

New members of a class of cyclometalated 1,3-di-(2-pyridyl)benzene platinum(II) complexes bearing a tetrazole-thiolate ancillary ligand

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Dedicated to Howard Alper, a great chemist and professor, full of boundless energy.

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ABSTRACT

Substitution of the chlorido ligand of the cyclometalated complexes [Pt(5-R-dpyb)Cl] (R = methyl, 2-thienyl; dpyb = 1,3-di(2-pyridyl)benzene) by 1-phenyl-1H-tetrazole-5-thiolate leads to the related thiolato complexes [Pt(5-R-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)], which have been fully characterised. Their photophysical properties were determined in degassed dichloromethane solution at room temperature. It turned out that the color of the phosphorescence can be tuned by the nature of the substituents on the benzene ring, with the introduction of a donor group such as 2-thienyl allowing a large red-shift of the emission. Substitution of the chloride ligand with 1-phenyl-1H-tetrazole-5-thiolate has a negligible effect on the emission maxima and lifetimes, since both parameters remain in a narrow range which is very close to the original value. However, the use of this thiolate as ancillary ligand can lead to very high quantum yields, approaching unity.

1. Introduction

In the last decade, there has been a growing interest in the study of cyclometalated platinum(II) complexes for a wide range of applications such as nonlinear optics [1–8], electroluminescent devices [9–21], bioimaging [22–26], photodynamic therapy [26–29], and sensing devices [30–35]. The important spin–orbit coupling due to the platinum atom helps intersystem crossing, and consequently emission of light from triplet excited states, a performance that is further enhanced by the introduction of Pt–C bonds [36–38]. Besides, an interesting aspect of square planar platinum(II) complexes is that their emitted colour can be easily controlled by the concentration of the complex, as a consequence of the parallel emissions coming from the mono-molecular and bi-molecular excited states; as a matter of fact, the square planar geometry allows the creation of bi-molecular states, both in the excited states (excimers) and in the ground states (dimers) by means of Pt–Pt and/or ligand–ligand intermolecular interactions [18,39–41].

Chlorido Pt(II) complexes bearing a cyclometalated 1,3-di(2-pyridyl)benzene (dpyb) ligand turned out to be very bright emitters, with the monomer emission colour easily modulated by the choice of the substituents on the phenyl or pyridyl rings of the cyclometalated dpyb ligand [9]. For example, the introduction of electron-acceptor groups on

the phenyl ring, where is mainly localized the highest occupied molecular orbital (HOMO), lowers the HOMO energy and thus increases the HOMO-LUMO gap leading to a blue shift of the emission. A further blue shift can be achieved by increasing the lowest unoccupied molecular orbital (LUMO) energy upon addition of electron-donor groups on the pyridines, where the LUMO is mostly localized. Vice-versa, introduction of electron-acceptor groups on the pyridines and/or electron-donor groups on the phenyl ring leads to a red-shift of the emission [9,42–44].

Recently, a topic of growing interest is the effect of the substitution of the chloride co-ligand on the emission properties of these platinum(II) complexes. Up to now, complexes with isothiocyanate [11,13,25], azide [28], acetylides [12,34,35,45–47], isocyanides [48,49], iodide [50], phenolates [51], and thiolates [19,52–54] instead of chloride have been prepared. It turned out that while substitution with isothiocyanate or acetylides maintains high Quantum Yields, the presence of a thiolate brings about different effects. Thus, differently substituted thio-phenolates [52] or a simple thioacetate [53] result in a much lower Quantum Yield with respect to the parent chlorido compound. On the contrary, we found that [Pt(5-mesityl-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (Fig. 1; complex 1) is characterized by a monomeric emissive colour similar to that of the related complex with chloride (complex A) [55] or 4-phenylthiazole-2-thiolate (complex 4) [54], but it is much

