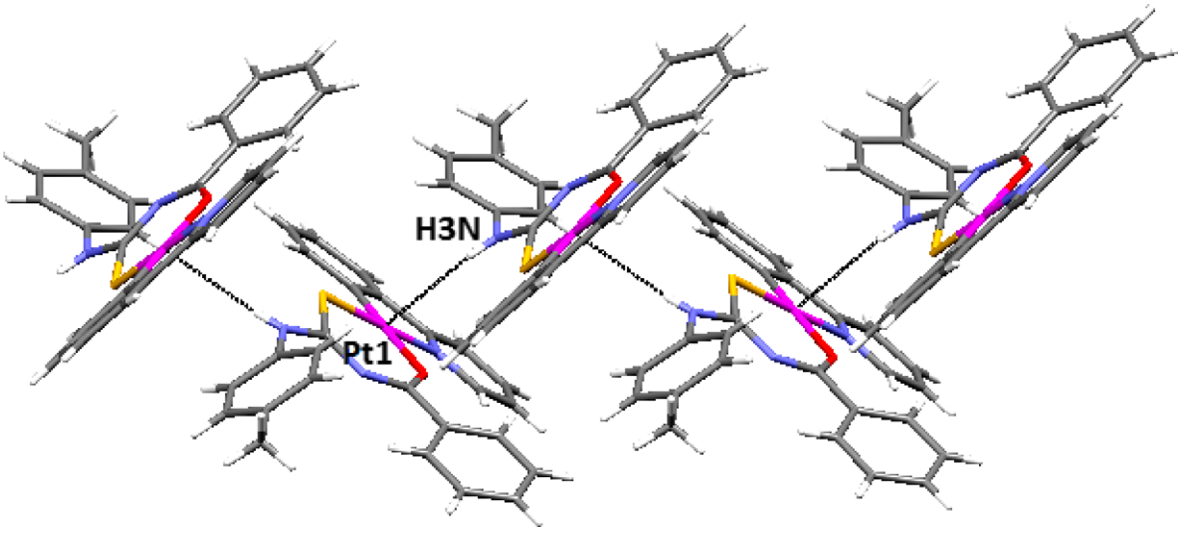

Fig. 3. The NH···Pt interactions between adjacent molecules of compound **8**.

available instrumental conditions. The extinction coefficient, ε, for the absorption maximum at 258 nm is around 40 000 M^{-1} cm^{-1} with a maximum of 46 500 M^{-1} cm^{-1} for complex **8**, except for compound **12**, which has an half-value extinction coefficient compared to the other compounds of the series.

The UV–Vis spectra of these complexes do not differ too much from the one of the homoleptic complex with 2-phenylpyridine ligand [$Pt(ppy)_2$] [6] and this is why the same electronic assignments are proposed.

The absorption bands located in the UV range can be assigned to intraligand n–π^* and π–π^* transitions (LC) which are perturbed by complexation to the Pt(II) metal. The free 2-phenylpyridine ligand show similar absorption bands in same region, at 248 and 276 nm whilst the free *N*-benzoyl thiourea derivatives show two absorption bands located in the range 240–280 nm and around 310 nm, respectively. The moderately intense absorptions around 375 nm for all prepared complexes **2**–**13** can be assigned to spin-allowed metal-to-ligand charge transfer MLCT ($d_{Pt} \rightarrow \pi^*_{ppy}$) transition by analogy with similar Pt(II) complexes containing 2-phenylpyridine as ligand [6]. The intensity of these absorption bands ($\varepsilon > 10^3$ M^{-1} cm^{-1}) rules

