

Article

A Novel Class of Cyclometalated Platinum(II) Complexes for Solution-Processable OLEDs

Dominique Roberto ¹, Alessia Colombo ¹, Claudia Dragonetti ¹, Francesco Fagnani ^{1,*}, Massimo Cocchi ²
and Daniele Marinotto ³

¹ Department of Chemistry, University of Milan, UDR-INSTM, Via C. Golgi 19, 20133 Milan, Italy

² Istituto per la Sintesi Organica e la Fotoreattività (ISOF), Consiglio Nazionale delle Ricerche (CNR), Via P. Gobetti 101, 40129 Bologna, Italy

³ Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta", Consiglio Nazionale delle Ricerche (CNR), Via C. Golgi 19, 20133 Milan, Italy

* Correspondence: francesco.fagnani@unimi.it; Tel.: +39-339-782-9874

Abstract: Substitution of the chlorido ligand of cyclometalated [Pt (5-R-1,3-di(2-pyridyl) benzene)Cl] (R = methyl, mesityl, 2-thienyl, or 4-diphenylamino-phenyl) by 4-phenylthiazole-2-thiolate leads to related thiolato complexes, which were fully characterized. Their photophysical properties were determined in degassed dichloromethane solution. The emission color of the novel complexes can be easily tuned by the nature of the substituents on the terdentate ligand, as is the case for the parent chlorido complexes. Their luminescence Quantum Yield is high, with that of the compounds with the 2-thienyl or 4-diphenylamino-phenyl substituents being much higher than that of the related chloride complexes. The platinum complex with the cyclometalated 5-(2-thienyl)-1,3-di(2-pyridyl) benzene was used as the emitter for the fabrication of a yellow solution-processable OLED.

Keywords: coordination compounds; cyclometalated platinum(II) complexes; dipyriddy benzene ligand



Citation: Roberto, D.; Colombo, A.; Dragonetti, C.; Fagnani, F.; Cocchi, M.; Marinotto, D. A Novel Class of Cyclometalated Platinum(II) Complexes for Solution-Processable OLEDs. *Molecules* **2022**, *27*, 5171. <https://doi.org/10.3390/molecules27165171>

Academic Editors: Paola Deplano, Flavia Artizzu and Luca Pilia

Received: 25 July 2022

Accepted: 11 August 2022

Published: 13 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Transition metal complexes can find very useful applications in different fields because of the luminescence characteristics provided by the presence of the heavy metal atom. In fact, this allows for an efficient intersystem crossing which populates the excited triplet states, from which radiative emission can occur, even if theoretically forbidden. These appealing luminescence properties of transition metals, such as Platinum [1,2], can find application in different fields, from the production of light-emitting devices [3–5] to the use as dyes for bio-imaging and as biological probes [6–8]. In particular, this phenomenon can be observed in the case of cyclometalated Pt(II) complexes belonging to the family of [Pt(dpyb)Cl] compounds (dpyb = 1,3-di(2-pyridyl) benzene, structure of the complex in Figure 2). The terdentate dpby chelating ligand offers a rigid environment around the platinum center, hampering non-radiative decays which could take place in the excited states. As a consequence, the absolute phosphorescence Quantum Yield of these complexes in deaerated solution reaches very high values ($\Phi_{lum} = 0.60$ for the unsubstituted [Pt(dpyb)Cl] [9]).

The main fields in which the emission characteristics of this family of Pt(II) complexes have been tested until now, and can be furtherly exploited within, are the production of sensing devices and OLEDs [10–16], photodynamic therapy [17,18] and for bio-imaging [19–23]. Remarkably, the emission color of the compounds (and therefore also of the prepared devices) can be tuned by varying the substituents on the main scaffold of the terdentate ligand. Different substituents can be introduced on both the central benzene ring and the pyridines. Depending on the electron-donating or accepting properties of the substituents, the HOMO-LUMO gap of the complex can be modified and therefore the emission color can be tuned.

Thanks to the cyclometalating carbon atom in the *trans* position with respect to the ancillary Cl ligand in the square planar geometry of these compounds, the chloride can be easily replaced by other anionic species. Up to now, various ligands have been introduced in this way including isothiocyanates [11,22–24], azides [25], acetylides [26–32], isocyanides [33–35], phenolates [36] and thiolates [37–41]. While substitution with NCS or an acetylide maintains high Quantum Yields, the presence of a thiolate brings about different effects. A simple thioacetate [40] or differently substituted thiophenolates [37] result in a much lower Quantum Yield with respect to the parent chlorido compound, while 1-phenyl-1*H*-tetrazole-5-thiolate [41] provides a record value of 0.90.

Another possibility is to introduce substituents (such as 4-NPh₂-phenyl [42]) on the pyridyl rings of the N[∩]C[∩]N ligands, leading to the expansion of the aromatic system and to higher QY (also in this case, up to 0.90).

In this work, we presented four new complexes bearing a new sulfur-based ancillary ligand, namely a 4-phenylthiazole-2-thiolate. These complexes present different substituents on the benzene ring of the N[∩]C[∩]N ligand, i.e., a methyl, a mesityl, a 2-thienyl and a 4-diphenylamino-phenyl group (structure of the complexes in Figure 1).