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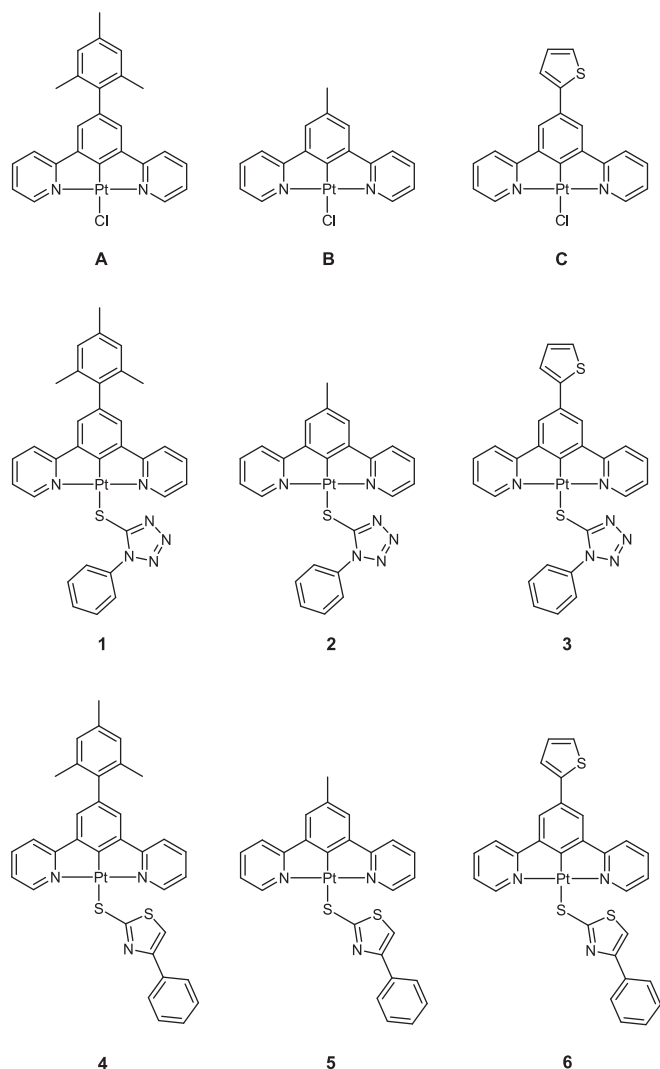


Fig. 1. Structure of the investigated complexes [Pt(5-R-dpyb)Cl] (R = mesityl for **A**, methyl for **B**, 2-thienyl for **C**), [Pt(5-R-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (R = mesityl for **1**, methyl for **2**, 2-thienyl for **3**) and [Pt(5-R-dpyb)(4-phenylthiazole-2-thiolate)] (R = mesityl for **4**, methyl for **5**, 2-thienyl for **6**).

more emissive ($\Phi_{lum} = 0.90, 0.62$ and 0.55 for **1**, **A** and **4**, respectively). These observations and the desire to gain a deeper understanding of the effect of a 1-phenyl-1H-tetrazole-5-thiolate co-ligand on the emission properties of Pt(II) complexes bearing a cyclometalated 1,3-di(2-pyridyl)benzene ligand prompted us to prepare complexes [Pt(5-R-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (R = Me, **2**; R = 2-thienyl, **3**) and compare their photophysical properties with that of the related complexes with chloride (**B**, **C**) and 4-phenylthiazole-2-thiolate (**5**, **6**).

2. Experimental

2.1. Materials and methods

All reaction solvents and reagents were purchased from Sigma-Aldrich, whereas deuterated solvents for NMR measurements were purchased from Eurisotop; all of them were used without further purification. Complexes [Pt(5-methyl-dpyb)Cl] (**B**) [56] and [Pt(5-(2-thienyl)-dpyb)Cl] (**C**) [55] were prepared by reaction of the suitable N^oC^oN ligand with 1.2 eq of K₂PtCl₄ in glacial acetic acid at reflux under argon for 24 h, according to literature [55,56]. ¹H and ¹³C{¹H} NMR spectra of the final complexes are reported in the SI.

Electronic absorption spectra were carried out in CH₂Cl₂ solution, at

room temperature, using a Shimadzu UV3600 spectrophotometer and quartz cuvettes with 1 cm optical path length. Luminescence measurements were recorded in CH₂Cl₂ solution after three Freeze-Pump-Thaw cycles in order to remove dissolved oxygen. Absolute photoluminescence quantum yields (QY) were measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer. Steady-state and time-resolved fluorescence data were obtained using a FLS980 spectrofluorimeter (Edinburgh Instrument Ltd). The measurement techniques are well described in the SI.