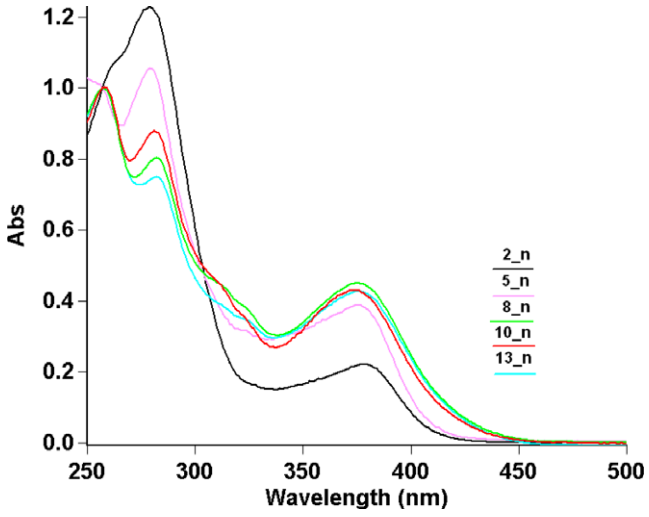

Fig. 4. Normalised spectra of 0.02 mM solutions of complexes **2**, **5**, **8**, **10** and **13** in dichloromethane (normalisation to the 258 nm peak).

Table 3
Absorption and emission data for complexes **2**–**13**.

Complex	Absorption λ_{max}/nm ($\varepsilon \times 10^{-3}$/M^{-1} cm^{-1})	Emission	Φ_{em}
2	260(sh), 279 (82.5), 378 (14.9)	482, 516	0.006
3	256(sh), 279 (38.3), 375 (8.5)	483, 515	0.005
4	257(sh), 282 (38.3), 323(sh), 378 (14.7)	483, 515	0.007
5	254(sh), 279 (26.7), 375 (9.9)	482, 515	0.009
6	256(sh), 280 (32.7), 375 (12.5)	483, 515	0.010
7	258 (41.1), 282 (37.7), 308(sh), 322(sh), 375(18.5)	482, 522	0.010
8	257 (46.5), 282 (37.5), 310(sh), 322(sh), 375 (21.0)	482, 522	0.010
9	258 (38.2), 282 (30.9), 309(sh), 324(sh), 375 (17.2)	482, 522	0.011
10	258 (40.3), 282(35.4), 310(sh), 373 (17.3)	482, 522	0.012
11	259 (40.4), 281 (34.3), 310(sh), 322(sh), 374 (18.9)	482, 531	0.007
12	256 (23.7), 278 (20.3), 308(sh), 320(sh), 374 (11.2)	482, 531	0.022
13	258 (43.2), 282 (32.4), 312(sh), 322(sh), 375 (18.5)	482, 531	0.063

out the possibility of the assignment to a purely d–d transition. Such an assignment could be further support by the fact that the position of the MLCT absorption band does not change when different *N*-benzoyl thiourea derivatives are introduced in the molecule as ancillary ligand.

All Pt(II) complexes show luminescence properties both in dichloromethane solution and in solid state at room temperature. The emission and excitation spectra in solution are presented in Figs. 5 and 6 whilst in Fig. 7 two examples of solid-state emission spectra are shown. The excitation spectra closely matched the absorption spectra. There is a clear difference between the complexes bearing *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives, complexes **2**–**6**, and the complexes with *N*-aryl-*N*′-benzoyl thiourea derivatives, **7**–**13**, in terms of luminescence properties. All prepared Pt(II) complexes show two emission bands in the 450–550 nm range. The first one has the same position at 482 nm for all complexes but its intensity in respect to the second one varies for the two groups of complexes introduced above. For complexes **2**–**6** the intensity of this band is higher than the one located at 515 nm, whilst for complexes **7**–**13** this band has lower intensity compare to the second emission band. Moreover, the second emission band is red shifted and display a broad maximum at 522 nm for complexes **7**–**10** and at 531 nm for complexes **11**–**13** when compare to complexes **2**–**6** which exhibit this emission band at 515 nm.

If we consider the highest energy feature of the luminescence emission maxima, there is no significant difference in the position of the emission maxima for complexes **2**–**13** compare to the Pt(II) complexes containing cyclometallated phenylpyridine and different ancillary ligands: acetylacetonate complexes exhibit emission at λ_{max} ~485 nm in 2-methyltetrahydrofuran solution [9]; complexes with phen or bpy [8] exhibit emission in DMF at λ_{max} ~486 nm and complexes with bis(pyrazolyl)borates [12] as ancillary ligands show the same features with λ_{max} = 488 nm in $CHCl_3$ solution. In fact for these complexes the emission maxima and quantum yields are similar to those of the homoleptic *cis*-[Pt(ppy)$_2$] complexes that display structured ligand-centred

