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Photophysical investigation of highly phosphorescent N^C^N platinum(II) azido complexes and their triazole derivatives

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ABSTRACT

Substitution of chloride by azide in cyclometalated 5-R-1,3-di(2-pyridyl)-benzene platinum(II) complexes (R = mesityl, methyl or 2-thienyl) leads to novel azido complexes with an intense phosphorescence that is modulated by the nature of R. An increase of the concentration brings about to the formation of aggregates with a red-shifted emission. Furthermore, the presence of the ancillary azido group allows, *via i*-click reaction, the obtainment of even more emissive 1,2,3-triazole derivatives. The 1,2,3-triazolate of the mesityl and 2-thienyl N^C^N–Pt(II) complexes were characterized by X-ray diffraction analysis and their photophysical properties were deeply investigated.

1. Introduction

Cyclometalated platinum(II) complexes are of growing interest since the advent of their applications as efficient molecular materials, *e.g.* for nonlinear optics [1] and Organic Light Emitting Diodes (OLEDs) [2], for bioimaging [3], photodynamic therapy, due to their ability to photogenerate reactive oxygen species which can kill cancer cells [4], and for sensing devices [5]. Their square planar geometry allows the creation of bi-molecular states, either in the ground (dimers) or in the excited states (excimers), by means of Pt–Pt and/or ligand-ligand intermolecular interactions [6]. These features have gained importance in the preparation of OLEDs because the parallel emissions from bi-molecular and mono-molecular excited states of Pt complexes allow the modulation of their efficiency and color [2,7]. In particular, Pt(II) chloride complexes with a cyclometalated 1,3-di(2-pyridyl)benzene (dipyb), which provides the platinum center a rigid N^C^N coordination environment, are really fascinating, being (to our knowledge) the most luminescent Pt emitters in solution at room temperature. For example, in deaerated CH_2Cl_2, [Pt(dipyb)Cl] has a luminescence quantum yield (φ_{lum}) of 0.60 [8], one order of magnitude greater than the related compound [Pt(N^C-ppy)(N-ppyH)Cl] (ppyH = 2-phenylpyridine) [9,] because the rigidity of the cyclometalated 1,3-di(2-pyridyl)benzene prevents distortion and therefore non-radiative decays, whereas the short Pt–C bond leads to a particularly high ligand-field strength [10] The charm of these N^C^N Pt(II) complexes is boosted by the possibility to tune the emission color by introducing substituents on the benzene or pyridyl rings, safekeeping large quantum yields [2a]. Astonishingly, whereas a lot of studies have been dedicated to unveil the influence of the substituents on the N^C^N ligand, the investigation of the role of the co-ligand on the emissive behavior is still in its infancy. Some of us found that the replacement of chloride by other species such as isothiocyanate [2c] or 1-phenyl-1-*H*-tetrazole-5-thiolate [2h] preserves the great luminescence in deaerated dichloromethane solution (φ_{lum} = 0.60–0.90) whereas replacement by a phenolate [11] or arenethiolate [12] leads to a large decrease of the quantum yields. These results prompted us to investigate the effect of the substitution of chloride by azide on the emissive properties of various Pt(II) complexes bearing a cyclometalated 1,3-di(2-pyridyl)benzene substituted in 5 position with a mesityl, a methyl or a 2-thienyl group. The substituents on the benzene ring were chosen in order to explore the effect of the presence of alkyl and (hetero)aryl groups on the luminescence of the obtained derivatives bearing an azide.

The use of an azide as co-ligand is particularly appealing because azido platinum complexes can find application in photoactivated chemotherapy due to the photorelease of azidyl radicals that can attack cancer cells [4b,13].

Furthermore, the well-known "click" reactions are a powerful tool in

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biochemistry and proteomics for inserting luminescent labels or for the facile synthesis of both bioactive small molecules as well as bio(macro) molecule conjugates [14]. In particular the 1,3-dipolar cycloaddition reaction between metal-azido complexes and alkynes (*i-click* reaction) is a method to introduce five-membered heterocyclic ligands directly in the inner coordination sphere of the metal centre. Recently, this approach was extended to CˆNˆN and unsubstituted NˆCˆN platinum complexes [15] but the photophysical properties of such new derivatives has not been investigated yet.

2. Materials and methods

In this contribution, we report the synthesis and characterization of three novel azido complexes and two triazole derivatives (**1-N$_3$**, **2-N$_3$**, **3-N$_3$**, **4** and **5**, Chart 1), thus adding new members to the interesting family of phosphorescent platinum(II) complexes.