2.2. Synthesis of the new complexes **2** and **3**

2.2.1. Synthesis of [Pt(5-methyl-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (**2**)

[Pt(5-methyl-dpyb)Cl] (14 mg, 0.029 mmol) was dissolved in a mixture of MeOH (3.0 mL) and CH₂Cl₂ (3.0 mL), and sodium 1-phenyl-1H-tetrazole-5-thiolate (89 mg, 0.44 mmol) was added. The obtained mixture was stirred at room temperature under argon atmosphere and in the dark. After 24 h the precipitation of an orange solid was observed. MeOH (5.0 mL) was added to precipitate all the product and to dissolve the sodium salt in excess; after 10 min of stirring the desired product was recovered by filtration, washed with MeOH and Et₂O, and dried (17 mg, 0.027 mmol, 94 %).

¹H NMR (400 MHz, CD₂Cl₂) δ (ppm): 9.14 (2H, s, with ¹⁹⁵Pt satellite peaks), 7.97 (2H, dd, $J = 7.3$ Hz, $J = 7.7$ Hz), 7.88 (2H, d, $J = 7.0$ Hz), 7.73 (2H, d, $J = 7.7$ Hz), 7.53–7.37 (5H, m), 7.23 (2H, m), 2.44 (3H, s).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂) δ (ppm): 153.14, 139.30, 128.89, 124.83, 123.46, 119.36, 21.71. Not all peaks are visible, due to the low solubility of the complex.

Elemental Analysis for C₂₄H₁₈N₆PtS: calcd. C 46.67 %; H 2.94 %; N 13.61 % found. C 46.98 %, H 2.92, N 13.70 %.

2.2.2. Synthesis of [Pt(5-(2-thienyl)-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (**3**)

[Pt(5-(2-thienyl)-dpyb)Cl] (36 mg, 0.066 mmol) was dissolved in a mixture of MeOH (6.0 mL) and CH₂Cl₂ (6.0 mL), and sodium 1-phenyl-1H-tetrazole-5-thiolate (200 mg, 0.99 mmol) was added. The obtained mixture was stirred at room temperature under argon atmosphere and in the dark. After 24 h the precipitation of an orange solid was observed. MeOH (10.0 mL) was added to precipitate all the product and to dissolve the sodium salt in excess; after 10 min of stirring the desired product was recovered by filtration, washed with MeOH and Et₂O, and dried (37 mg, 0.055 mmol, 83 %).

¹H NMR (300 MHz, CD₂Cl₂) δ (ppm): 9.19 (2H, s, with ¹⁹⁵Pt satellite peaks), 8.07–7.99 (2H, t, $J = 5.5$ Hz), 7.92–7.77 (5H, m), 7.53–7.42 (3H, m), 7.40 (1H, d, $J = 3.7$ Hz), 7.33–7.25 (2H, m), 7.20–7.15 (1H, m).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂) δ (ppm): 139.36, 129.10, 128.23, 124.37, 123.71, 122.74, 121.84, 119.68. Not all peaks are visible, due to low solubility of the complex.

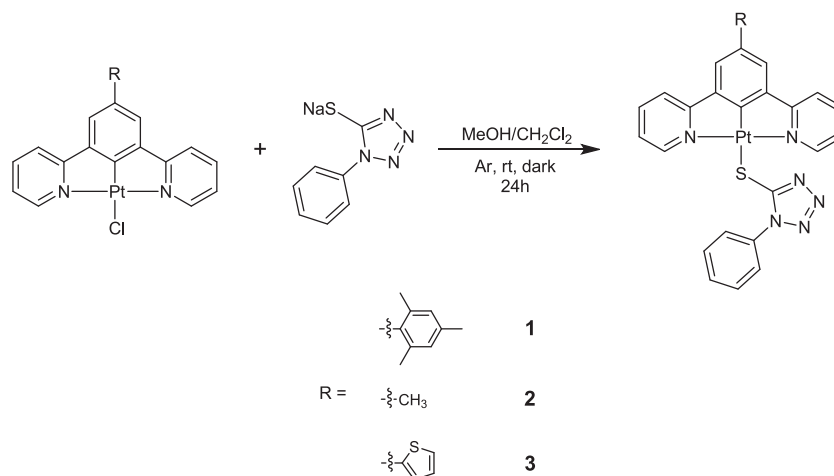
Elemental Analysis for C₂₇H₁₈N₆PtS₂: calcd. C 47.29 %; H 2.65 %; N 12.26 % found. C 46.99 %, H 2.68, N 12.13 %.