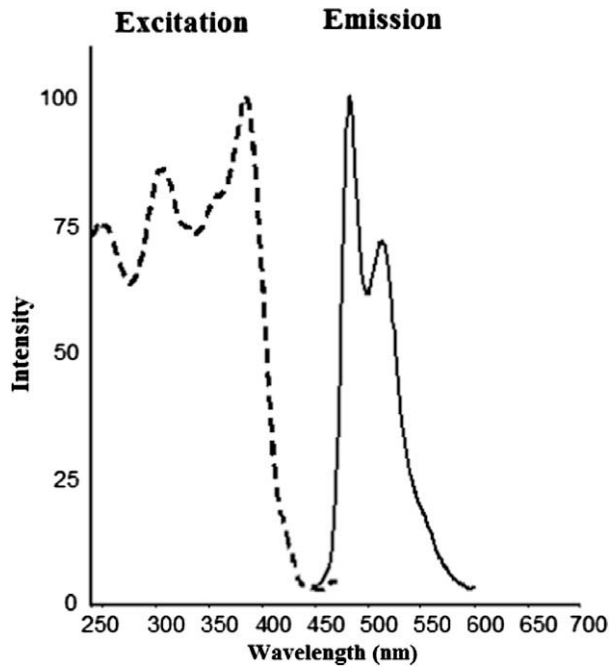

Fig. 5. Excitation and emission spectra of compound **2** in CH_2Cl_2 at 298 K with excitation at 375 nm and emission monitored at 482 nm.

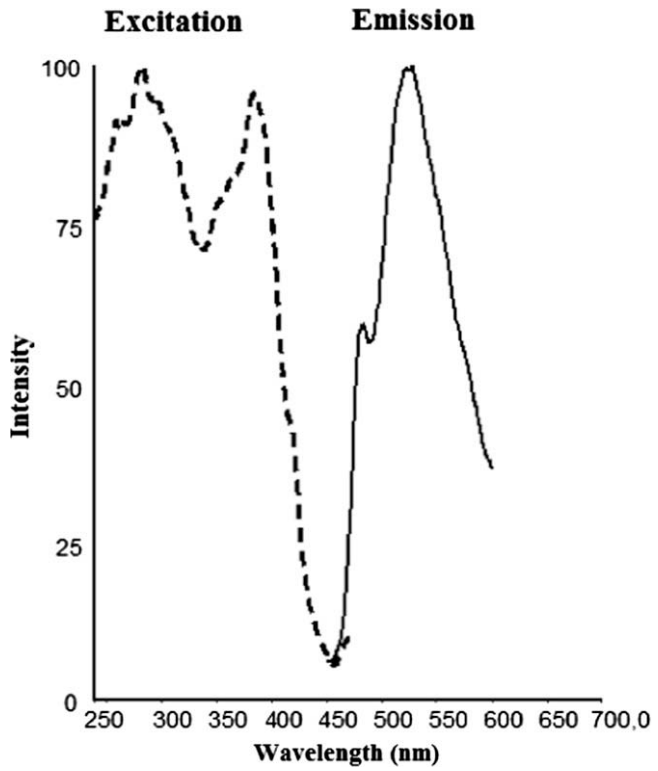

Fig. 6. Excitation and emission spectra of compound **10** in CH_2Cl_2 at 298 K with excitation at 375 nm and emission monitored at 522 nm.

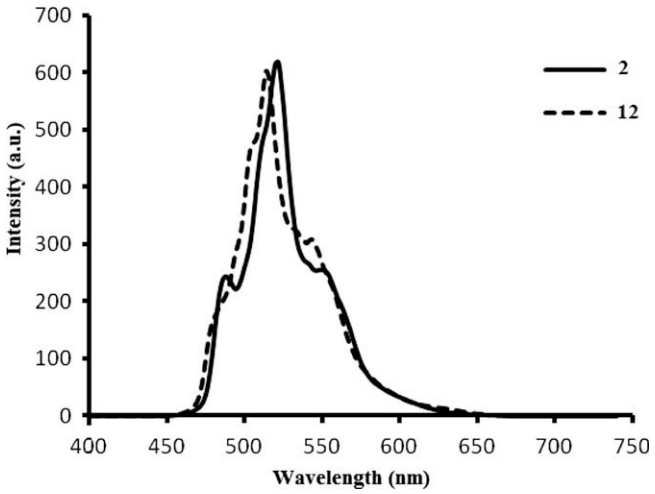

Fig. 7. Solid state emission spectra of complexes **2** and **12** (λ_{exc} = 380 nm).