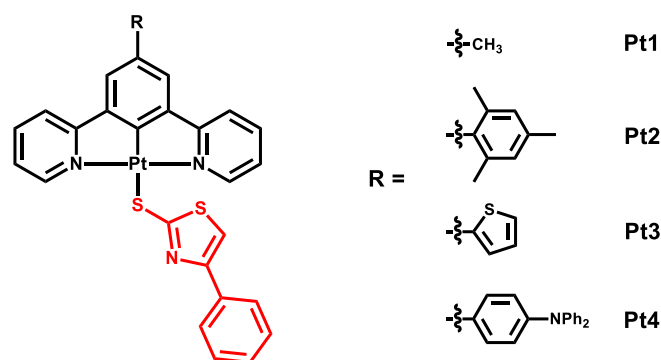


Figure 1. Structure of complexes **Pt1–Pt4**; in red, the new thiolate employed as ancillary ligand.

All complexes were characterized from the absorption and luminescence point of view (Figures S7–S18), and compound **Pt3** was employed for the production of a yellow solution-processable OLED device.

2. Results and Discussion

Starting with the already known chlorido complexes **PtCl1–PtCl4** ([9,43], structures in Figure 2), four new compounds were synthesized with 4-phenylthiazole-2-thiolate as the ancillary ligand on the Pt(II) center (Figure 1). For all **Pt1–Pt4** complexes, UV-Vis absorption spectra were registered, together with emission, excitation, absolute Quantum Yield and lifetime measurements; the luminescence studies were carried out in deaerated dichloromethane solutions. Since the long-living triplet states of the platinum(II) complexes are efficiently quenched by molecular oxygen, three Freeze–Pump–Thaw (FPT) cycles were performed to remove the O₂ present in the air and in the solution.

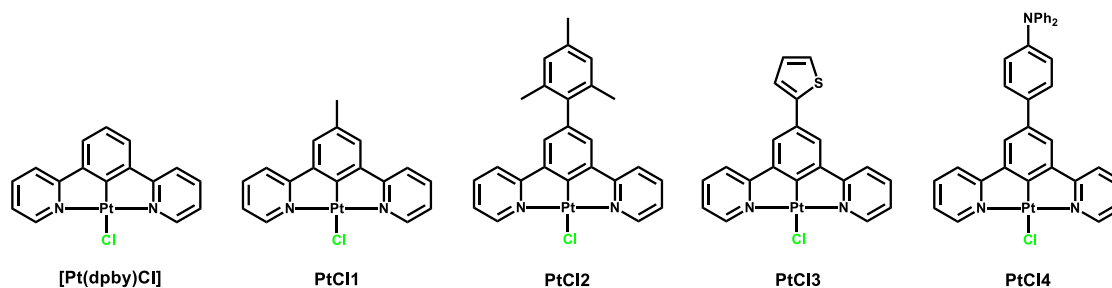


Figure 2. Structure of complexes **[Pt(dpby)Cl]** and **PtCl1–PtCl4**.

2.1. Photophysical Properties

Figure 3 shows the UV-Vis absorption spectra of the four new compounds **Pt1–Pt4**, while Figure 4 reports their normalized emission spectra; in both cases, the complexes were studied as dichloromethane solutions with a concentration of 1×10^{-6} M. The absorption spectra in CH_2Cl_2 at different concentrations were registered in order to calculate the molar extinction coefficients (ϵ); the spectra and a table with ϵ values are reported in the Supplementary Information. For all complexes, no aggregation was observed neither in absorption nor in the emission measurements.

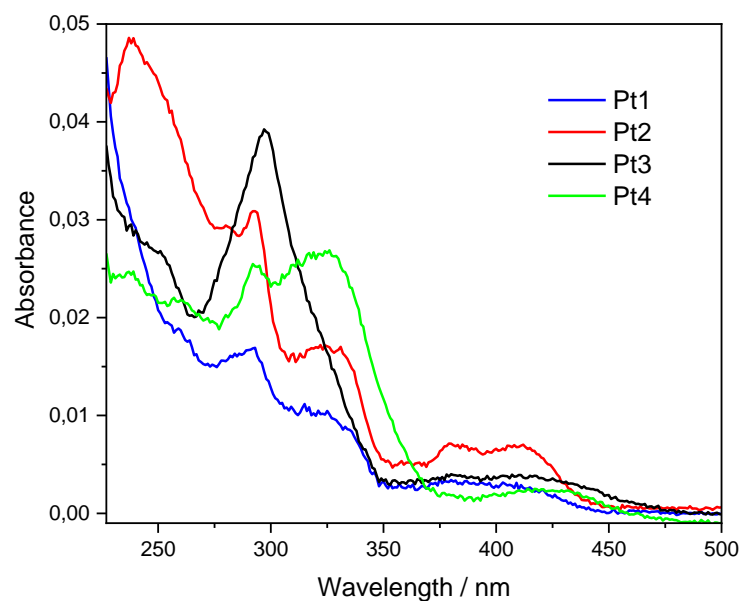


Figure 3. UV-Vis absorption spectra of **Pt1–Pt4** in dichloromethane, at a concentration of 1×10^{-6} M.

