

Luminescent Cycloplatinated(II) Complexes: Impact of Ancillary Ligands and Second Metals

Hamid R. Shahsavari*, Sareh Paziresh, Reza Babadi Aghakhanpour and Samira Chamyani

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

This paper is dedicated to the memory of our great mentor Prof. Dr. Mehdi Rashidi

(Received 16 August 2020, Accepted 22 September 2020)

Cycloplatinated(II) complexes are an important class of organoplatinum(II) compounds with impressive photophysical properties. The luminescent cycloplatinated(II) complexes have been employed in many aspects such as optoelectronic devices and bio-imaging applications. The center of emission in these complexes is significantly attributed to the cyclometalated ligand. The emission properties of this chromophoric ligand is perturbed by Pt(II) center as a heavy metal ion and also can be controlled by other ancillary ligands. The role of ancillary ligand seems to be crucial in tuning the photophysical properties of such complexes. In addition to the normal emissions that arise from the cyclometalated ligand, the ancillary ligand(s) may induce some emissions which are created by intra- or inter-molecular Pt...Pt and π ... π interactions. In this regard, the presence of the other metal centers like Ag(I), Au(I), Tl(I) and Pb(II) in the structures of cycloplatinated(II) complexes may considerably affect their emission properties. Since almost 10 years ago, we have started to employ different kinds of ancillary ligands toward different cycloplatinated(II) precursor complexes and study their influences on the structural and photophysical properties of these complexes. In this direction, the new complexes were predominantly identified by means of NMR and Mass spectroscopies together with X-ray crystallography. For photophysical investigations, the UV-Vis and photoluminescence spectroscopies were applied and the obtained results were rationalized with the help of DFT calculation method. In this review article, we tried to share our experiences in this attractive field of research and mention how some of these luminescent complexes synthesized during these years.

Keywords: Cyclometalated ligand, Platinum, Photophysical properties, Heterobimetallic

INTRODUCTION

Among the heavy metal complexes, platinum(II) compounds can be considered as luminescent materials [1-4]. The cycloplatinated(II) complexes are a category of Pt complexes that exhibit outstanding luminescence properties [3,5-21]. Therefore, these complexes are suitable choices for many different research areas such as light emitting devices [22-25], dye sensitized solar cell [26], photo-switches [27-29], photocatalysts [30], and chemical or biochemical sensors [31].

The C^N-based cycloplatinated(II) complexes have

shown to be more attractive than the other cyclometalated complexes. They have been investigated by many research groups [32-42] and their emission properties have remarkably been studied previously [43-50]. A C^N ligand imposes a strong ligand field on the Pt(II) center which arises from its strong σ -donating C atom and π -accepting N atom. It causes the $d-d$ transitions to be energetically non-accessible in the C^N cycloplatinated(II) complexes and consequently the non-radiative pathway is minimized. Also, the emission properties of these complexes can be tuned by functionalization of phenyl and pyridyl rings of C^N ligands [51]. This modification leads to stabilization or destabilization of HOMO and/or LUMO energy levels [48,50,52,53]. The electron-withdrawing groups such as F

*Corresponding author. E-mail: shahsavari@iasbs.ac.ir

and CF₃ groups on the phenyl part of C[^]N ligand (*e.g.* ppy) normally induce the blue shift in the emission of cycloplatinated complexes by stabilization in the HOMO level. On the other hand, the electron-donating groups like NMe₂ similarly make blue shifts *via* destabilization of LUMO [51]. However, there are some factors such as extending π -conjugation [43,44,54] (in some cases blue shift) [6] or the presence of an electron-donating sulfur-containing heterocycle [55] that cause spectral red-shift in the luminescence of the cycloplatinated(II) complexes. Also, a strong electronegative nitrogen atom, when located as a member of the aryl ring, theoretically increases the ligand-centered energy gap of these cyclometalated ligands [56-59].

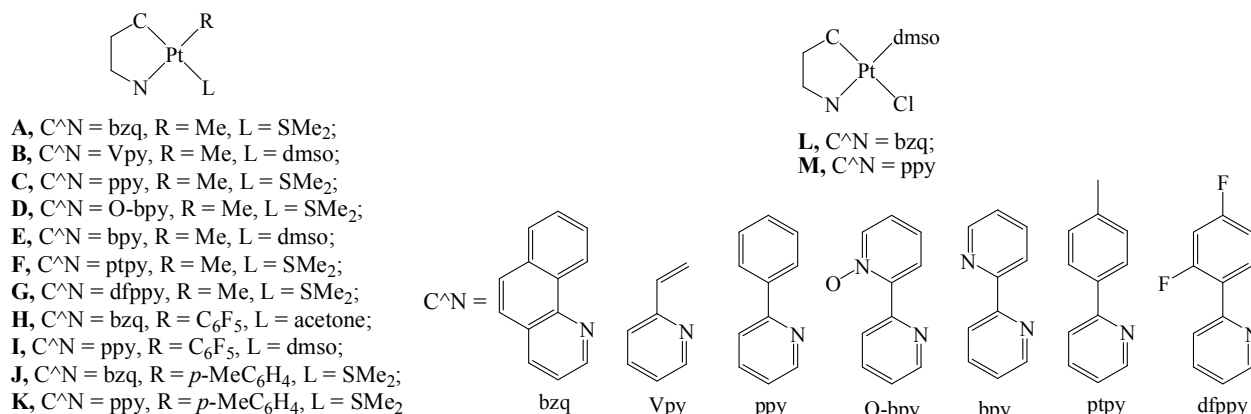
Predominantly, the luminescence of cycloplatinated(II) complexes is attributed to a lowest energy triplet excited state (phosphorescence nature). In order to make a room temperature phosphorescence emitter, two basic components seem to be essential. The first one is a cyclometalated ligand which plays the role of a chromophoric part while the second one is the presence of Pt as a heavy metal center. In the presence of Pt or any other heavy metal, because of the high spin-orbit coupling constant, singlet-triplet intersystem crossing can be allowed. Given the above-mentioned reason, there are many cycloplatinated(II) complexes which are still weak or non-emissive materials at room temperature. Therefore, a third factor is required to influence the luminescence properties of such complexes. In this condition, the modification of chromophoric ligands or presence of an appropriate ancillary ligand (or ligands) can be remedial for creating a strong emission in these complexes. The vital role of the ancillary ligands is referred to their control on the electron density at the metal center and somehow the amount of MLCT (L = cyclometalated ligand) at the lowest energy. There are many reports on different types of ancillary ligands in the structure of cycloplatinated(II) complexes, including neutral (L) or anionic (X), chelating (\wedge) and non-chelating (\prime) ligands (L[^]X [6,39,60,61], L[^]L [14,62,63] L/X [8,38,64-67], L/L [42,68] and X/X [69-71]). Depending on the nature of ancillary ligands, these complexes display highly efficient and tunable phosphorescence attributed to ³ILCT or mixed ³ILCT/³MLCT and ³MLCT/³L/LCT (L' = ancillary ligand) states [23,72-74].