phosphorescence at 450–550 nm [25]. The solid-state emission spectra displayed in Fig. 7 show compounds **2** and **12** having λ_{max} at 521 and 514 nm, respectively. These two complexes also exhibit some structure on the emission bands with high- and low-energy shoulders at 488 and 552 nm and at 484 and 544 nm, respectively. Also, complexes **2** and **12** exhibit a slightly red shift in the value of λ_{max} in going from solution to the solid state. The solid-state emission spectra are not significantly different from those recorded in dichloromethane solution which suggests that there is a negligible Pt–Pt interaction resulted from crystal packing as it is supported by the X-ray analysis data.

3. Conclusions

A series of cyclometallated 2-phenylpyridine (ppy) Pt(II) complexes bearing *N*-benzoyl thiourea derivatives as ancillary ligands were prepared and characterised, and their absorption spectra and luminescence properties were investigated. These complexes were isolated as single isomers with the sulfur atom in *trans* position versus the nitrogen atom of the ppy ligand as confirmed by X-ray diffraction studies and NMR spectroscopy. The platinum(II) complexes show good photoluminescence properties both in dichloromethane solution and in solid state at room temperature and their emission maxima are similar to other cyclometallated 2-phenylpyridine Pt(II) complexes with different ancillary ligands, resulting in a very little influence of the type of *N*-benzoyl thiourea derivatives employed.

4. Experimental

Dichloromethane was distilled over phosphorus pentaoxide; other chemicals were used as supplied. Melting points were measured using a Linkam THMS600 hot stage and a TMS94 temperature controller attached to a Nikon 50i Pol microscope. The FT-IR spectra were recorded in the range 4000–400 cm^{-1} using a BioRad FTS-135 instrument. Proton and carbon NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using $CDCl_3$ as solvent. ^1H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. X-ray data for crystals **2** and **8** were collected at room temperature on a STOE IPDS II diffractometer. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. The UV–Vis absorption spectra of Pt(II) complexes **2**–**13** were recorded in dichloromethane using a Cary 100 Bio (Varian Inc.) spectrophotometer. Solid state fluorescence spectra were recorded using a JASCO FP6500 spectrofluorimeter whilst fluorescence spectra in solution were recorded using a Perkin–Elmer LS 50B spectrofluorimeter with the following instrumental parameters: excitation wavelengths 259, 282 and 375 nm, excitation slit 5 nm, emission slit 5 nm, scanning speed 200 nm/min and 290 nm cut-off filter except for the λ_{exc} = 375 nm. For each excitation (emission) wavelength a spectrum of the solvent was also recorded in the same conditions. Absorption and emission spectra of a 1 μM quinine sulfate solution in 0.5 M H_2SO_4 were used for the determination of the fluorescence quantum yield of the compounds. The quantum yield was computed according to the following equation:

$$\Phi_u = \Phi_{st}\frac{I_u q_{st} A_{st}}{I_{st} q_u A_u}$$

where Φ is the quantum yield, I is the integrated area of the emission spectrum corrected for the solvent signal, q is the photon output of the source at the excitation wavelength (the emission intensity measured directly on the curve) and A is the absorbance of the solutions at the excitation wavelengths, whereas indexes u and st denote the unknown (new) compound and the quinine sulfate (standard) solutions [26]. The Pt precursor [Pt(Hppy)(ppy)(Cl)] used in the preparation of the mononuclear complexes **2**–**13** was prepared according to the literature data [9,19]. The *N*-benzoyl thiourea derivatives as well as their sodium salts used in this work were prepared according to the methods published in the literature [16,17].