2.1. Synthesis of the Pt-azido complexes

Compounds **1-N$_3$**, **2-N$_3$**, and **3-N$_3$** were readily prepared by

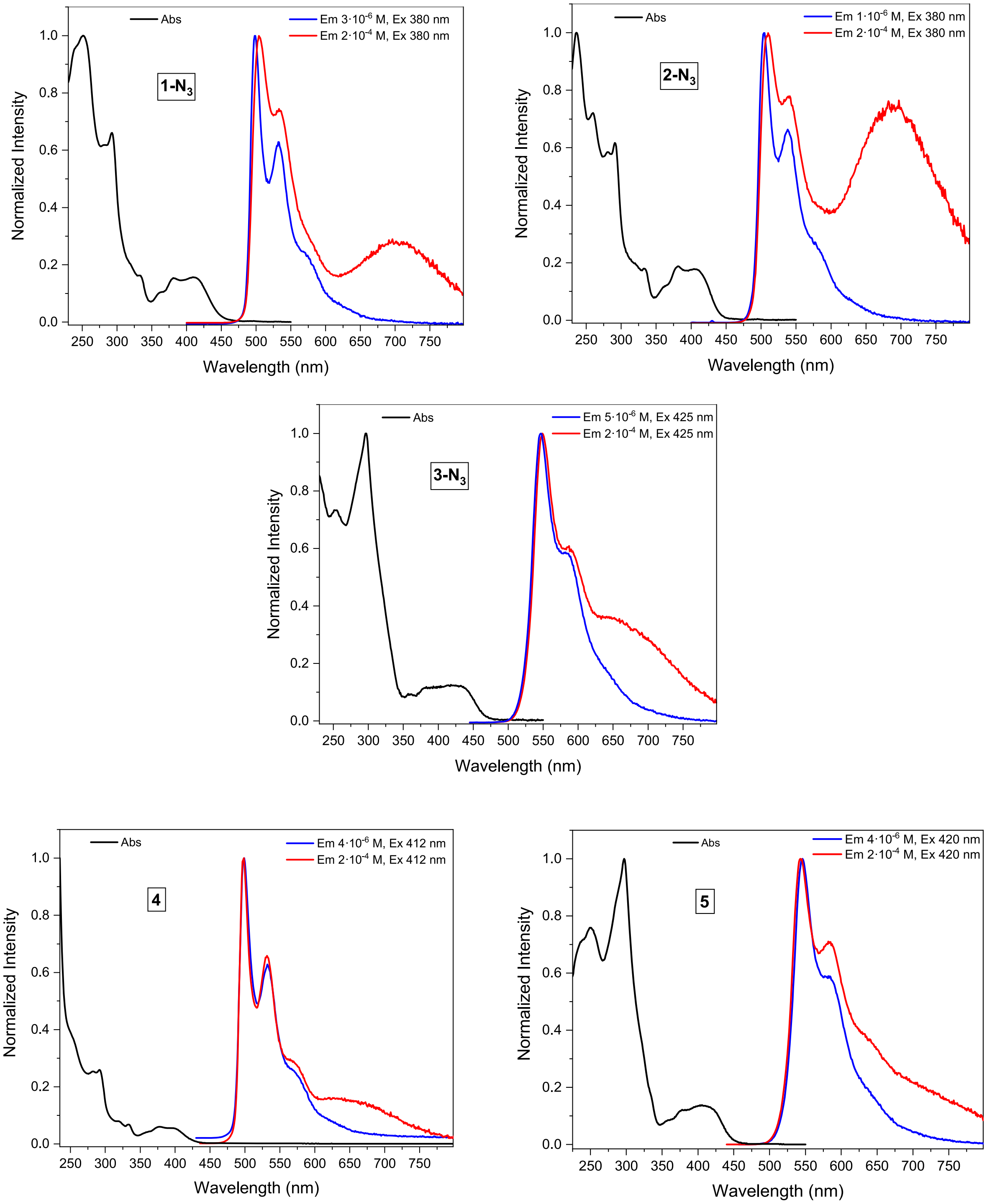

Fig. 1. Normalized absorption (black lines) and emission (blue and red lines) spectra of complexes **1-N$_3$**, **2-N$_3$**, **3-N$_3$**, **4** and **5** in CH_2Cl_2 at 298 K. Emission spectra refer to dilute (blue) and concentrated (red) solutions in degassed solvent.

treatment of the parent chloride derivatives with sodium azide in methanol at room temperature; the products were fully characterized by NMR spectroscopy and elemental analysis (details are given in the ESI) [16].

2.2. Synthesis of the Pt-1,2,3-triazole complexes

Derivatives **4** and **5** were easily prepared at room temperature by *i*-click reaction in dichloromethane between **1-N$_3$** or **3-N$_3$** and diethyl acetylenedicarboxylate (Chart 2, the details are given in the ESI) [15b]. Unfortunately, the same reaction on complex **2-N$_3$** did not lead to a single stable isomer but to a mixture, therefore it was not possible to proceed with the photophysical characterization.

Chart 2 shows the synthetic pathway from the chlorido complex to azido and triazole derivatives.

2.3. Photophysical characterization of the complexes

The normalized absorption and photoluminescence spectra of the platinum(II) azido complexes in dichloromethane at low (1–5 $\cdot 10^{-6}$ M) and high ($2\cdot 10^{-4}$ M) concentrations are shown in Fig. 1, whereas key data are listed in Table 1.