3. Results and discussion

Complexes [Pt(5-methyl-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (**2**) and [Pt(5-(2-thienyl)-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (**3**) were prepared by reaction of the related chlorido complex with sodium 1-phenyl-1H-tetrazole-5-thiolate (Scheme 1, see Experimental).

The UV–vis absorption spectra of complexes **2** and **3** in dichloromethane (CH₂Cl₂) solution at the concentration of $1 \cdot 10^{-6}$ M are shown in Fig. 2, along with that of the related **1** complex. In addition, the UV–vis absorption spectra at different concentrations in CH₂Cl₂ solution were registered in order to calculate the molar extinction coefficients (ϵ), see Figs. S1 and S2, and Table S1 in the SI.

The two new complexes show intense absorption bands at 237–325 nm which can be attributed to intraligand ¹ π - π^* transitions of the N^oC^oN



Scheme 1. General reaction for the substitution of the -Cl ligand with the thiolate.

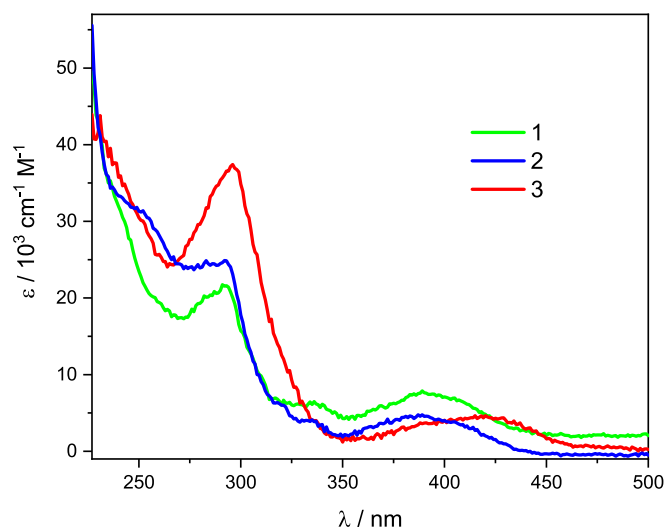


Fig. 2. UV-vis absorption spectra of **1–3** in CH_2Cl_2 , at a concentration of $1 \cdot 10^{-6}$ M.

ligand and less intense bands at 350–450 nm assigned to charge-transfer transitions involving the cyclometalated ligand and the metal [13]. In addition, a very weak absorption band at lower energy (around 492 nm) is distinguishable in the absorption spectrum of **2** at the concentration of $2 \cdot 10^{-4}$ M (see inset expansion in Fig. S1 panel A). This weak absorption band is probably composed by the overlapping of two absorption bands: one due to direct population of $^3\pi\text{-}\pi^*$ states of **2**, as observed for similar complexes [21], and the other by the absorption of the aggregates (see below).

Fig. 3 reports the normalized emission spectra of complexes **2** and **3** studied in deaerated CH_2Cl_2 solutions at the concentration of $1 \cdot 10^{-6}$ M, along with that of the related complex **1**. The emission wavelengths, a comparison of the Quantum Yields before ($\text{QY}_{\text{before}}$) and after (QY_{after}) three Freeze-Pump-Thaw (FPT) cycles, and the lifetimes of **2** and **3** are reported in Table 1, together with the values relative to complex **1** and of the related complexes with chloride (A–C) and 4-phenylthiazole-2-thiolate (4–6). Complete data and spectra are reported in the SI.