Besides the mentioned characters, ³MMLCT and/or ³ $\pi\pi^*$ excimeric excited states are the transitions that might be established between two vicinal molecules in a cycloplatinated(II) complex [42,75-78]. The lengths of Pt...Pt or π ... π intermolecular interactions outstandingly affect the luminescence of these complexes. These interactions are influenced by the factors such as temperature, crystallization, concentration, solvent and the nature of counteranion [42,79,80]. In the solvent, such interactions may remarkably become weaker or vanish.⁸¹ In addition to the pure cycloplatinated(II) complexes, heteronuclear cycloplatinated complexes form another class of cycloplatinated(II) complexes. In these complexes the platinum metal center can be bound through metallophilic interactions with another metal [18,82-90], or remotely connected through a bridging ligand without any metallophilic interaction [91-99]. They have been remarkably discussed in the literature which is significantly corresponded to their marvelous emission properties, although the logical relationship between their structures and their emissions is not completely clear [21].

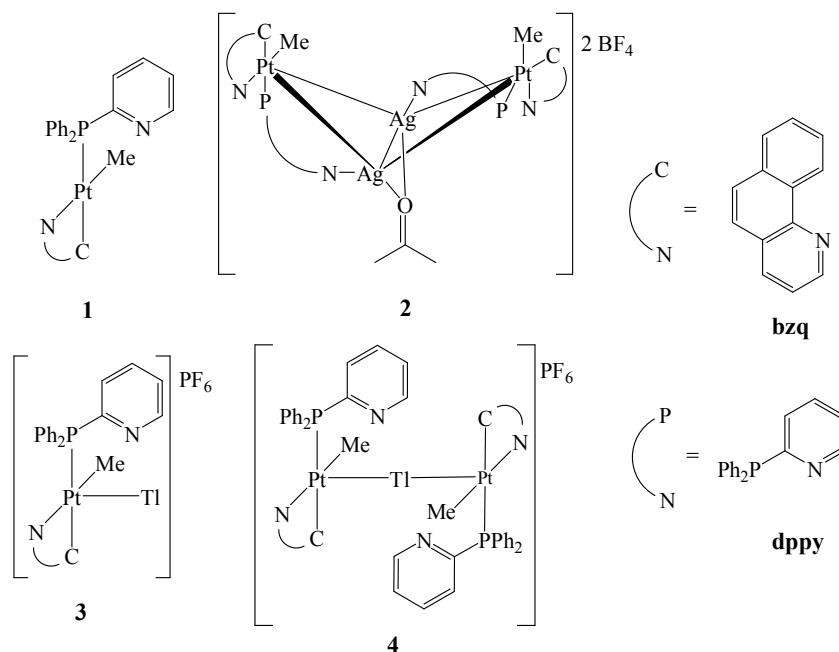
In this review article, we tried to overlook our photophysical investigations on the cycloplatinated(II) complexes in the last decade. Our works in this research field are divided into three main themes *i.e.* our luminescent cycloplatinated(II) complexes are prepared from the precursor complexes containing I) Me, II) aryl and III) Cl ancillary ligands (Scheme 1). These precursor complexes were used for the synthesis of new luminescent cycloplatinated(II) complexes and discussed here.