4.1. Synthesis of complexes 2–13

The solid sodium salt of *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivative (0.15 mmol) was added to a solution of the Pt precursor complex (0.10 mmol) in CH_2Cl_2 (15 ml) and the resulting mixture was stirred at room temperature for 1 day. The solvent was removed and the solid was purified on silica using CH_2Cl_2 as eluant. The crude yellow solid was recrystallised from a mixture of CH_2Cl_2/C_2H_5OH (1/1) at −25 °C to give a bright yellow crystalline product.

The yields, elemental analysis results as well as ^1H and selected ^{13}C NMR and IR data are presented below:

Compound **2**. Yield 83%, yellow crystals, m.p. 187 °C. *Anal.* Calc. for $C_{23}H_{24}N_3OPtS$: C, 47.2; H, 4.1; N, 7.2. Found: C, 46.9; H, 4.5; N, 7.0%.

^1H NMR (300 MHz, $CDCl_3$) δ: 1.30, 1.44 (2t, 6H, J = 7.1 Hz, $2CH_3$); 3.88, 3.96 (q, 4H, J = 7.1 Hz, $2CH_2N$); 7.04–7.14 (m, 2H, H-4′, H-5′); 7.33 (ddd, 1H, J = 1.4, 5.0, 7.4 Hz, H-5); 7.40–7.46 (m, 2H, *meta*-Ph-BTU); 7.49–7.60 (m, 3H, H-3′, H-6′, *para*-Ph-BTU); 7.74 (dt, 1H, J = 0.8, 7.5 Hz, H-3); 7.88 (ddd, 1H, J = 1.6, 7.4, 7.5 Hz, H-4); 8.20–8.23 (m, 2H, *ortho*-Ph-BTU); 9.29 (ddd, 1H, J = 0.8, 1.6, 5.0 Hz, H-6).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3 (C=S), 165.8 (C=O), 145.2 (C-2, ppy), 138.3 (C-4, ppy), 132.9 (C-3′, ppy), 131.2 (Ph-BTU), 129.9 (C-4′, ppy), 129.4 (Ph-BTU), 128.4 (Ph-BTU), 123.9 (C-6′, ppy), 123.7 (C-5′, ppy), 122.1 (C-5, ppy), 118.9 (C-3, ppy), 47.2, 46.1 (CH_2), 13.5, 12.9 (CH_3).

IR (KBr, cm^{-1}): (ν_{C-H}), 2960w, 2930w, 2870w, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1608m, 1520s, 1483s, 1420vs, 745m.

Compound **3**. Yield 82%, yellow crystals, m.p. 148 °C. *Anal.* Calc. for $C_{25}H_{28}N_3OPtS$: C, 48.9; H, 4.6; N, 6.8. Found: C, 48.5; H, 4.9; N, 6.5%.

^1H NMR (300 MHz, $CDCl_3$) δ: 0.96, 1.05 (2t, 6H, J = 7.1 Hz, $2CH_3$); 1.70–2.00 (m, 4H, $2CH_2$); 3.75–3.86 (m, 4H, $2CH_2N$); 7.07–7.11 (m, 2H, H-4′, H-5′); 7.32 (ddd, 1H, J = 1.4, 5.0, 7.4 Hz, H-5); 7.40–7.45 (m, 2H, *meta*-Ph-BTU); 7.48–7.53 (m, 3H, H-3′, H-6′, *para*-Ph-BTU);

7.75 (dt, 1H, J = 0.8, 7.5 Hz, H-3); 7.90 (ddd, 1H, J = 1.6, 7.4, 7.5 Hz, H-4); 8.19–8.21 (m, 2H, *ortho*-Ph-BTU); 9.28 (ddd, 1H, J = 0.8, 1.6, 5.0 Hz, H-6).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.9 (C=S), 165.8 (C=O), 145.1 (C-2, ppy), 138.4 (C-4, ppy), 132.7 (C-3′, ppy), 131.3 (Ph-BTU), 130.0 (C-4′, ppy), 129.4 (Ph-BTU), 128.5 (Ph-BTU), 124.0 (C-6′, ppy), 123.7 (C-5′, ppy), 122.2 (C-5, ppy), 119.0 (C-3, ppy), 54.8, 53.7, 21.6, 21.0 (CH_2), 11.9 (CH_3).