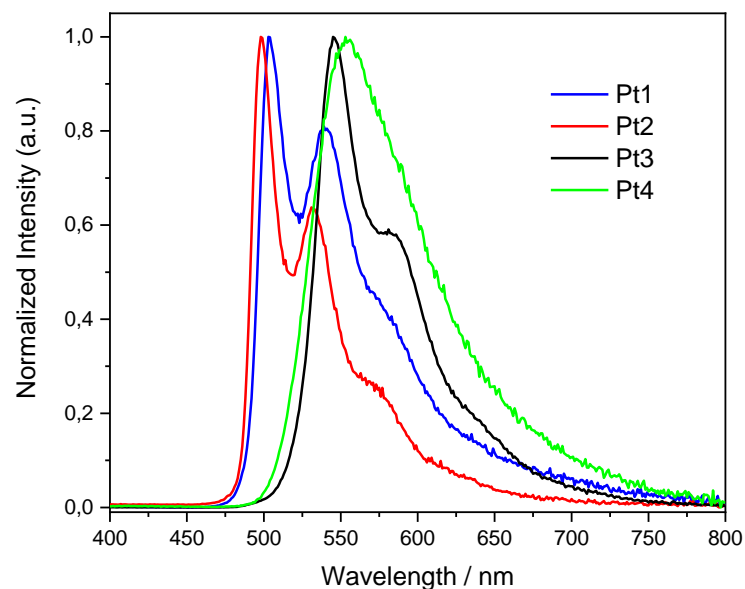


Figure 4. Emission spectra of **Pt1–Pt4** in deaerated dichloromethane, at a concentration of 1×10^{-6} M.

The emission wavelengths, a comparison of the Quantum Yields before and after the FPT cycles, and the lifetimes are reported in Table 1, together with the values corresponding to the parent chlorido complexes **PtCl1–PtCl4**. Complete data and spectra are reported in the Supplementary Information.

Table 1. Key luminescence values for complexes **PtC11–PtC14** and **Pt1–Pt4**.

Complex	λ_{\max} , em/nm	Φ_{lum} before FPT/%	Φ_{lum} after FPT/%	$\tau/\mu\text{s}$
PtC11 ¹	505	-	68	7.8
PtC12 ¹	501	-	62	7.9
PtC13 ¹	548	-	54	20.5
PtC14 ²	557	-	29	9.0
Pt1 ³	503	2.5	65	7.9
Pt2 ³	498	3.5	55	7.7
Pt3 ³	545	3.0	89	19.1
Pt4 ³	554	2.5	72	13.6

¹ From Ref. [9]. Luminescence Quantum Yields were determined by the method of continuous dilution, using quinine sulfate in 1 M H₂SO₄ as the standard; the estimated uncertainty is 20% or better. ² From Ref. [43]. Luminescence Quantum Yield determined using [Ru(bpy)₃]Cl₂ as the standard. ³ This work; measured in dichloromethane solution (10⁻⁶ M) using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer.

It can be observed that the substitution of chloride with the 4-phenylthiazole-2-thiolate ligand exerts a very limited effect on the emission wavelength of the complexes, since a difference of only a few nm is present. Thus, the spectral region in which emission occurs is mainly determined by the substituent on the terdentate ligand. Nevertheless, by looking at **Pt3** and **Pt4**, an important effect on the absolute Φ_{lum} can be noticed upon the substitution of chloride with thiolate. Considering the reference values taken from literature [9,43], both the thienyl- and the 4-NPh₂-phenyl-substituted complexes undergo a remarkable increase in Φ_{lum} , from 54% to 89% and from 29% to 72%, respectively. Up to now, since very few studies exist in the field of NCN-Pt(II) complexes bearing thiolate ancillary ligands, it was not possible to point out a general trend in the QY values. Nevertheless, it can be noticed that the highest values among **Pt1–Pt4** were reached in the case of electron-rich substituents such as 2-thienyl and 4-NPh₂-phenyl. As a future perspective, new thiolates and substituents could be tested, together with a theoretical investigation of the photophysical properties of such complexes.

Considering the lifetimes, it can be pointed out that the presence of the thiazole-based ancillary ligand did not bring about a change in the values in the case of **Pt1** (7.9 μs vs. 7.8 μs), **Pt2** (7.7 μs vs. 7.9 μs) and **Pt3** (19.1 μs vs. 20.5 μs); instead, only for **Pt4** was a remarkable increase observed, from 9.0 μs to 13.6 μs .

2.2. OLED Device Produced with Pt3

Since the novel complexes bearing a 4-phenylthiazole-2-thiolate ligand (**Pt1–Pt4**) are characterized by a high solubility in chlorinated solvents, they represent good candidates for application in the production of solution-processable devices, obtaining thin films of the compound by means of the spin-coating technique. Therefore, **Pt3**, i.e., the complex showing the highest value of Quantum Yield in the new class of dyes, was employed for the production of a solution-processable OLED device.

The EL spectrum of the OLED is shown in Figure 5. The OLED emission is in the yellow region, with CIE coordinates of (0.42, 0.52). The EL spectrum closely matches the emission of **Pt3** at a concentration of 1 \times 10⁻⁶ M in dichloromethane (Figure 5). There is no significant contribution to the EL emission bands from the TBPI electron-transporting (hole-blocking) or TCTA binder layers, which is in agreement with a good charge carrier confinement within the EML and complete energy transfer from the excited states of TCTA (formed by charge carrier recombination) to the Pt complex.

The luminance as a function of the applied voltage of the OLED is shown in Figure 6. It is worth pointing out that the OLED performance observed with **Pt3** as the emitter is much better than that reported for a solution-processed OLED built with an N[^]C[^]N Pt complex bearing a chloride ancillary ligand [24] and similar to that observed for an OLED based on an N[^]C[^]N Pt complex having a 1-phenyl-1H-tetrazole-5-thiolate ancillary ligand [41].