Me-Cycloplatinated(II) Complexes

Successful routes for the preparation of cycloplatinated(II) complexes using the precursor complexes comprising Me group are stated in this section. The precursor complex [PtMe(bzq)(SMe₂)], A, [100] was employed to synthesize the complex [PtMe(bzq)(dppy)], 1 [85] whereas the other heteronuclear complexes (Pt-Ag and Pt-Tl) were prepared from 1 (Scheme 2). The factors influence the luminescence properties of polymetallic cycloplatinated complexes were studied. All the complexes have intense emissions in the solid state (298 K and 77 K) and glassy solution excluding 1 which is emissive only in glassy state. The monomer entity 1 depicts a structured



Scheme 1. The structure of the precursor complexes for the preparation of luminescent cycloplatinated(II) complexes



Scheme 2. The structures of 1-4

emission band in this condition and it is attributed to the admixture of ³IL³MLCT (L = bzq) excited state. The non-structured profile of the emission band (590 nm, τ = 8.3 μs) for cluster [Pt₂Me₂(bzq)₂(μ-dppy)₂Ag₂(μ-acetone)](BF₄)₂, **2**, indicates the role of Pt₂Ag₂ core in the excited state whereas **1** is non-emissive in the solid state (77 K). In glassy CH₂Cl₂ and acetone diluted solutions (5 × 10⁻⁵ M), **2** shows the non-

structured emission band (λ_{max} = 560 nm) with a concentration-dependent broad shoulder (660 nm). The DFT results show that the high energy band orientates from ³MM'LCT (M = Pt, M' = Ag, L = bzq) with a somewhat ³L'LCT (L' = dppy) character. The intensity of the low energy band (shoulder) increases by raising the concentration (10⁻³ M) having a different excitation profile

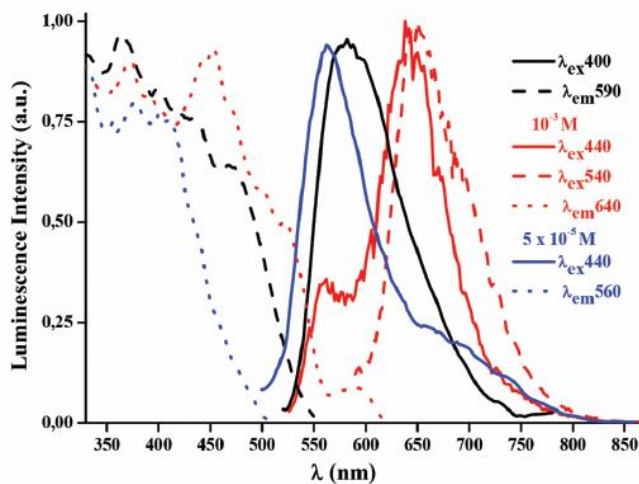


Fig. 1. Emission spectra of 2 in the solid state at 77 K (black lines) and in the glassy solution (CH_2Cl_2 5×10^{-5} and 10^{-3} M at 77 K). Adapted with permission from Ref. [101]. Copyright 2014 The Royal Society of Chemistry.

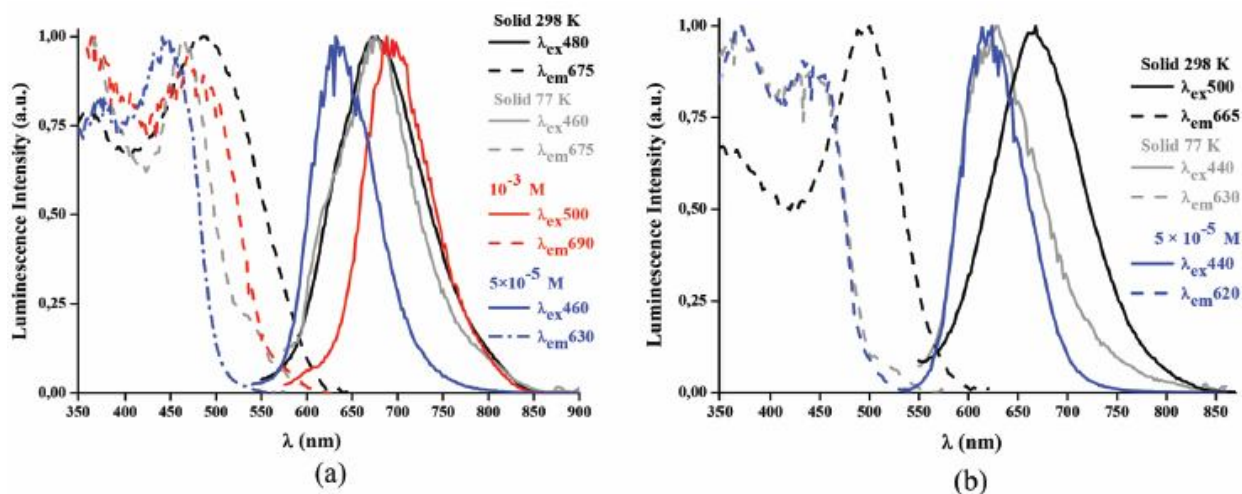
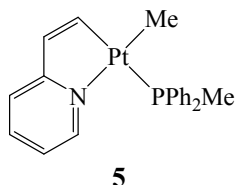


Fig. 2. Normalized excitation and emission spectra of (a) 3 and (b) 4 in the solid state at 298 K and 77 K and in CH_2Cl_2 glasses at 77 K. Adapted with permission from Ref. [101]. Copyright 2014 The Royal Society of Chemistry.

in its maximum compared with high-energy band. It suggests that this low energy band comes from $\pi \cdots \pi$ or Pt \cdots Pt intermolecular interactions in ground state aggregates, being formed specifically at higher concentrations (Fig. 1). The heteropolymetallic Pt-Tl derivatives $[\{\text{PtMe}(\text{bzq})(\text{dppy})\}\text{Tl}]\text{PF}_6$, 3, and $[\{\text{Pt}_2\text{Me}_2(\text{bzq})_2(\text{dppy})_2\}\text{Tl}]\text{PF}_6$, 4, are red emitters in the

solid state with unstructured emission bands at room temperature. For 3 in the solid state, the main emission band is observed at 675 nm (298 K and 77 K) with an additional shoulder at 620 nm (77 K), indicating that the emission band is attributed to the mixed excited states (Fig. 2a). In glassy solution, the emission profile is concentration-dependent. It is suggested that, in glassy concentrated