As expected, complex **2**, bearing a methyl group on the phenyl ring, shows intense phosphorescent bands with a maximum wavelength at 504 nm, slightly red-shifted with respect to **1**, whereas a much larger red-shift is observed for **3**, in agreement with the presence of the much stronger electron-donor thienyl group on the phenyl ring (Fig. 3). The same trend has been observed for the complexes bearing a chloride (A–C)

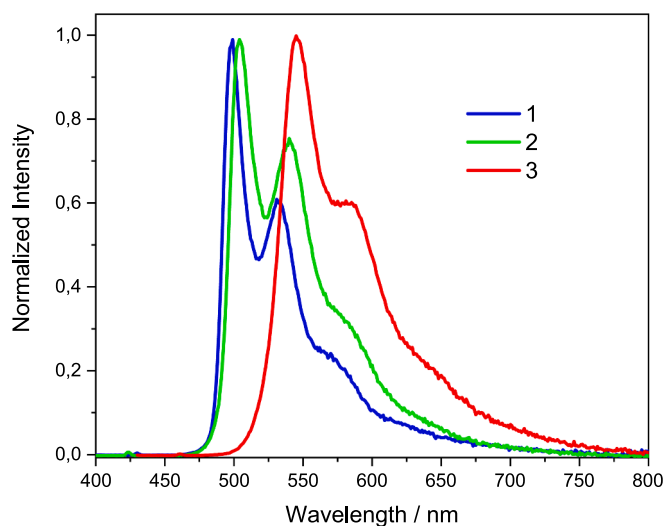


Fig. 3. Emission spectra of **1–3** in deaerated CH_2Cl_2 at a concentration of $1 \cdot 10^{-6}$ M.

[55,56] or a 4-phenylthiazole-2-thiolate (4–6) [54] ligand.

When the concentration of the **2** and **3** complexes is increased up to $2 \cdot 10^{-4}$ M, new broad structureless emission bands arise at around 690 nm (Figs. S4 and S6), which are slightly blue shifted compared to the **1** complex (733 nm) (Fig. 4). These new bands at lower energy can be ascribed to the emission from bi-molecular emissive excited states (excimers and aggregates) of the platinum(II) complexes, as previously reported for related complexes. [19,53,57,58] It is worth noting that the excitation spectrum profile of the **2** and **3** complexes recorded at the wavelength of 503 and 545 nm, respectively, and those of the structureless emission bands at around 690 nm are quite different between 440 ÷ 550 nm, see Figs. S4 and S6. This difference is attributed to the absorption of the aggregates of the two complexes which are excited between 440 ÷ 550 nm and then decay radiatively at 690 nm.

As a general consideration arising from the comparative data reported in Table 1, substitution of the chloride ligand with 1-phenyl-1*H*-tetrazole-5-thiolate or 4-phenylthiazole-2-thiolate doesn't exert a noticeable effect on the emission maxima. Therefore, in the case of derivatives of complex **B**, the $\lambda_{\text{em}}^{\text{max}}$ has values of 504 nm and 503 nm for **2** and **5** respectively, starting from a maximum at 505 nm; the same is valid also for compounds **3** and **6** ($\lambda_{\text{em}}^{\text{max}} = 545$ nm for both, from an original 548 nm for **C**), and for compounds **1** and **4** ($\lambda_{\text{em}}^{\text{max}} = 498$ nm for both, from an original 501 nm for **A**). Similarly, the lifetimes of the

Table 1

Key luminescence data for complexes 1–3, related chloride compounds A–C and complexes 4–6 bearing a 4-phenylthiazole-2-thiolate ancillary ligand at the concentration of $1 \cdot 10^{-6}$ M.

Complex	λ_{em}^{max} / nm	QY _{after} / %	QY _{before} / %	τ / μ s	k_r / s^{-1}	k_{nr} / s^{-1}
A ^a	501	62	4.5	7.9	$7.9 \cdot 10^4$	$4.8 \cdot 10^4$
B ^b	505	68	2.4	7.8	$8.7 \cdot 10^4$	$4.1 \cdot 10^4$
C ^a	548	54	1.5	20.5	$2.6 \cdot 10^4$	$2.2 \cdot 10^4$
1 ^c	498	90	5.0	7.39	$1.2 \cdot 10^5$	$1.3 \cdot 10^4$
2 ^d	504	42	5.0	7.90	$5.3 \cdot 10^4$	$7.3 \cdot 10^4$
3 ^d	545	93	3.3	19.2	$4.8 \cdot 10^4$	$3.0 \cdot 10^3$
4 ^e	498	55	3.5	7.7	$7.1 \cdot 10^4$	$5.8 \cdot 10^4$
5 ^e	503	65	2.5	7.9	$8.2 \cdot 10^4$	$4.4 \cdot 10^4$
6 ^e	545	89	3.0	19.1	$4.7 \cdot 10^4$	$6.0 \cdot 10^3$