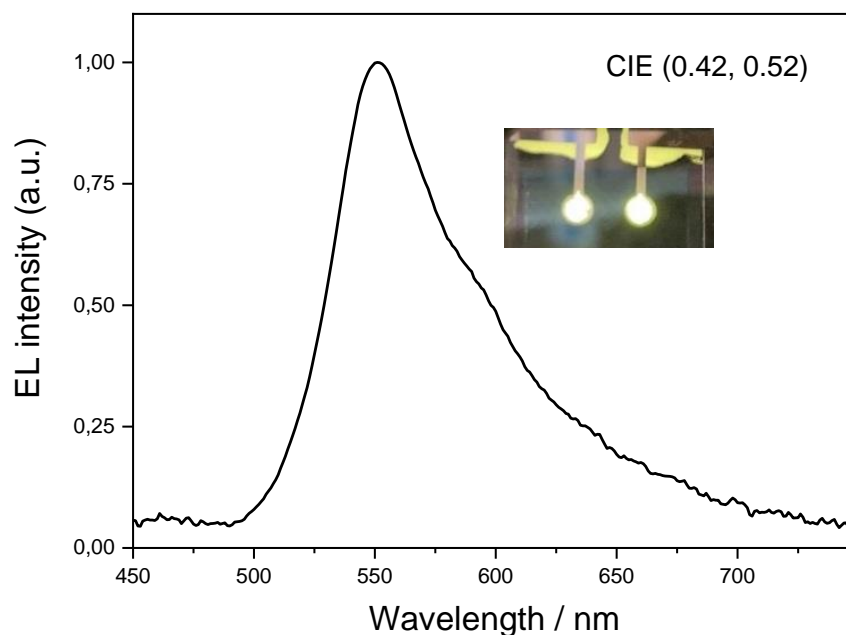


Figure 5. Electroluminescence spectra at 15 V of OLEDs based on **Pt3**. In the inset there is the photo of the resulting yellow OLED.

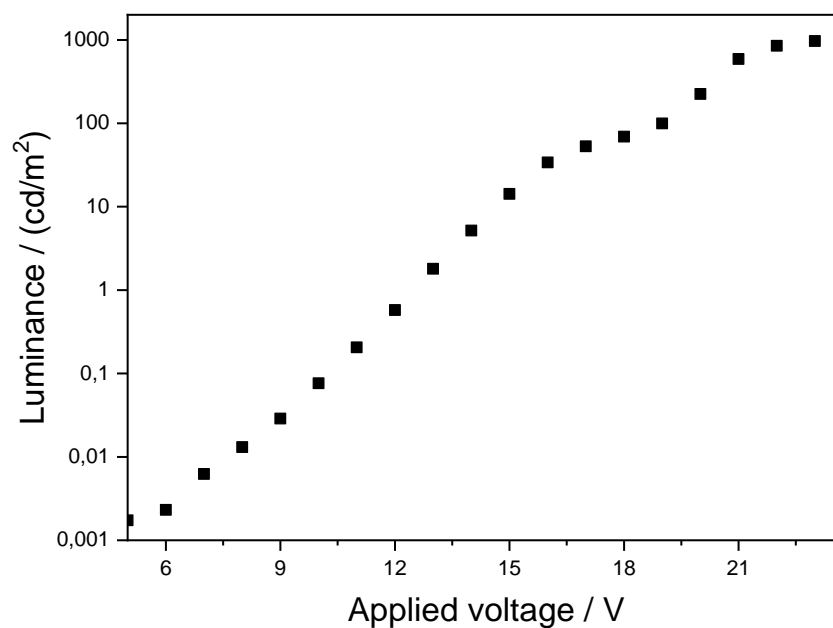


Figure 6. Luminance vs. applied voltage for the OLED device produced with 8% **Pt3** in the emissive layer.

3. Materials and Methods

All reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and were used without further purification. The deuterated solvents for NMR measurements were purchased from Eurisotop (Saint-Aubin, France).

Ligands **L1–L4** (structure in Figure 7) were synthesized starting with 3,5-dibromotoluene (in the case of **L1**) or 1,3,5-tribromobenzene (for **L2–L4**) and by employing Pd-catalyzed Suzuki–Miyaura and/or Stille cross-coupling reactions to introduce the proper moieties on the N[∞]C[∞]N ligand.