Scheme 3. The structure of 5

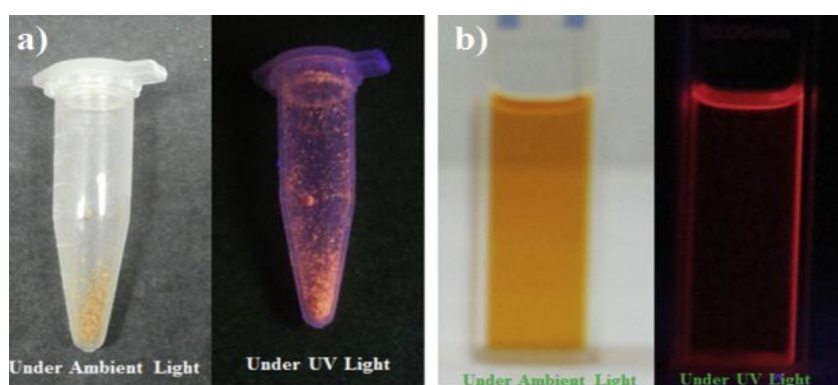
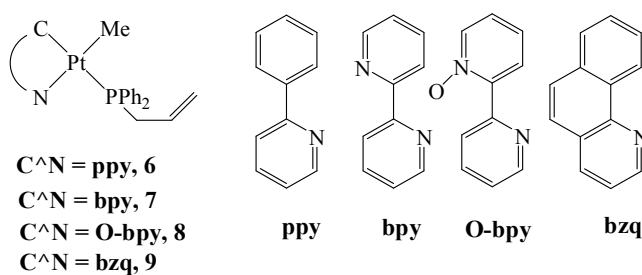


Fig. 3. Photographic images showing the luminescence color change under UV light irradiation (365 nm) a) in solid state and b) in CH₂Cl₂ solution. Adapted with permission from Ref. [103]. Copyright 2016 Elsevier.



Scheme 4. The structures of 6-9

solution (10^{-3} M) the emission band appears at low energies coming from intermolecular $\pi\cdots\pi$ interactions excited state as the extensive $\pi\cdots\pi$ network observed in the crystal of 3. In the case of 4 (Fig. 2b), the emission is similar to the emission profile of 3 and suggesting the emissive state is probably originated from a mixed $^3\text{LL}'\text{CT}/^3\text{LM}'\text{CT}$ ($M' = \text{TI}$) which modified by the Pt-TI bonds [101].

Reaction of the precursor complex [PtMe(Vpy)(dmsO)], B [102,103], with PPh₂Me gave the luminescent complex

[PtMe(Vpy)(PPh₂Me)], 5, (Scheme 3). This complex exhibit deep orange luminescence in solid and solution states at room temperature (Fig. 3). The absorption spectrum of 5 shows high intense $\pi\text{-}\pi^*$ intra-ligand transition (^1IL , L = Vpy) around 230 nm and a band with less intensity at 418 nm which attributed to the mixture of ^1IL and $^1\text{MLCT}$. The emission spectrum of 5 indicates a structured emission band with a maximum at 550 nm with the vibronic progression spacing *ca.* 1400 cm^{-1} in diluted solution with

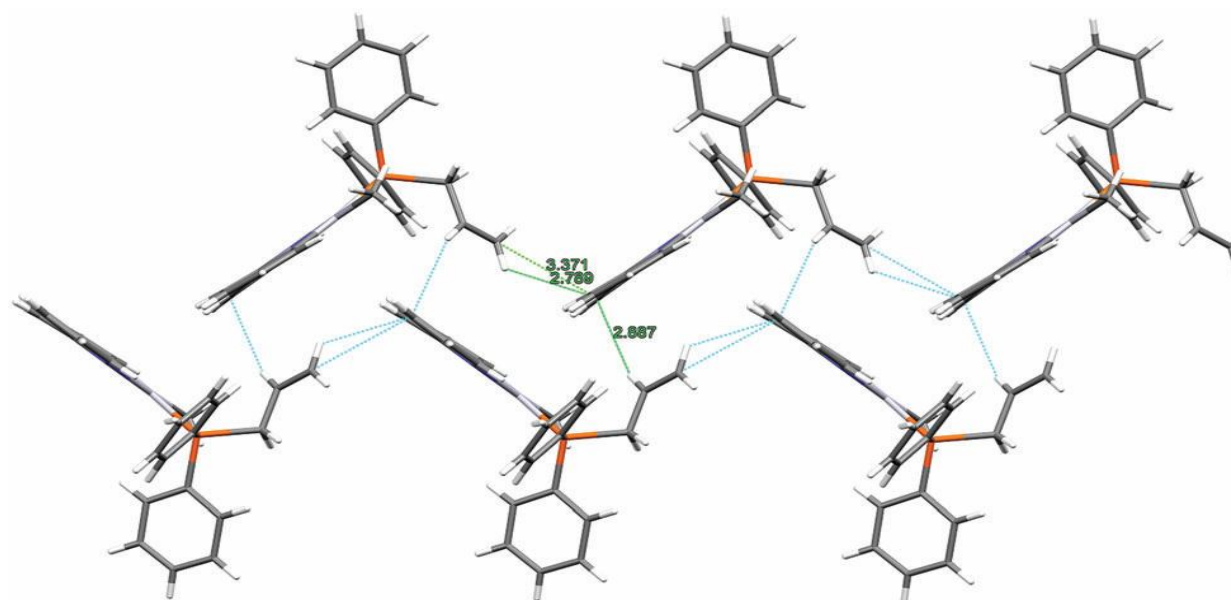
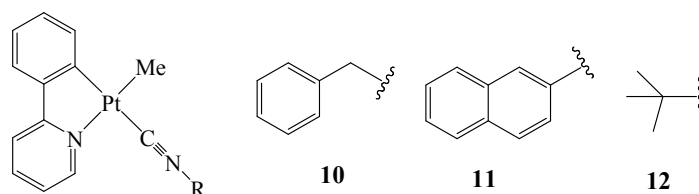