Like their parent chloride derivatives [17], **1-N$_3$**, **2-N$_3$**, and **3-N$_3$** are characterized by very intense absorption bands below 330 nm ($\varepsilon > 18\cdot 10^3$ M^{-1}cm^{-1}), because of $^1\pi$-π* transitions localized on the cyclometalated 1,3-di(2-pyridyl)benzene ligands, together with weaker bands at 350–450 nm caused by charge-transfer transitions concerning the cyclometalated ligand and the metal (Fig. 1). An increase of the concentration of the complexes leads to the appearance of a new band at lower energy, especially for the azido derivatives (see ESI, Fig. S9, **S14** and **S19**) ascribed to the formation of dimeric species by analogy with other N^C^N platinum(II) complexes [2h], as confirmed by a deviation from the Beer–Lambert law (See ESI, Figs. S1b and S2b).

Similar features are also observed for derivatives **4** and **5**, in which the involved transitions present the same nature of those of the parent azido compounds.

2.4. X-ray structure determination of complexes 4 and 5

Crystals of complex **4** (yellow) and complex **5** (dark orange) suitable for X-ray structure determination were obtained by slow evaporation from dichloromethane solutions. Single crystal X-ray diffraction experiments were performed at RT for **4** and at 150 K for **5** using a Rigaku XtaLAB Synergy-S diffractometer, operating with Cu-Kα (λ = 1.54184 Å) radiation and equipped with HyPix-6000HE detector. Data were corrected for absorption, scaled and integrated with CrysAlis$^{\text{Pro}}$ software [18]. The structure of both complexes was solved with SHELXT and refined by iterative cycles of full-matrix least-squares on Fo^2 and Fourier-difference synthesis with SHELXL2018/3 [19], within the WinGX suite of programs [20]. Additional details on structure determination and refinement are provided in the ESI. Full crystallographic data are deposited within the CSD with CCDC codes 2309868 and 2309869 for complex **4** and **5**, respectively. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44– 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Photophysical parameters of dilute solutions in degassed CH_2Cl_2 at 298 K for complexes **1-Cl**, **2-Cl** and **3-Cl**, and for their derivatives **1-N$_3$**, **2-N$_3$**, **3-N$_3$**, **4** and **5**.

Complex	Monomer emission [excimer or aggregate]λ_{max}/nm	φ_{lum} degassed (aerated)	τ/μs
1-Cl[a]	501, 534, 574(sh) [690][b]	0.62 (0.045)	7.90
1-N$_3$[c]	500, 532, 572(sh) [703][d]	0.87 (0.059)	7.48
2-Cl[a]	505, 539, 578(sh) [690][b]	0.68 (0.024)	7.80
2-N$_3$[e]	504, 538, 575(sh) [687][d]	0.66 (0.040)	8.07
3-Cl[a]	548, 584, 641(sh) [690][b]	0.54 (0.015)	20.5
3-N$_3$[f]	547, 582, 638(sh) [686][d]	0.79 (0.022)	17.8
4[g]	498, 531, 570(sh) [634][d]	0.96 (0.067)	7.44
5[g]	543, 582, 632(sh) [684][d]	0.94 (0.017)	18.1

[a] From Ref. [17].
[b] Excimer.
[c] At $3\cdot 10^{-6}$ M.
[d] Aggregate at $2\cdot 10^{-4}$ M.
[e] At $1\cdot 10^{-6}$ M.
[f] At $5\cdot 10^{-6}$ M.
[g] At $4\cdot 10^{-6}$ M.