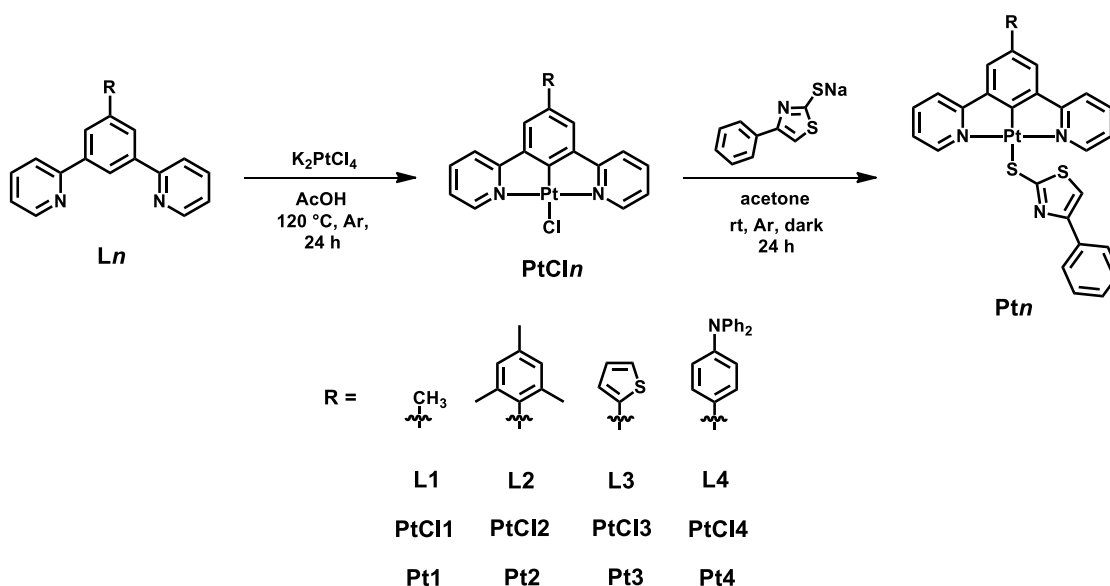


Figure 7. General synthesis of complexes **Pt1–Pt4**, starting from ligands **L1–L4**.

In all cases, the known parent chlorido complexes **PtCl1–PtCl4** [9,43] were obtained by refluxing a mixture of the proper ligand (1 eq.) and K_2PtCl_4 (1.2 eq.) in glacial AcOH for 24 h under Argon atmosphere. The obtained precipitate was filtered, washed with H_2O , MeOH and Et_2O , and dried. Synthetic details and procedures are provided in the Supplementary Information.

Electronic absorption spectra were recorded at room temperature in CH_2Cl_2 solution, using a Shimadzu UV3600 spectrophotometer and quartz cuvettes with a 1 cm optical path length. Absolute photoluminescence Quantum Yields (Φ_{lum}) were measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer. Steady-state and time-resolved fluorescence data were obtained using an FLS980 spectrofluorometer (Edinburg Instruments Ltd., Livingston, UK). A detailed description of the measurement techniques can be found in the Supplementary Information, together with the absorption and the luminescence spectra.

The device was built by using both dry and wet processes (sublimation in high vacuum and spin coating) in a pre-cleaned glass substrate made of indium tin oxide (ITO). Holes were injected from the ITO anode and passed through a 40 nm thick transporting layer made of PEDOT:PSS. Electrons were injected from an Al/LiF cathode and transported to the emitting layer (EML) by means of a layer of 2,2',2''-(1,3,5-benzinetriyl)-tris (1-phenyl-1*H*-benzimidazole) (TPBi, 30 nm thick). Charges recombined in the 40 nm thick EML made of a 4,4',4''-tris (N-carbazolyl)-triphenylamine (TCTA) matrix, hosting **Pt3** (8% wt) as the emitter.

General Synthesis of Complexes **Pt1–Pt4**

Compounds **Pt1–Pt4** were obtained (57–90% yields, see Supplementary Information) by stirring a mixture of the proper parent chloride complex (1 eq.) and of the sodium salt of 4-phenylthiazole-2-thiol (10 eq.) in acetone at room temperature in the dark under Argon atmosphere. After 24 h, the solution was evaporated to dryness under reduced pressure and dichloromethane was added to the solid residue in order to dissolve only the product. The sodium salt was filtered and the evaporation of the dichloromethane resulted in the desired product as an orange solid (Figure 2). All synthetic details and NMR spectra are reported in the Supplementary Information.

4. Conclusions

In conclusion, four novel cyclometalated Pt(II) complexes, bearing a variously substituted N²C¹N¹ 1,3-di(2-pyridyl) benzene ligand and a 4-phenylthiazole-2-thiolate ancillary ligand, were easily prepared and well characterized. Their emission color can be easily tuned by the nature of the substituents on the terdentate ligand, as is the case for the parent chlorido complexes. However, their luminescence Quantum Yield can be much higher. Clearly, there is a need for the preparation and characterization of platinum(II) complexes with other sulfur co-ligands in order to understand the relationship between their nature and the emission properties of the compounds. In any case, the novel complexes with a 4-phenylthiazole-2-thiolate ligand reported here represent the first members of an interesting new class of soluble Pt(II) compounds which can be used as emitters for the fabrication of solution-processable OLEDs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27165171/s1>, Figures S1–S6: synthetic pathways; Figures S7–S10: UV-Vis absorption spectra; Figures S11–S14: Emission and Excitation spectra; Figures S15–S18: lifetime measurements; Figures S19–S39: NMR spectra; Table S1: absorption maxima and ϵ values [44].

Author Contributions: Conceptualization, D.R., C.D. and F.F.; methodology, A.C. and F.F.; formal analysis, F.F., M.C. and D.M.; investigation, F.F., M.C. and D.M.; data curation, F.F.; writing—original draft preparation, F.F.; writing—review and editing, D.R., A.C., C.D., F.F., M.C. and D.M.; supervision, D.R. and C.D.; project administration, F.F.; funding acquisition, A.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Interuniversity Consortium of Materials Science and Technology (Project INSTM21MIROBERTO) and Università degli Studi di Milano (Project PSR2020_DIP_005_PI_ACOLO “Synthesis and characterization of organic and coordination compounds for application in luminescent devices or in bioimaging”).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Material.

Acknowledgments: F.F. thanks MUR and Università degli Studi di Milano for a PhD fellowship. Fondazione Cariplo and Regione Lombardia are acknowledged for the instrumentation bought during the *SmartMatLab Centre* project (2014).

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available.