Fig. 4. Crystal packing of 6 displaying intermolecular short contacts between the allyl and ppy groups. Adapted with permission from Ref. [64]. Copyright 2017 The Royal Society of Chemistry.



Scheme 5. The structures of 10-12

the similar emission profile in the solid state. The emissive state is originated from the $^3\text{ILCT}/^3\text{MLCT}$ excited state. By lowering the temperature to 77 K, 5 become a strong emitter, due to the structural rigidity, with a hypsochromic shift compared to its emission at 298 K [103].

The precursor complexes $[\text{PtMe}(\text{C}^{\wedge}\text{N})(\text{SMe}_2)]$, $\text{C}^{\wedge}\text{N}$ = bzq, A; ppy, C [104]; O-bpy, D [105], and $[\text{PtMe}(\text{bpy})(\text{dmsO})]$, E [106], were reacted with PPh_2allyl ligand to give complexes $[\text{PtMe}(\text{C}^{\wedge}\text{N})(\text{PPh}_2\text{allyl})]$, $\text{C}^{\wedge}\text{N}$ = ppy, 6; bpy, 7; O-bpy, 8; bzq, 9 (Scheme 4). In UV-Vis spectra, the bands appear between 300 and 400 nm have mixed $^1\text{ILCT}/^1\text{MLCT}$ ($\text{L} = \text{C}^{\wedge}\text{N}$ ligand) character with contributions of $^1\text{ML}'\text{CT}$ and $^1\text{LL}'\text{CT}$ ($\text{L}' = \text{PPh}_2\text{allyl}$) at higher energies. Except 8, all the complexes are strong green emitters at 298 K and 77 K in the solid state and

glassy solution (CH_2Cl_2) under photoexcitation. The emissive states of 6, 7 and 9 are originated from the mixed $^3\text{ILCT}/^3\text{MLCT}$ excited state, depicting a large participation of cyclometalated ligands in the emissive state. DFT and TD-DFT calculations support the origin of photophysical data. The reason for the quenching of emission in 8, even at low temperature, is probably due to the interruption of the electronic transitions in the presence of oxygen in the O-bpy moiety. The emission band wavelengths follow the trend of $\text{bpy} < \text{ppy} < \text{bzq}$, showing the slight red shift. However, the trend of $\text{ppy} > \text{bpy} > \text{bzq}$ for the quantum efficiency values, were observed. In the crystal packing of 6, the ppy ligand is surrounded on two sides by two distinct $\text{C}(\text{sp}^2)\text{-H}\cdots\pi$ interactions from two allyl groups (Fig. 4). As a result, 6 had a high luminescence quantum efficiency due to