IR (KBr, cm^{-1}): (ν_{C-H}), 2950w, 2930w, 2870w, ($\nu_{C=N}$, $\nu_{C=C}$), 1635m, 1606m, 1514s, 1482s, 1423vs, 746m.

Compound **4**. Yield 70%, yellow crystals, m.p. 143 °C. *Anal.* Calc. for $C_{27}H_{32}N_3OPtS$: C, 51.8; H, 5.2; N, 6.7. Found: C, 51.9; H, 5.5; N, 6.4%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.98, 1.05 (2t, 6H, J = 7.3 Hz, $2CH_3$); 1.35–1.55 (m, 4H, $2CH_2$); 1.65–1.95 (m, 4H, $2CH_2$); 3.80–3.93 (m, 4H, $2CH_2N$); 7.10 (m, 2H, H-4′, H-5′); 7.32 (ddd, 1H, J = 1.4, 5.0, 7.4 Hz, H-5); 7.40–7.45 (m, 2H, *meta*-Ph-BTU); 7.48–7.53 (m, 3H, H-3′, H-6′, *para*-Ph-BTU); 7.75 (dt, 1H, J = 0.8, 7.5 Hz, H-3); 7.90 (ddd, 1H, J = 1.6, 7.4, 7.5 Hz, H-4); 8.20–8.22 (m, 2H, *ortho*-Ph-BTU); 9.29 (ddd, 1H, J = 0.8, 1.6, 5.0 Hz, H-6).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.9 (C=S), 165.8 (C=O), 145.2 (C-2, ppy), 138.4 (C-4, ppy), 132.8 (C-3′, ppy), 131.3 (Ph-BTU), 130.0 (C-4′, ppy), 129.4 (Ph-BTU), 128.5 (Ph-BTU), 124.0 (C-6′, ppy), 123.7 (C-5′, ppy), 122.2 (C-5, ppy), 119.0 (C-3, ppy), 52.8, 51.8, 30.4, 29.7, 20.7 (CH_2), 14.3 (CH_3).

IR (KBr, cm^{-1}): (ν_{C-H}), 2957m, 2930m, 2870w, ($\nu_{C=N}$, $\nu_{C=C}$), 1634m, 1607m, 1518s, 1494s, 1484s, 1418vs, 745m.

Compound **5**. Yield 80%, yellow crystals, m.p. 79 °C. *Anal.* Calc. for $C_{31}H_{40}N_3OPtS$: C, 53.4; H, 5.8; N, 6.0. Found: C, 53.1; H, 6.0; N, 5.7%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86, 0.94 (2t, 6H, J = 7.1 Hz, $2CH_3$); 1.21–1.56 (m, 8H, $4CH_2$); 1.60–1.78 (m, 4H, $2CH_2$); 1.80–1.99 (m, 4H, $2CH_2$); 3.77–3.87 (m, 4H, $2CH_2N$); 7.06–7.11 (m, 2H, H-4′, H-5′); 7.32 (ddd, 1H, J = 1.4, 5.0, 7.4 Hz, H-5); 7.41–7.46 (m, 2H, *meta*-Ph-BTU); 7.49–7.52 (m, 3H, H-3′, H-6′, *para*-Ph-BTU); 7.73 (dt, 1H, J = 0.8, 7.5 Hz, H-3); 7.88 (ddd, 1H, J = 1.6, 7.4, 7.5 Hz, H-4); 8.18–8.21 (m, 2H, *ortho*-Ph-BTU); 9.28 (ddd, 1H, J = 0.8, 1.6, 5.0 Hz, H-6).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.9 (C=S), 165.8 (C=O), 145.1 (C-2, ppy), 138.4 (C-4, ppy), 132.8 (C-3′, ppy), 131.3 (Ph-BTU), 130.0 (C-4′, ppy), 129.4 (Ph-BTU), 128.4 (Ph-BTU), 124.0 (C-6′, ppy), 123.7 (C-5′, ppy), 122.2 (C-5, ppy), 119.0 (C-3, ppy), 52.8, 53.1, 52.1, 31.9, 28.2, 27.4, 27.2, 23.0 (CH_2), 14.4 (CH_3).