References

1. Puttock, E.V.; Melissa, T.W.; Williams, J.A.G. The luminescence properties of multinuclear platinum complexes. *Coord. Chem Rev.* **2018**, *367*, 127–162. [CrossRef]
2. Yam, V.W.-W.; Law, A.S.-Y. Luminescent d⁸ metal complexes of platinum(II) and gold(III): From photophysics to photofunctional materials and probes. *Coord. Chem. Rev.* **2020**, *414*, 213298. [CrossRef]
3. Tang, M.-C.; Chan, A.K.-W.; Chan, M.-Y.; Yam, V.W.-W. Platinum and Gold Complexes for OLEDs. *Top. Curr. Chem.* **2016**, *374*, 46. [CrossRef] [PubMed]
4. Williams, J.A.G.; Develay, S.; Rochester, D.L.; Murphy, L. Optimising the luminescence of platinum (II) complexes and their application in organic light emitting devices (OLEDs). *Coord. Chem. Rev.* **2008**, *252*, 2596–2611. [CrossRef]
5. Kalinowski, J.; Fattori, V.; Cocchi, M.; Williams, J.A.G. Light-emitting devices based on organometallic platinum complexes as emitters. *Coord. Chem. Rev.* **2011**, *255*, 2401–2425. [CrossRef]
6. Baggaley, E.; Weinstein, J.A.; Williams, J.A.G. Lighting the way to see inside the live cell with luminescent transition metal complexes. *Coord. Chem. Rev.* **2012**, *256*, 1762–1785. [CrossRef]
7. Zhao, Q.; Huang, C.; Li, F. Phosphorescent heavy-metal complexes for bioimaging. *Chem. Soc. Rev.* **2011**, *40*, 2508–2524. [CrossRef] [PubMed]
8. Lo, K.K.-W.; Choi, A.W.-T.; Law, W.H.-T. Applications of luminescent inorganic and organometallic transition metal complexes as biomolecular and cellular probes. *Dalton Trans.* **2012**, *41*, 6021–6047. [CrossRef]