3. Results and discussion

3.1. DFT calculations

To understand the electronic and optical properties of Pt-based complexes **1-N$_3$**, **2-N$_3$**, **3-N$_3$**, **4** and **5**, Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations have been carried out in dichloromethane solution, this being the solvent used for the experimental absorption and photoluminescence spectra. All the computational details are accurately described in ESI (Section S3). The molecular geometry of the five complexes has been optimized, exhibiting comparable core Pt-di(2-pyridyl)benzene structures, which differ for the orientation of the substituent on the central benzene ring (see Fig. 2). The analysis of the main frontier orbitals of the investigated Pt(II) complexes, in terms of energy and electronic density distribution, are reported in Figs. 2 and 3. The frontier orbitals of **1-N$_3$** and **2-N$_3$** are very similar and the two complexes show the same $\Delta E_{H\text{-}L}$, testifying that the presence of methyl or mesityl group in 5 position of the cyclometalated 1,3-di(2-pyridyl)benzene electronically does not affect the first HOMOs and LUMOs (see Fig. 2). The HOMO of both **1-N$_3$** and **2-N$_3$** is linearly delocalized on azide, Pt(II) and on the N^C^N benzene, while the HOMO-1 involves mainly azide and Pt. The HOMO/HOMO-1 of **3-N$_3$** are slightly destabilized with respect to the corresponding orbitals of **1-N$_3$** and **2-N$_3$**, due to the involvement of the 2-thienyl moiety in the orbitals; this fact reflects in a small decrease of the **3-N$_3$** $\Delta E_{H\text{-}L}$ gap, as shown in Fig. 2. The LUMO and LUMO+1 of the three complexes show similar electronic delocalization, being the result of the antibonding combinations of Pt and cyclometalated 1,3-di(2-pyridyl)benzene orbitals. The HOMO of **4** and **5** complexes is linearly delocalized on the triazole, Pt(II) and the N^C^N benzene similarly the corresponding azido complexes, but stabilized by 0.50 eV and 0.31 eV with respect to the azido counterparts (see Fig. 3). The HOMO of **5** shows electron density delocalized on the 2-thienyl analogously to what happens with **3-N$_3$**. The HOMO-1/HOMO-2 are almost degenerate, on **4** the HOMO-1 is delocalized on the mesityl ligand and the HOMO-2 is the Pt d_z^2, while in **5** they are reversed. The LUMO and LUMO+1 pair of **4** and **5** are similar for energy and character to the corresponding orbitals of the azido complexes, indeed all the pairs lie in the range 2.16–2.23 eV and are the antibonding combinations of the orbitals of Pt(II)-1,3di(2-pyridyl)benzene. In the triazole derivatives **4** and **5** the $\Delta E_{H\text{-}L}$ gap is increased due to the stabilization of the HOMO, being in **4** (**5**) 0.5 eV (0.32 eV) larger than in **1-N$_3$** (**3-N$_3$**).

We simulated the UV–vis spectra of complexes **1-N$_3$**, **2-N$_3$**, **3-N$_3$**, **4** and **5** (Fig. S31 in ESI), showing a good agreement with their experimental counterparts (Fig. 1). The transitions associated to the lower energy bands can be related to the HOMO→LUMO transitions and therefore reflect the HOMO-LUMO gaps, with the lowest absorption band of **3-N$_3$** being red-shifted with respect to the same spectral feature of **1-N$_3$**, **2-N$_3$**, **4** and **5**, and with the lowest absorption band of **5** red-shifted with respect to that of **4** because of the 2-thienyl moiety.

3.2. Luminescence properties of the complexes

Upon excitation in the 290–425 nm range, the three new azido

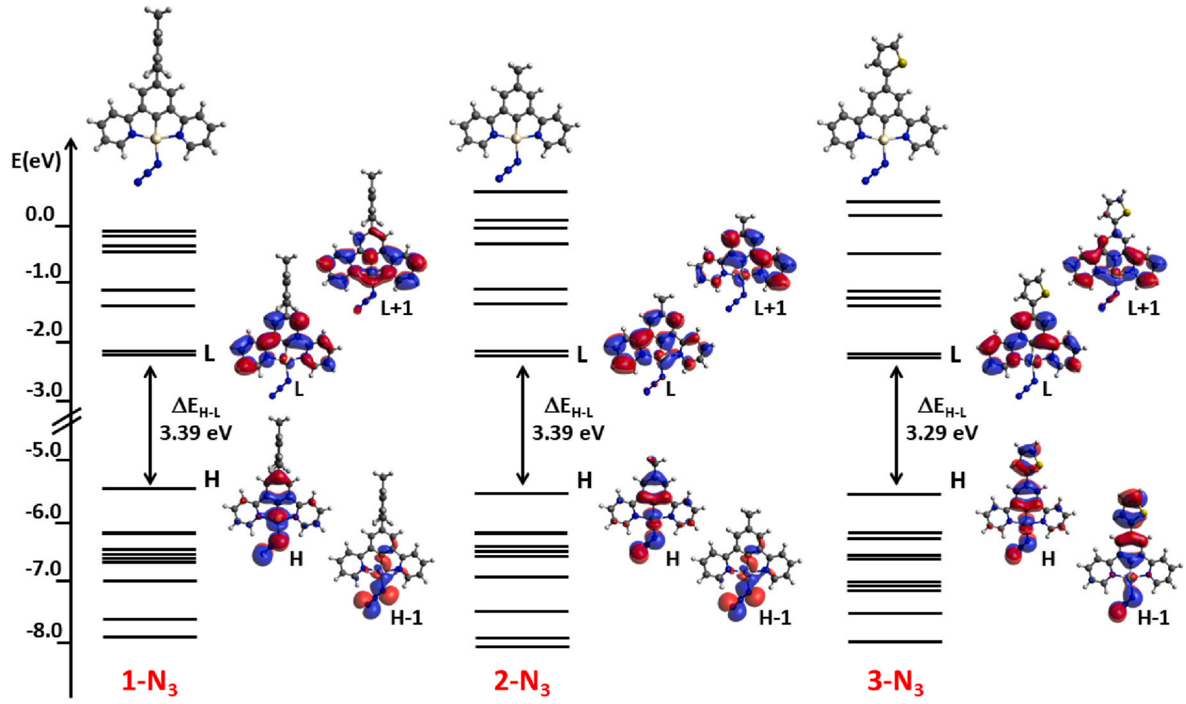

Fig. 2. Optimized geometries and main frontier molecular orbitals energies of **1-N$_3$**, **2-N$_3$** and **3-N$_3$** complexes along with the isodensity plots of HOMO/HOMO-1 and LUMO-LUMO+1 (isodensity value = 0.02).