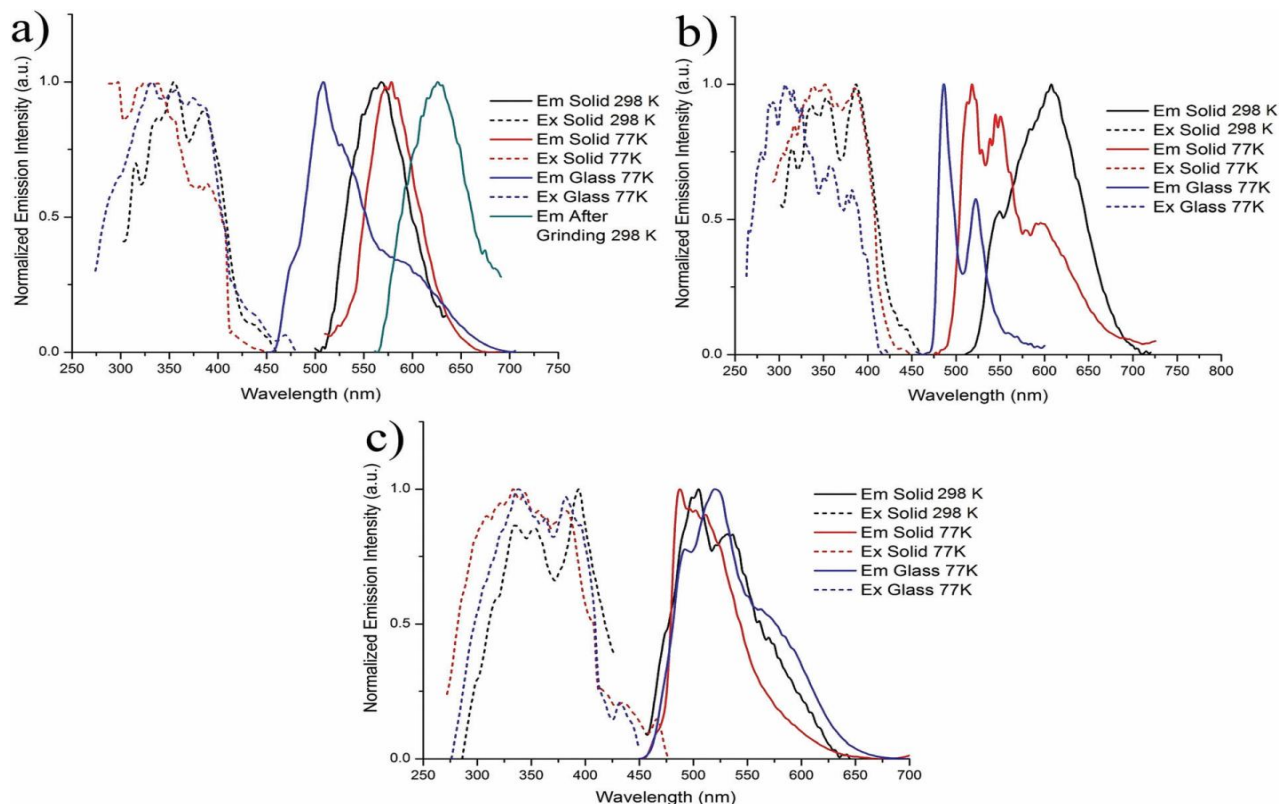


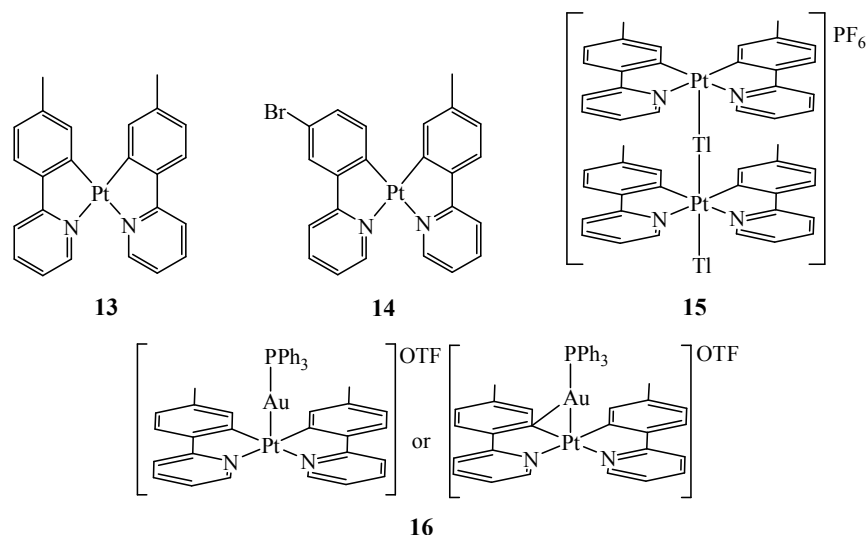
Fig. 5. Normalized emission (solid lines) and excitation (dashed lines) spectra in the solid state at 298 K, the solid state at 77 K and the CH_2Cl_2 glassy state at 77 K for (a) 10, (b) 11 and (c) 12. Adapted with permission from Ref. [65]. Copyright 2017 The Royal Society of Chemistry.

restriction the motions of the ppy ligand. This kind of interaction is not present in the crystal packing of 9 [64].

The complex C was reacted with three different isocyanide ligands giving the cycloplatinated(II) complexes $[\text{PtMe}(\text{ppy})(\text{Me})(\text{CN-R})]$, R = benzyl, 10, 2-naphtyl, 11, *tert*-butyl, 12, (Scheme 5). The photophysical properties of these complexes were investigated in different states and temperature conditions (Fig. 5). In the luminescence study of the complexes, the role of R substituents on the structures of isocyanide ligands seems to be vital. It can explain the different behavior of 11 with aromatic backbone in relation to 10 and 12 with aliphatic backbones. At room temperature in solid state, 10 and 12 show unsymmetrical unstructured bands which are originated from $^3\text{ILCT}/^3\text{MLCT}$ ($L = \text{ppy}$) excited state with more contribution of $^3\text{ILCT}$ for 12. For 11, in addition to $^3\text{ILCT}$ and $^3\text{MLCT}$, the $^3\text{ML}'\text{CT}$ and

$^3\text{IL}'\text{CT}$ ($L' = 2\text{-naphtyl isocyanide}$) characters can be seen. Extended π -conjugation system in 11 causes a red shift in emission band in comparison to those of 10 and 12. By lowering the temperature, for 10 and 11, a hypsochromic shift in the emission bands is occurred. Interestingly, 10 has mechanochromic behavior during the grinding process, showing a remarkable red shift in the emission band. This bathochromic shift can probably be attributed to the existence of metallophilic interactions. It should be mentioned that the obtained photophysical data have been supported by DFT calculations. The complexes had high quantum yield values 0.41, 10; 0.56, 11; and 0.40, 12. It was due to the presence of two strong carbon-donor ancillary ligands (Me and isocyanide) in the structure of complexes [65].