IR (KBr, cm^{-1}): (ν_{C-H}), 2925m, 2857m, ($\nu_{C=N}$, $\nu_{C=C}$), 1635m, 1606m, 1514s, 1482s, 1419vs, 747m.

Compound **6**. Yield 75%, yellow crystals, m.p. 71 °C. *Anal.* Calc. for $C_{35}H_{48}N_3OPtS$: C, 55.8; H, 6.4; N, 5.6. Found: C, 55.5; H, 6.8; N, 5.4%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86, 0.90 (2t, 6H, J = 7.1 Hz, $2CH_3$); 1.25–1.44 (m, 16H, $8CH_2$); 1.63–178 (m, 4H, $2CH_2$); 1.80–1.98 (m, 4H, $2CH_2$); 3.78–3.89 (m, 4H, $2CH_2N$); 7.08–7.11 (m, 2H, H-4′, H-5′); 7.30 (ddd, 1H, J = 1.4, 5.0, 7.4 Hz, H-5); 7.40–7.45 (m, 2H, *meta*-Ph-BTU); 7.49–7.54 (m, 3H, H-3′, H-6′, *para*-Ph-BTU); 7.75 (dt, 1H, J = 0.8, 7.5 Hz, H-3); 7.89 (ddd, 1H, J = 1.6, 7.4, 7.5 Hz, H-4); 8.20–8.22 (m, 2H, *ortho*-Ph-BTU); 9.29 (ddd, 1H, J = 0.8, 1.6, 5.0 Hz, H-6).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3 (C=O), 165.5 (C=S), 144.9 (C-2, ppy), 138.0 (C-4, ppy), 132.4 (C-3′, ppy), 130.9 (Ph-BTU), 129.6 (C-4′, ppy), 129.1 (Ph-BTU), 128.1 (Ph-BTU), 123.6 (C-6′, ppy), 123.4 (C-5′, ppy), 121.8 (C-5, ppy), 118.6 (C-3, ppy), 52.8, 51.7, 31.8, 29.3, 27.9, 27.2, 22.6 (CH_2), 14.1 (CH_3).

IR (KBr, cm^{-1}): (ν_{C-H}), 2950m, 2925m, 2870m, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1607m, 1517s, 1497s, 1483s, 1420vs, 742m.

Compound **7**. Yield 77%, yellow crystals, m.p. 220 °C. *Anal.* Calc. for $C_{25}H_{19}N_3OPtS$: C, 49.7; H, 3.2; N, 7.0. Found: C, 49.5; H, 3.6; N, 6.8%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.02–7.05 (m, 2H, H-4′, H-5′); 7.29 (ddd, 1H, J = 1.4, 6.0, 7.1 Hz, H-5); 7.33–7.56 (m, 12H, H-3′, H-6′, 8H-BTU); 7.71 (m, 1H, H-3); 7.86 (m, 1H, H-4); 8.15–8.17 (m, 2H, *ortho*-Ph-BTU); 9.18 (dd, 1H, J = 0.8, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3054w, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1608m, 1518s, 1501s, 1485s, 1427vs, 752m.

Compound **8**. Yield 72%, yellow crystals, m.p. 228 °C dec. *Anal.* Calc. for $C_{26}H_{21}N_3OPtS$: C, 50.5; H, 3.4; N, 6.8. Found: C, 50.3; H, 3.7; N, 6.5%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.38 (s, 1H, *p*-CH_3); 7.07–7.10 (m, H-4′, H-5′); 7.21 (d, 2H, J = 8.6 Hz, 2H-BTU); 7.35 (ddd, 1H, J = 1.6, 6.0, 7.4 Hz, H-5); 7.41–7.58 (m, 7H, H-3′, H-6′, 5H-BTU); 7.75–7.77 (m, 1H, H-3); 7.88–7.93 (m, 1H, H-4); 8.20–8.23 (m, 2H, *ortho*-Ph-BTU); 9.23 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3051w, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1608m, 1518s, 1485s, 1431vs, 754m.