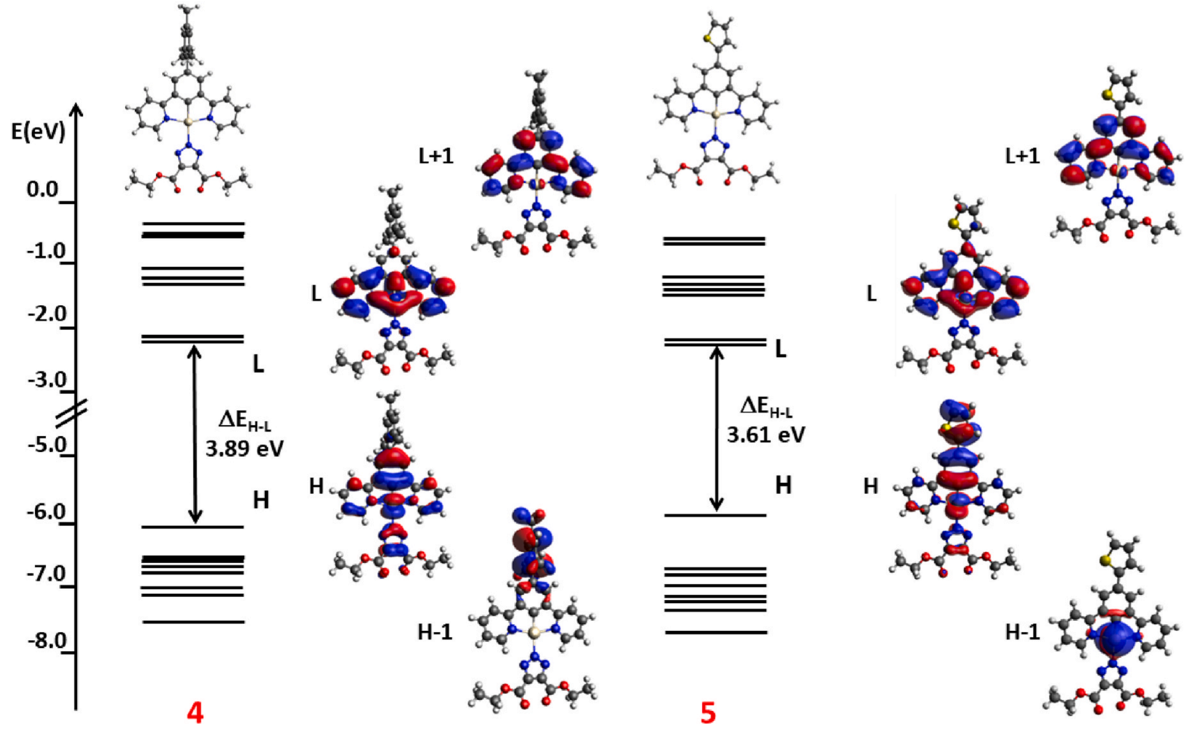

Fig. 3. Optimized geometries and main frontier molecular orbitals energies of **4** and **5** complexes along with the isodensity plots of HOMO/HOMO-1 and LUMO-LUMO+1 (isodensity value = 0.02).

complexes are strongly luminescent at room temperature (Fig. 1 and Table 1). Remarkably, the luminescence quantum yields in diluted degassed dichloromethane solution of **1-N$_3$** and **3-N$_3$** are very large, being higher than that of the related chloride complex (0.87 and 0.79 *vs* 0.62 and 0.54, respectively), whereas that of **2-N$_3$** is somewhat lower (0.66) and similar to that of **2-Cl** (Table 1). The luminescence of **1-N$_3$** is of particular interest: the quantum yield is higher and the emission is more shifted in the NIR region (703 nm) than that previously reported in the same solvent for the related **1-NCS** derivative [2c] (φ_{lum}: 0.60, excimer emission at 670 nm).

The emission spectra are highly structured (Fig. 1), as expected for luminescence from states of primarily ^{3}LC character, and it can be attributed to the monomeric complexes. The emission maxima are quite similar to those of the parent chloride derivatives (Table 1), being increasingly red-shifted by the nature of the substituent in the order methyl < mesityl < 2-thienyl. The lifetimes of **1-N$_3$** and **2-N$_3$** are comparable (7–8 μs), with that of the thienyl-bearing compound **3-N$_3$** being much longer (17.8 μs), as previously observed for the parent chloride complexes [17].