9. Farley, S.J.; Rochester, D.L.; Thompson, A.L.; Howard, J.A.K.; Williams, J.A.G. Controlling Emission Energy, Self-Quenching, and Excimer Formation in Highly Luminescent N[^]C[^]N-Coordinated Platinum(II) Complexes. *Inorg. Chem.* **2005**, *44*, 9690–9703. [[CrossRef](#)] [[PubMed](#)]
10. Murphy, L.; Brulatti, P.; Fattori, V.; Cocchi, M.; Williams, J.A.G. Blue-Shifting the Monomer and Excimer Phosphorescence of Tridentate Cyclometallated Platinum(II) Complexes for Optimal White-Light OLEDs. *Chem. Commun.* **2012**, *48*, 5817–5819. [[CrossRef](#)]
11. Rossi, E.; Colombo, A.; Dragonetti, C.; Roberto, D.; Demartin, F.; Cocchi, M.; Brulatti, P.; Fattori, V.; Williams, J.A.G. From Red to near Infra-Red OLEDs: The Remarkable Effect of Changing from X = -Cl to -NCS in a Cyclometallated [Pt(N[^]C[^]N)X] Complex (N[^]C[^]N = 5-Mesityl-1,3-Di-(2-Pyridyl)Benzene). *Chem. Commun.* **2012**, *48*, 3182–3184. [[CrossRef](#)] [[PubMed](#)]
12. Rossi, E.; Murphy, L.; Brothwood, P.L.; Colombo, A.; Dragonetti, C.; Roberto, D.; Ugo, R.; Cocchi, M.; Williams, J.A.G. Cyclometallated Platinum(II) Complexes of 1,3-Di(2-Pyridyl)Benzenes: Tuning Excimer Emission from Red to near-Infrared for NIR-OLEDs. *J. Mater. Chem.* **2011**, *21*, 15501–15510. [[CrossRef](#)]
13. Nisic, F.; Colombo, A.; Dragonetti, C.; Roberto, D.; Valore, A.; Malicka, J.M.; Cocchi, M.; Freeman, G.R.; Williams, J.A.G. Platinum(II) Complexes with Cyclometallated 5- π -Delocalized-Donor-1,3-Di(2-Pyridyl)Benzene Ligands as Efficient Phosphors for NIR-OLEDs. *J. Mater. Chem. C* **2014**, *2*, 1791–1800. [[CrossRef](#)]
14. Rao, Y.L.; Schoenmakers, D.; Chang, Y.L.; Lu, J.S.; Lu, Z.H.; Kang, Y.; Wang, S. Bluish-Green BMes₂-Functionalized PtII Complexes for High Efficiency PhOLEDs: Impact of the BMes₂ Location on Emission Color. *Eur. J. Chem.* **2012**, *18*, 11306–11316. [[CrossRef](#)] [[PubMed](#)]
15. Cocchi, M.; Kalinowski, J.; Fattori, V.; Williams, J.A.G.; Murphy, L. Color-Variable Highly Efficient Organic Electrophosphorescent Diodes Manipulating Molecular Exciton and Excimer Emissions. *Appl. Phys. Lett.* **2009**, *94*, 073309. [[CrossRef](#)]
16. Cocchi, M.; Virgili, D.; Fattori, V.; Rochester, D.L.; Williams, J.A.G. N[^]C[^]N-Coordinated Platinum(II) Complexes as Phosphorescent Emitters in High-Performance Organic Light-Emitting Devices. *Adv. Funct. Mater.* **2007**, *17*, 285–289. [[CrossRef](#)]
17. Doherty, R.E.; Sazanovich, I.V.; McKenzie, L.K.; Stasheuski, A.S.; Coyle, R.; Baggaley, E.; Bottomley, S.; Weinstein, J.A.; Bryant, H.E. Photodynamic Killing of Cancer Cells by a Platinum(II) Complex with Cyclometallating Ligand. *Sci. Rep.* **2016**, *6*, 22668. [[CrossRef](#)] [[PubMed](#)]
18. Chatzisideri, T.; Thysiadis, S.; Katsamakakos, S.; Dalezis, P.; Sigala, I.; Lazarides, T.; Nikolakaki, E.; Trafalis, D.; Gederaas, O.A.; Lindgren, M.; et al. Synthesis and Biological Evaluation of a Platinum(II)-c(RGDyK) Conjugate for Integrin-Targeted Photodynamic Therapy. *Eur. J. Med. Chem.* **2017**, *141*, 221–231. [[CrossRef](#)] [[PubMed](#)]
19. Baggaley, E.; Sazanovich, I.V.; Williams, J.A.G.; Haycock, J.W.; Botchway, S.W.; Weinstein, J.A. Two-Photon Phosphorescence Lifetime Imaging of Cells and Tissues Using a Long-Lived Cyclometallated Npyridyl[^]Cphenyl[^]N Pyridyl Pt(II) Complex. *RSC Adv.* **2014**, *4*, 35003–35008. [[CrossRef](#)]
20. Botchway, S.W.; Charnley, M.; Haycock, J.W.; Parker, A.W.; Rochester, D.L.; Weinstein, J.A.; Williams, J.A.G. Time-Resolved and Two-Photon Emission Imaging Microscopy of Live Cells with Inert Platinum Complexes. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 16071–16076. [[CrossRef](#)]
21. Raza, A.; Colley, H.E.; Baggaley, E.; Sazanovich, I.V.; Green, N.H.; Weinstein, J.A.; Botchway, S.W.; MacNeil, S.; Haycock, J.W. Oxygen Mapping of Melanoma Spheroids Using Small Molecule Platinum Probe and Phosphorescence Lifetime Imaging Microscopy. *Sci. Rep.* **2017**, *7*, 10743. [[CrossRef](#)] [[PubMed](#)]
22. Colombo, A.; Fiorini, F.; Septiadi, D.; Dragonetti, C.; Nisic, F.; Valore, A.; Roberto, D.; Mauro, M.; de Cola, L. Neutral N[^]C[^]N Tridentate Luminescent Pt(II) Complexes: Their Synthesis, Photophysical Properties, and Bio-Imaging Applications. *Dalton Trans.* **2015**, *44*, 8478–8487. [[CrossRef](#)] [[PubMed](#)]
23. Baggaley, E.; Botchway, S.W.; Haycock, J.W.; Morris, H.; Sazanovich, I.V.; Williams, J.A.G.; Weinstein, J.A. Long-Lived Metal Complexes Open up Microsecond Lifetime Imaging Microscopy under Multiphoton Excitation: From FLIM to PLIM and Beyond. *Chem. Sci.* **2014**, *5*, 879–886. [[CrossRef](#)]
24. Mróz, W.; Botta, C.; Giovanella, U.; Rossi, E.; Colombo, A.; Dragonetti, C.; Roberto, D.; Ugo, R.; Valore, A.; Williams, J.A.G. Cyclometallated Platinum(II) Complexes of 1,3-Di(2-Pyridyl)Benzenes for Solution-Processable WOLEDs Exploiting Monomer and Excimer Phosphorescence. *J. Mater. Chem.* **2011**, *21*, 8653–8661. [[CrossRef](#)]
25. Shi, H.; Clarkson, G.J.; Sadler, P.J. Dual Action Photosensitive Platinum(II) Anticancer Prodrugs with Photoreleasable Azide Ligands. *Inorg. Chim. Acta* **2019**, *489*, 230–235. [[CrossRef](#)]
26. Scarpaci, A.; Monnereau, C.; Hergué, N.; Blart, E.; Legoupy, S.; Odobel, F.; Gorfo, A.; Pérez-Moreno, J.; Clays, K.; Asselberghs, I. Preparation and Characterization of Second Order Non-Linear Optical Properties of New “Push-Pull” Platinum Complexes. *Dalton Trans.* **2009**, 4538–4546. [[CrossRef](#)] [[PubMed](#)]
27. Lien, C.Y.; Hsu, Y.F.; Liu, Y.H.; Peng, S.M.; Shinmyozu, T.; Yang, J.S. Steric Engineering of Cyclometallated Pt(II) Complexes toward High-Contrast Monomer-Excimer-Based Mechanochromic and Vapochromic Luminescence. *Inorg. Chem.* **2020**, *59*, 11584–11594. [[CrossRef](#)] [[PubMed](#)]
28. Lin, C.J.; Liu, Y.H.; Peng, S.M.; Shinmyozu, T.; Yang, J.S. Excimer-Monomer Photoluminescence Mechanochromism and Vapochromism of Pentiptycene-Containing Cyclometallated Platinum(II) Complexes. *Inorg. Chem.* **2017**, *56*, 4978–4989. [[CrossRef](#)]
29. Rossi, E.; Colombo, A.; Dragonetti, C.; Roberto, D.; Ugo, R.; Valore, A.; Falciola, L.; Brulatti, P.; Cocchi, M.; Williams, J.A.G. Novel N[^]C[^]N-Cyclometallated Platinum Complexes with Acetylide Co-Ligands as Efficient Phosphors for OLEDs. *J. Mater. Chem.* **2012**, *22*, 10650–10655. [[CrossRef](#)]