9. Yield 83%, yellow crystals, m.p. 150 °C. *Anal.* Calc. for $C_{26}H_{21}N_3OPtS$: C, 50.5; H, 3.4; N, 6.8. Found: C, 50.2; H, 3.6; N, 6.5%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 1H, *m*-CH_3); 7.01–7.03 (m, 2H, H-4′, H-5′); 7.23–7.52 (m, 10H, H-5, H-3′, H6′, 7H-BTU); 7.69 - 7.71 (m, 1H, H-3); 7.82–7.88 (m, 1H, H-4); 8.15–8.18 (m, 2H, *ortho*-Ph-BTU); 9.17 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3047w, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1607m, 1512s, 1485s, 1431vs, 751m.

Compound **10**. Yield 82%, yellow crystals, m.p. 229 °C dec. *Anal.* Calc. for $C_{25}H_{18}FN_3OPtS$: C, 48.2; H, 2.9; N, 6.7. Found: C, 47.9; H, 3.3; N, 6.4%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.00–7.08 (m, 4H, H-4′, H-5′, 2H-BTU); 7.19–7.52 (m, 8H, H-5, H-3′, H-6′, 5H-BTU); 7.69–7.72 (m, 1H, H-3); 7.82–7.85 (m, 1H, H-4); 8.10–8.13 (m, 2H, *ortho*-Ph-BTU); 9.16 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3077w, ($\nu_{C=N}$, $\nu_{C=C}$), 1637m, 1607m, 1522s, 1508s, 1485s, 1431vs, 755m.

Compound **11**. Yield 85%, yellow crystals, m.p. 232 °C. *Anal.* Calc. for $C_{25}H_{18}ClN_3OPtS$: C, 47.0; H, 2.8; N, 6.6. Found: C, 46.8; H, 3.1; N, 6.4%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.01–7.08 (m, 4H, H-4′, H-5′, 2H-BTU); 7.29–7.54 (m, 8H, H-5, H-3′, H-6′, 5H-BTU); 7.70–7.72 (m, 1H, H-3); 7.83–7.89 (m, 1H, H-4); 8.11–8.14 (m, 2H, *ortho*-Ph-BTU); 9.15 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3052w, ($\nu_{C=N}$, $\nu_{C=C}$), 1635m, 1607m, 1519s, 1485s, 1431vs, 754m.

Compound **12**. Yield 80%, yellow crystals, m.p. 239 °C. *Anal.* Calc. for $C_{25}H_{18}BrN_3OPtS$: C, 43.9; H, 2.7; N, 6.1. Found: C, 43.7; H, 3.0; N, 5.9%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.08–7.11 (m, 4H, H-4′, H-5′, 2H-BTU); 7.35–7.60 (m, 8H, H-5, H-3′, H-6′, 5H-BTU); 7.76–7.79 (m, 1H, H-3); 7.89–7.95 (m, 1H, H-4); 8.18–8.21 (m, 2H, *ortho*-Ph-BTU); 9.22 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3053w, ($\nu_{C=N}$, $\nu_{C=C}$), 1635m, 1608m, 1517s, 1485s, 1431vs, 754m.

Compound **13**. Yield 77%, yellow crystals, m.p. 220 °C. *Anal.* Calc. for $C_{26}H_{21}N_3O_2PtS$: C, 49.2; H, 3.3; N, 6.6. Found: C, 48.9; H, 3.6; N, 6.4%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.85 (s, 1H, OCH_3); 6.94 (d, 2H, J = 8.0 Hz, BTU); 7.05–7.07 (m, 2H, H-4′, H-5′); 7.21–7.57 (m, 6H, H-5, H-3′, H-6′, 3H-BTU); 7.75–7.77 (m, 1H, H-3); 7.87–7.93 (m, 1H, H-4); 8.11–8.20 (m, 4H, BTU); 9.24 (dd, 1H, J = 1.6, 6.0 Hz, H-6).

IR (KBr, cm^{-1}): (ν_{N-H}), 3044w, ($\nu_{C=N}$, $\nu_{C=C}$), 1636m, 1607m, 1509s, 1484s, 1435vs, 751m.

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Appendix A. Supplementary data

CCDC 740820 and 740821 contain the supplementary crystallographic data for **2** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.08.015.

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