The room temperature emission of the dilute solution is very efficiently quenched by oxygen: the luminescence quantum yield is 15–36 times lower in air-equilibrated dichloromethane, the greatest quenching being observed for the compound with the 2-thienyl substituent (Table 1). This oxygen quenching efficacy is expected to afford an efficient production of singlet oxygen, of particular interest for photodynamic therapy [4].

The increase of the concentration of the novel azido complexes up to $2{\cdot}10^{-4}$ M leads to the appearance of a structureless band around 690 nm (Fig. 1). This new band at lower energy, which can change in intensity by varying the excitation wavelength, can be reasonably attributed to the emission from excited-state aggregates rather than to excimers. In fact, by increasing the concentration of the solution, the normalized excitation spectra at the emission wavelength of the monomer and structureless band around 690 nm are different and change shape when compared to those obtained at the more diluted concentration (Fig. S6, **S11** and **S16**). The inner filter effect is avoided by using quartz cuvettes of 1 mm optical path length for concentrated solutions.

The emissive low energy band of complexes **1-N$_3$**, **2-N$_3$**, and **3-N$_3$** at $2{\cdot}10^{-4}$ M is probably due to the excited state of dimeric species [6], in contrast to the behaviour of the parent chloride complexes (forming excimers), but in agreement with the behaviour of the related [Pt(5-mesityl-dpyb)(1-phenyl-1*H*-tetrazole-5-thiolate)] complex [2h].

As a consequence of the increased concentration of the novel complexes (from $1{\cdot}10^{-6}$ M to $2{\cdot}10^{-4}$ M) in deaerated dichloromethane solution, the aggregation causes a quenching of the luminescence quantum yield (presenting values of 0.27, 0.18, and 0.54 for **1-N$_3$**, **2-N$_3$**, and **3-N$_3$**, respectively), the decrease of φ_{lum} in the case of the complex bearing the 2-thienyl group being less pronounced.

Moving to complexes **4** and **5**, their emission maxima are very close to the values registered for parent compounds **1-N$_3$** and **3-N$_3$**: 498, 531 and 570 nm for monomeric **4** *vs* 500, 532 and 572 for **1-N$_3$**; 543, 582 and 632 nm *vs* 547, 582 and 638 nm for **5** and **3-N$_3$**, respectively. The same is valid also when considering the lifetimes of the discussed compounds, the values being 7.44 and 7.48 μs for the mesityl-bearing complexes, while 18.1 and 17.8 μs for the thienyl-substituted ones. Complete data are reported in Table 1.

The major effect brought about by the reaction of the azido complex with the electron-poor alkyne is on the emission quantum yield, showing a remarkable increase from 0.87 to 0.96 when passing from **1-N$_3$** to **4**, and from 0.79 to 0.94 in the case of diluted dearated solutions of **3-N$_3$** and **5**.

As it can be observed from the presented data, the emission maxima and the lifetimes values are essentially due to the substituents inserted onto the NˆCˆN scaffold of the molecule, while the effect of the replacement of the ancillary ligand on the metal center is on the absolute quantum yield, as already shown in previous works about this class of compound, where the chloride has been substituted with various thiolates [2h,21,22].

As it can be pointed out, the ancillary ligand plays a key role not only to enhance the photophysical properties of this family of Pt(II) compounds (reaching a QY exceeding 0.9), but also as precursor for further functionalizations or as anchoring point to biomolecules.

Considering the more concentrated solutions ($2{\cdot}10^{-4}$ M in degassed CH_2Cl_2), graphs reported in Fig. 1 clearly show how the presence of the more sterically hindered triazole ligand bearing COOEt chains limits the aggregation usually observed for complexes having the same NˆCˆN ligand studied at the same concentrations; this feature can be particularly useful for applications in which the aggregation-caused quenching of the emission represents a limit, since QY values close to unity can be retained even at very high concentrations. Fig. S21-**26** show the detailed luminescence spectra of derivatives **4** and **5** under different experimental conditions.

3.3. Crystal structure description

The structures of **4** and **5** are shown in Fig. 4, while selected bond distances and angles are given in Table 2. Both complexes crystallize in the triclinic crystal system, space group $P\,\overline{1}$, with an asymmetric unit containing one molecule for complex **4**, and three molecules for complex **5**. In both cases, the metal centre exhibits a square planar coordination environment, with three positions occupied by the 1,3-di(2-pyridyl)benzene ligand and one by the triazolate anion. The bond lengths and angles are in line with those found in known cyclometalated platinum(II) complexes. The strongest interaction is with the carbon atom of the aryl ring, with a Pt–C distance around 1.9 Å. However, the steric demand of the pincer ligand causes a distortion of the coordination geometry. Indeed, the bond angles C–Pt–N and N–Pt–N referred to the NˆCˆN scaffold are about 80° and 160° respectively and deviate from their ideal values of 90° and 180° [23–26]. The X-ray structure determination confirms that the triazolate ligand binds symmetrically to Pt through its central N atom in a κ^1-fashion. Furthermore, the plane of the triazolate anion is twisted with respect to the plane of the Pt(NˆCˆN) unit, with a dihedral angle of about 74° in the structure of **4** and ranging from 58° to 75° in **5**. On the other hand, the moiety in position 5 of the 1,3-di(2-pyridyl)benzene ligand shows different conformations in the two complexes. While the mesityl group in **4** is almost orthogonal the benzene ring, the thienyl moiety in **5** is only slightly tilted, with a dihedral angle ranging from 5° to 25°.