The substitution of SMe_2 ligand in the complex



Scheme 6. The structures of 13-16

[PtMe(pty)(SMe₂)], F [107] with nitrogen atom of ptpy or bppy cyclometalating ligands followed by the addition of B(C₆F₅)₃ to yield bis-cyclometalated complexes [Pt(pty)₂], 13, and [Pt(pty)(bppy)], 14. The reaction of 13 with one equivalent of [TlPF₆] or [Au(PPh₃)]OTf [108] gave [{Pt(pty)₂}Tl]PF₆, 15, or [{Pt(pty)₂}Au(PPh₃)]OTf, 16. The X-ray determination indicated 15 or 16 exist as an infinite helical chain [-Pt(II)-Tl(I)-]_∞ structure or as a mixture of supported and unsupported Pt(II)-Au(I)-bonded structures, respectively (Scheme 6). Different spectroscopies such as absorption, emission and NMR revealed that both Pt-Tl and Pt-Au bonds in 15 and 16 have dynamic behavior. All complexes are bright emitters in the solid state, and their photophysical properties were studied. The emission spectrum of 13 and 14 in the solid state show structured bands, originated from ³ILCT/³MLCT (L = C[^]N ligand) excited state. According to the experimental data and DFT calculations, the red emission of 15 originates from Pt-Tl chromophore. At 77 K, as a result of shorter Pt-Tl distance, the emission band slightly red-shifted (Fig. 6a). Emission spectrum of 16 in the solid state at 298 K shows a band with maximum at 592 nm with a high energy shoulder at 530 nm. This observation related to the supported and unsupported Pt-Au bond forms of 16 (Fig. 6b). Based on the calculation data, supported Pt-Au bond causes formation of the intense band, originating from an excited state which is

localized on Au and Pt metal centers. On the other hand, unsupported Pt-Au causes formation of the shoulder and originated from the ³MLCT excited state. The obtained T₁ → S₀ emission energies are also in compliance with the experimental data for both complexes (Fig. 6c). The lowest-energy triplet emission in 15, the contribution of the thallium and platinum atoms becomes more significant and the emission is associated with the Pt-Tl chromophore. For 16 with the supported Au-C_{ipso} bond, the transition density is predominantly localized on the ptpy moieties and Pt center (MLCT), while the gold atoms play a less important role (Fig. 6c) [107].

The photoluminescence properties of a series of binuclear cycloplatinated(II) complexes [Pt₂Me₂(C[^]N)₂(μ-P[^]P)], C[^]N = Vpy, P[^]P = dppm, 17; C[^]N = O-bpy, P[^]P = dppm, 18; C[^]N = O-bpy, P[^]P = dppa, 19; C[^]N = dfppy, P[^]P = dppm, 20; C[^]N = dfppy, P[^]P = dppa, 21, were investigated (Scheme 7). These complexes can be provided by the reaction of the precursor complexes B, E and [PtMe(dfppy)(SMe₂)], G [109,110] with 0.5 equivalent of dppm and dppa as bridging ligands. Consistent with the DFT investigations, the UV-Vis spectra of 17-21 in both solution and solid states indicated the same electronic transition of ¹MMLCT (M = Pt, L = cyclometalated ligand) at higher wavelengths (> 425 nm). As a result, the presence of Pt...Pt interaction is confirmed in both states. Emission

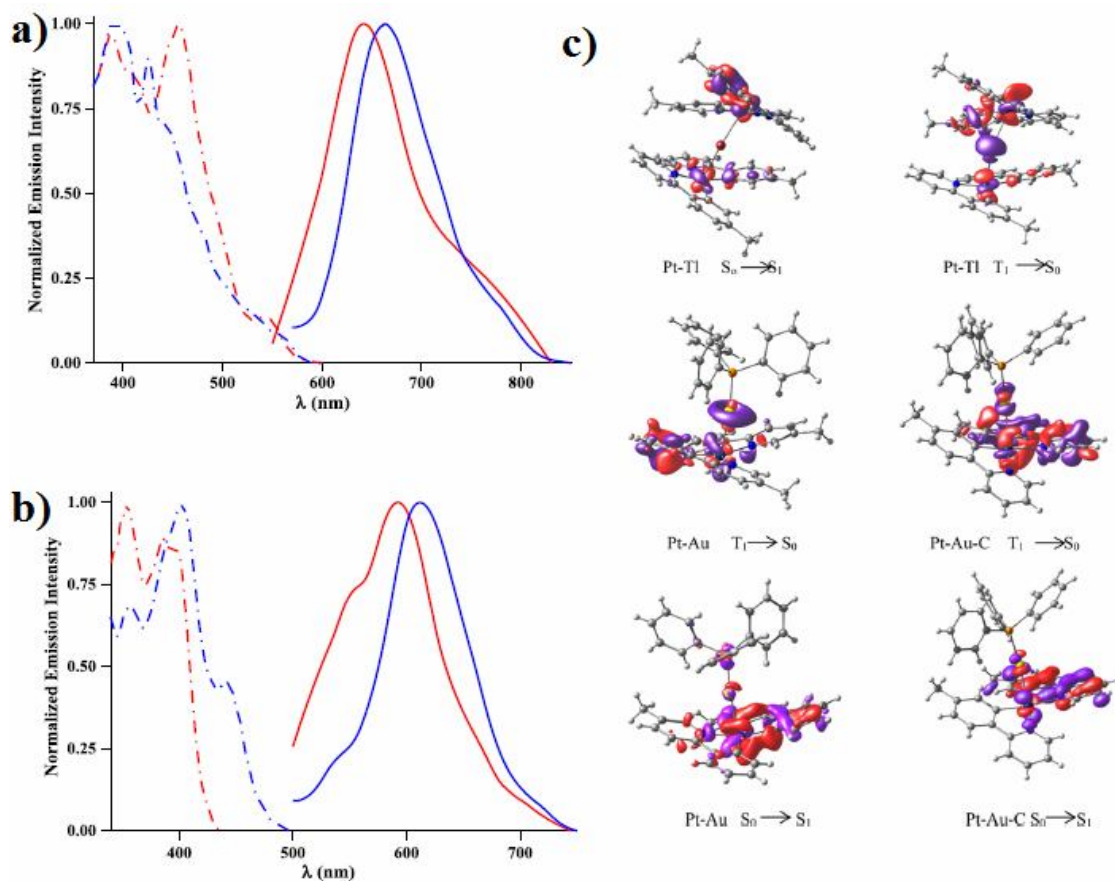
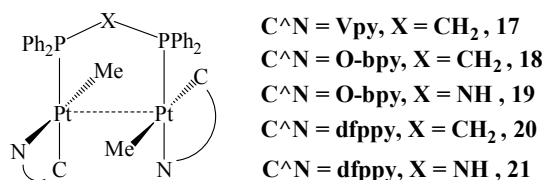