^a From reference [55]. Luminescence quantum yields were determined by the method of continuous dilution, using quinine sulfate in 1 M H₂SO₄ (QY = 0.546) as the standard.

^b From reference [56]. The reported value represents the mean obtained from measurements using three standards: [Ru(bpy)₃]Cl₂ in H₂O (QY = 0.028), fluorescein in 0.1 M NaOH (QY = 0.90) and quinine sulfate in 1 M H₂SO₄ (QY = 0.546).

^c From reference [19] Absolute QY were measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer.

^d This work. Absolute QY were measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer.

^e From reference [54] Absolute QY were measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer.

^f Lifetimes were recorded in deaerated solutions.

^g Formulas for calculating k_r and k_{nr} are reported in the supporting information.

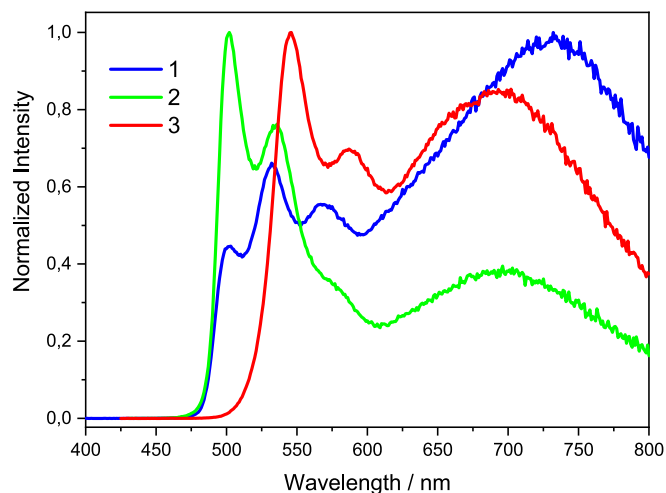


Fig. 4. Emission spectra of 1–3 in deaerated CH₂Cl₂ at a concentration of $2 \cdot 10^{-4}$ M.

complexes with the investigated thiolates remain very close to the original value of the chlorido parent. They are in the range 7.4–7.9 μ s for the mesityl- and methyl-substituted complexes, while longer lifetimes characterize the compounds with a 2-thienyl moiety, reaching values of 19–20 μ s. Increasing the concentration of complexes 2 and 3 to $2 \cdot 10^{-4}$ M leads to a drastic decrease of the lifetimes at 0.72 and 1.85 μ s, respectively.

Moving to the absolute Quantum Yields, the effect of the replacement of the chloride appears more evident. Complex 3, having the 1-phenyl-1H-tetrazole-5-thiolate as ancillary ligand and the 2-thienyl group on the phenyl ring, is the best-performing among all the investigated compounds (Table 1), with a QY of 93 %, a value slightly higher than that of the related 4-phenylthiazole-2-thiolate complex 6 (89 %) [54] and much higher than that of the parent chlorido complex C (54 %