The analysis of the crystal packing reveals distinct features in the two compounds as well. Considering the unit cell content in the structure of **4**, staggered complexes interact in a head-to-tail arrangement; no appreciable $\pi\cdots\pi$ interactions can be recognized between the aromatic rings, although the overall interplanar separation is around 3.38 Å. The Pt⋯Pt interatomic distance within the dimer is 4.93 Å, whereas the shortest Pt⋯Pt separation between two pairs of dimers is 5.25 Å. The dimers of complex **4** stacks together along the b axis, having the plane of the Pt(NˆCˆN) unit oriented parallel to (110) plane.

The asymmetric unit in the structure of complex **5** shows three molecules offset around a pseudo-3-fold axis (Fig. S32), forming a helix-like arrangement. Centroid-centroid distances of 3.50 and 3.72 Å (see Fig. S33) between pyridyl rings in the trimeric unit strongly indicate the presence of $\pi\cdots\pi$ interactions [27]. Two Pt⋯Pt separations of 4.94 and 4.40 Å are found within the trimer, while the shortest Pt⋯Pt distance between two adjacent units is 5.71 Å. The trimers stack with their pseudo-3-fold axis roughly parallel to the [100] direction.

4. Conclusions

In conclusion, we have synthesized and well characterized three novel azido platinum(II) complexes and the 1,2,3-triazole derivatives of two of them, particularly we focused our attention on their photophysical properties. Their intense luminescence, that is quenched by oxygen, combined with the presence of an azide as co-ligand, opens an appealing route for photoactivated chemotherapy and for the synthesis of bioactive molecules. In fact, starting from the azido complexes, via *i*-click reaction, it is possible to obtain even more emissive Pt(II) derivatives. The photophysical properties of the new mesityl and 2-thienyl cyclometalated NˆCˆN–Pt(II) 1,2,3 triazolate complexes were deeply investigated and here reported for the first time, giving rise to chromophores with quantum yields approaching unity.

As a possible development of the suggested strategy, new moieties could be tested on both the benzene and the pyridine rings, to observe the effect exerted on the photophysical properties of the resulting

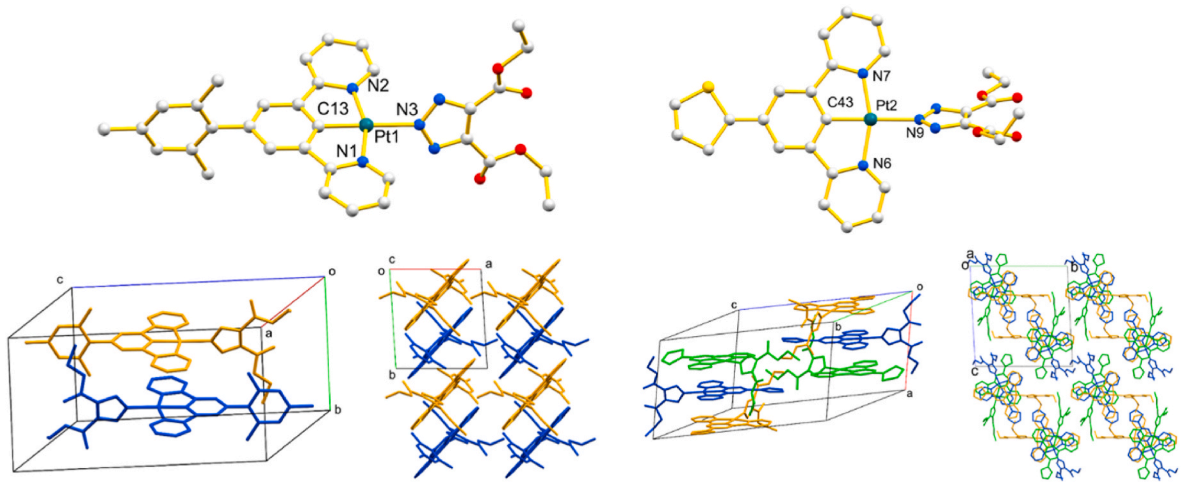

Fig. 4. Molecular structure and crystal packing of (left) complex **4** and (right) complex **5**. The molecules are colored by symmetry equivalence in the crystal packing diagrams. Hydrogen atoms are omitted for clarity.