30. Ai, Y.; Chan, M.H.-Y.; Chan, A.K.-W.; Ng, M.; Li, Y.; Yam, V.W.-W. A platinum(II) molecular hinge with motions visualized by phosphorescence changes. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 13856–13861. [[CrossRef](#)] [[PubMed](#)]
31. Li, B.; Li, Y.; Chan, M.H.Y.; Yam, V.W.W. Phosphorescent Cyclometalated Platinum(II) Enantiomers with Circularly Polarized Luminescence Properties and Their Assembly Behaviors. *J. Am. Chem. Soc.* **2021**, *143*, 21676–21684. [[CrossRef](#)] [[PubMed](#)]
32. Garoni, E.; Boixel, J.; Dorcet, V.; Roisnel, T.; Roberto, D.; Jacquemin, D.; Guerschais, V. Controlling the Emission in Flexibly-Linked (N⁺C⁻N)Platinum Dyads. *Dalton Trans.* **2018**, *47*, 224–232. [[CrossRef](#)]
33. Yamaguchi, K.; Yamawaki, K.; Kimura, T.; Kuwabara, J.; Yasuda, T.; Nishimura, Y.; Kanbara, T. Multi-Molecular Emission of a Cationic Pt(II) Complex through Hydrogen Bonding Interactions. *Dalton Trans.* **2018**, *47*, 4087–4092. [[CrossRef](#)] [[PubMed](#)]
34. Kuwabara, J.; Yamaguchi, K.; Yamawaki, K.; Yasuda, T.; Nishimura, Y.; Kanbara, T. Modulation of the Emission Mode of a Pt(II) Complex via Intermolecular Interactions. *Inorg. Chem.* **2017**, *56*, 8726–8729. [[CrossRef](#)] [[PubMed](#)]
35. Chen, Y.; Lu, W.; Che, C.M. Luminescent Pincer-Type Cyclometalated Platinum(II) Complexes with Auxiliary Isocyanide Ligands: Phase-Transfer Preparation, Solvatomorphism, and Self-Aggregation. *Organometallics* **2013**, *32*, 350–353. [[CrossRef](#)]
36. Wang, Z.; Turner, E.; Mahoney, V.; Madakuni, S.; Groy, T.; Li, J. Facile Synthesis and Characterization of Phosphorescent Pt(N⁺C⁻N)X Complexes. *Inorg. Chem.* **2010**, *49*, 11276–11286. [[CrossRef](#)] [[PubMed](#)]
37. Tarran, W.A.; Freeman, G.R.; Murphy, L.; Benham, A.M.; Katakay, R.; Williams, J.A.G. Platinum(II) Complexes of N⁺C⁻N- Coordinating 1,3-Bis(2-Pyridyl)Benzene Ligands: Thiolate Coligands Lead to Strong Red Luminescence from Charge-Transfer States. *Inorg. Chem.* **2014**, *53*, 5738–5749. [[CrossRef](#)]
38. Zheng, Q.; Borsley, S.; Tu, T.; Cockroft, S.L. Reversible Stimuli-Responsive Chromism of a Cyclometallated Platinum(Ii) Complex. *Chem. Commun.* **2020**, *56*, 14705–14708. [[CrossRef](#)] [[PubMed](#)]
39. Zheng, Q.; Borsley, S.; Nichol, G.S.; Duarte, F.; Cockroft, S.L. The Energetic Significance of Metallophilic Interactions. *Angew. Chem. Int. Ed.* **2019**, *58*, 12617–12623. [[CrossRef](#)]
40. Fagnani, F.; Colombo, A.; Dragonetti, C.; Roberto, D.; Marinotto, D. The Intriguing Effect of Thiolates as Co-Ligands in Platinum(II) Complexes Bearing a Cyclometalated 1,3-Di(2-Pyridyl)Benzene. *Inorg. Chim. Acta* **2022**, *532*, 120744. [[CrossRef](#)]
41. Dragonetti, C.; Fagnani, F.; Marinotto, D.; di Biase, A.; Roberto, D.; Cocchi, M.; Fantacci, S.; Colombo, A. First Member of an Appealing Class of Cyclometalated 1,3-Di-(2-Pyridyl)Benzene Platinum(II) Complexes for Solution-Processable OLEDs. *J. Mater. Chem. C* **2020**, *8*, 7873–7881. [[CrossRef](#)]
42. Dragonetti, C.; Colombo, A.; Fagnani, F.; de Soricellis, G.; Cocchi, M.; Carboni, B.; Guerschais, V.; Marinotto, D. Introduction of a Triphenylamine Substituent on Pyridyl Rings as a Springboard for a New Appealing Brightly Luminescent 1,3-Di-(2-Pyridyl)Benzene Platinum(II) Complex Family. *Dalton Trans.* **2022**. [[CrossRef](#)]
43. Rochester, D.L.; Develay, S.; Zališ, S.; Williams, J.A.G. Localised to Intraligand Charge-Transfer States in Cyclometalated Platinum Complexes: An Experimental and Theoretical Study into the Influence of Electron-Rich Pendants and Modulation of Excited States by Ion Binding. *Dalton Trans.* **2009**, *10*, 1728–1741. [[CrossRef](#)] [[PubMed](#)]
44. Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishic, S.; Tobita, S. Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850–9860. [[CrossRef](#)]