[55]). A similar excellent QY (90 %) was previously observed with the related 1-phenyl-1H-tetrazole-5-thiolate complex 1, having a mesityl instead of a 2-thienyl group on the phenyl ring [19]. However, the QY measured for complex 2 is lower (42 %). Increasing the concentration of 2 and 3 leads to a strong decrease in QY up to 14.1 % and 18.5 %, respectively, due to quenching caused by the presence of aggregates and excimers. To get a better understanding of the observed trends in the quantum yield, radiative (k_r) and nonradiative (k_{nr}) rate constants have been calculated (see Table 1 and Table S2, details in the supporting information, Equations 3–4). k_r represents the rate constant for the radiative deactivation of the excited state of a molecule (in this case as phosphorescence), in which no competitive radiationless pathways are present from the emitting state; on the other side, k_{nr} represents the sum of all rate constants deactivating the excited state in a non-radiative way. Although photophysical data for groups A–C, 1–3 and 4–6 in Table 1 are obtained from different sources, a qualitative rationalization of the results can still be obtained. It is observed that the complexes bearing the 2-thienyl substituent on the phenyl ring always show a lower k_r with respect to complexes with mesityl and methyl substituent in each of the three groups; moreover, the complexes with the methyl substituent have the highest k_r , except for that of 1 which is higher than the value of 2. These behaviours suggest that the stronger the donor group, the lower the k_r ; however, the high value of k_r obtained for 1 cannot be justified without a deeper quantummechanic analysis which allows to calculate the transition dipole moment from the triplet excited state to the ground state of the two complexes. Interestingly, 1 displays not only a high k_r but also a very low k_{nr} and this can explain the high value (90 %) of QY recorded for this complex. Molecules that possess rigid structures, for which twisting and stretching of bonds is inhibited, tend to decrease the radiationless transition rate [59]. In 1, steric hindrance of the methyl groups of the mesityl ligand decreases the rotation of the mesityl group itself with respect to the terdentate ligand; as well as the steric interactions between the terdentate ligand and the phenyl group of the tetrazole-bearing phenyl moiety prevent the twisting of the latter [19]. On the contrary, in 2 the rotations of the methyl group on the central phenyl ring result in a higher k_{nr} value, which ultimately causes a low QY. In general, the complexes with the 2-thienyl substituent present a lower k_{nr} than the complexes with mesityl and methyl substituents in each of the three groups, due to the coplanarity of the 2-thienyl and the terdentate ligand. In particular, these low k_{nr} values for 3 and 6 are responsible for the excellent measured quantum yield values, 93 % and 89 %, respectively. As the concentration of complexes 2 and 3 is increased up to around $2 \cdot 10^{-4}$ M, the k_{nr} values increase by at least one order of magnitude with respect to the diluted solution at $1 \cdot 10^{-6}$ M and this is compatible with the presence of excimers and aggregates.

As for the related complexes in dilute aerated dichloromethane solution (Table 1), the luminescence of 2 and 3 is very efficiently quenched by oxygen at room temperature, this species being detrimental for light-emitting devices; however, the production of singlet oxygen could be interesting for other applications such as sensors and photodynamic therapy.

4. Conclusion

In conclusion, two new luminescent complexes, namely [Pt(5-R-dpyb)(1-phenyl-1H-tetrazole-5-thiolate)] (R = methyl for 2; R = 2-thienyl for 3), have been prepared. In this thiolate N³C²N-platinum(II) family, it was shown how the color of the phosphorescence can be tuned by the nature of the substituents on the benzene ring, with the presence of a donor group such as 2-thienyl allowing a large red-shift of the emission. It appeared that, in this kind of platinum(II) complexes, substitution of the chloride ligand with a thiolate ligand such as 1-phenyl-1H-tetrazole-5-thiolate or 4-phenylthiazole-2-thiolate has a negligible effect on the emission maxima and on the lifetimes, since both parameters remain in a narrow range which is very close to the original value. However, the use of 1-phenyl-1H-tetrazole-5-thiolate as ancillary ligand

can be useful for the photophysical properties because it can lead, although not always, to very high quantum yields, approaching unity. Complex Pt3 is characterized by a quantum yield of 93 % in diluted deaerated solution which decreases by a factor of almost 30 (QY = 3.3 %) in the presence of oxygen, an interesting aspect for sensors and photodynamic therapy.

CRediT authorship contribution statement

Francesco Fagnani: Investigation, Writing – original draft, Writing – review & editing. **Alessia Colombo:** Conceptualization, Investigation, Writing – review & editing. **Claudia Dragonetti:** Conceptualization, Investigation, Writing – review & editing. **Dominique Roberto:** Conceptualization, Investigation, Writing – review & editing. **Daniele Marinotto:** Conceptualization, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2023.121446>.

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