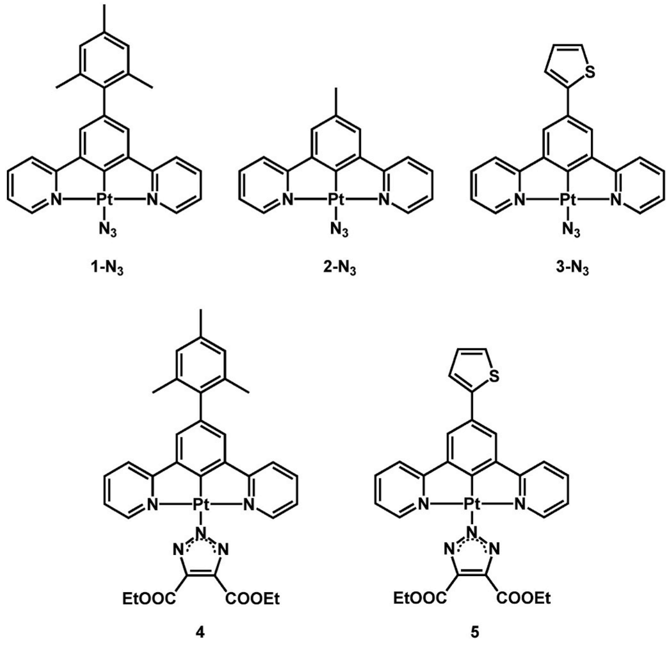

Chart 1. Structure of the investigated complexes.

complexes. Moreover, substituents able to allow for solubility in aqueous media (to be inserted on the aryl rings and/or as alkyls on the ester functional groups of the reacting alkyne) would remarkably extend the application of such compounds, which can nevertheless be tested as dyes in biological environments by starting from a solution containing a small amount of DMSO, as often done in such experiments. Various cyclometalated platinum(II) complexes have already provided remarkable results in biological applications. In the near future, the novel compounds prepared in the present work will be investigated in the dark and under irradiation to assess their cito-toxicity and their efficiency as chromophores in Photodynamic Therapy.

Associated content

Supporting Information: General information for the experimental section, synthetic procedures, NMR spectra, absorption and luminescence spectra, computational details, X-ray structure determination and refinement.

CRediT authorship contribution statement

Francesco Fagnani: Writing – review & editing, Methodology, Investigation, Data curation. **Giulia De Soricellis:** Methodology, Investigation, Formal analysis, Data curation. **Alessia Colombo:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Conceptualization. **Claudia Dragonetti:** Supervision, Methodology, Conceptualization. **Dominique Roberto:** Writing – original draft, Supervision, Data curation, Conceptualization. **Armando di Biase:** Methodology, Formal analysis, Data curation, Conceptualization. **Simona Fantacci:** Investigation, Formal analysis, Data curation, Conceptualization. **Daniele Marinotto:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

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.

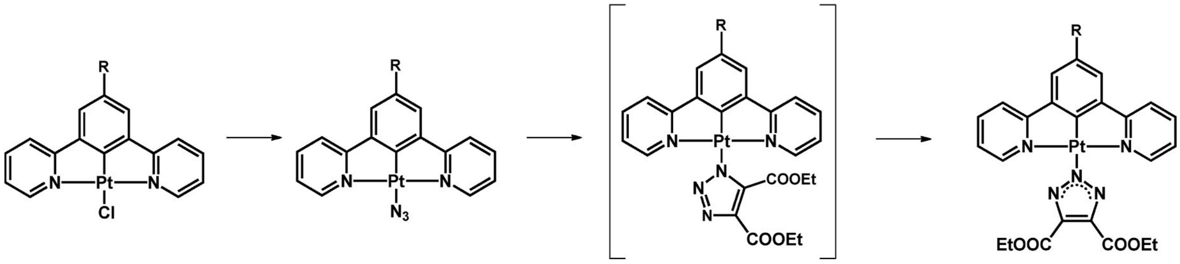

Chart 2. Schematic synthetic pathway for the azido and triazole complexes.

Table 2
Selected bond lengths [Å] and angles [°] for complexes **4** and **5**.

4				5			
Pt1–C13	1.907(6)	C13–Pt1–N1	80.3(2)	Pt2–C43	1.919(9)	C43–Pt2–N6	80.9(3)
Pt1–N1	2.039(6)	C13–Pt1–N2	80.3(2)	Pt2–N6	2.034(7)	C43–Pt2–N7	80.4(3)
Pt1–N2	2.039(5)	N2–Pt1–N3	99.0(2)	Pt2–N7	2.026(8)	N7–Pt2–N9	99.8(3)
Pt1–N3	2.133(5)	N1–Pt1–N3	100.4(2)	Pt2–N9	2.118(8)	N6–Pt2–N9	98.9(3)
		C13–Pt1–N3	178.5(2)			C43–Pt2–N9	179.3(3)
		N2–Pt1–N1	160.6(2)			N7–Pt2–N6	161.3(3)

Data availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2024.112064.

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