Fig. 6. Normalized excitation and emission spectra of a) 15 ($\lambda_{\text{ex}} = 440$ nm) and b) 16 ($\lambda_{\text{ex}} = 400$ nm) in solid states at 298 K (red) and at 77 K (blue). c) PBE0-DFT transition densities for the lowest-energy singlet excitations and triplet emissions of 15 and 16. During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Adapted with permission from Ref. [107]. Copyright 2019 American Chemical Society.



Scheme 7. The structures of 17-21

properties of the complexes are strongly affected by the nature of Pt...Pt interaction and cyclometalated ligands. It can be seen that in the luminescence spectra of 17 in the

solid state, the wavelength of bell-shaped emission bands are higher than 600 nm (Fig. 7a). The band shape and wavelength show obviously the large amount of $^3\text{MMLCT}$

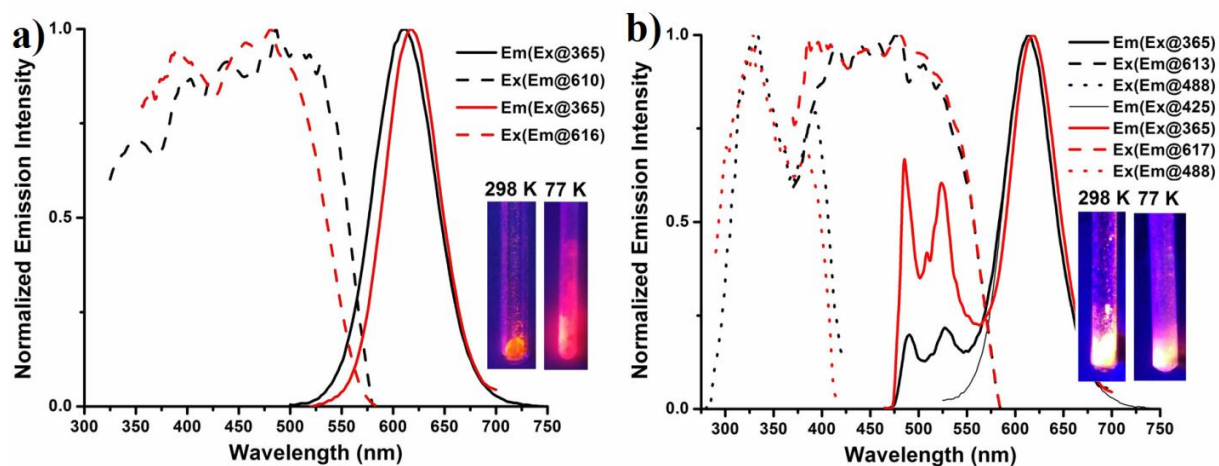


Fig. 7. Emission (solid) and excitation (dashed) spectra for a) 17 and b) 21 in solid state at 298 K (black) and 77 K (red). Adapted with permission from Ref. [109]. Copyright 2019 Wiley-VCH.

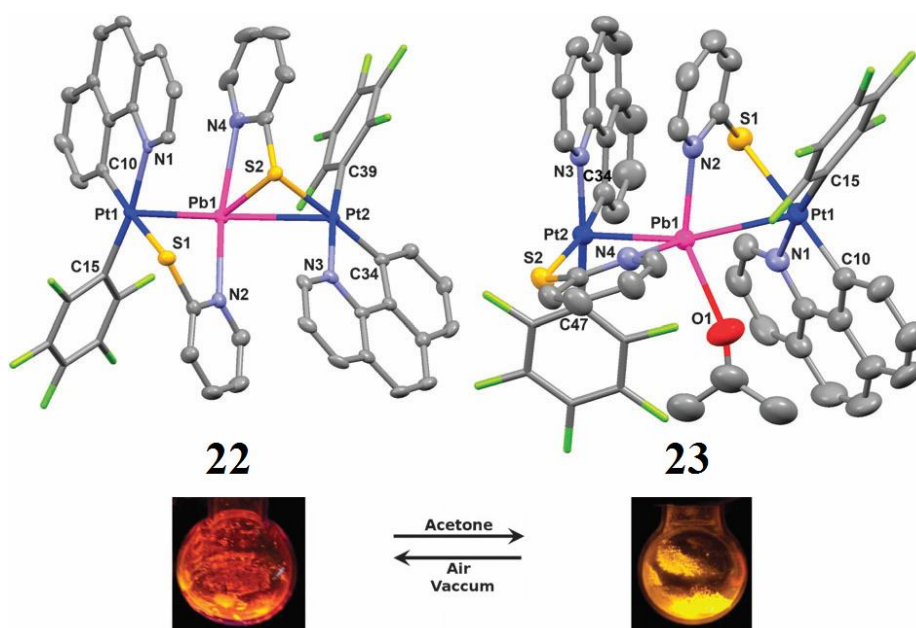
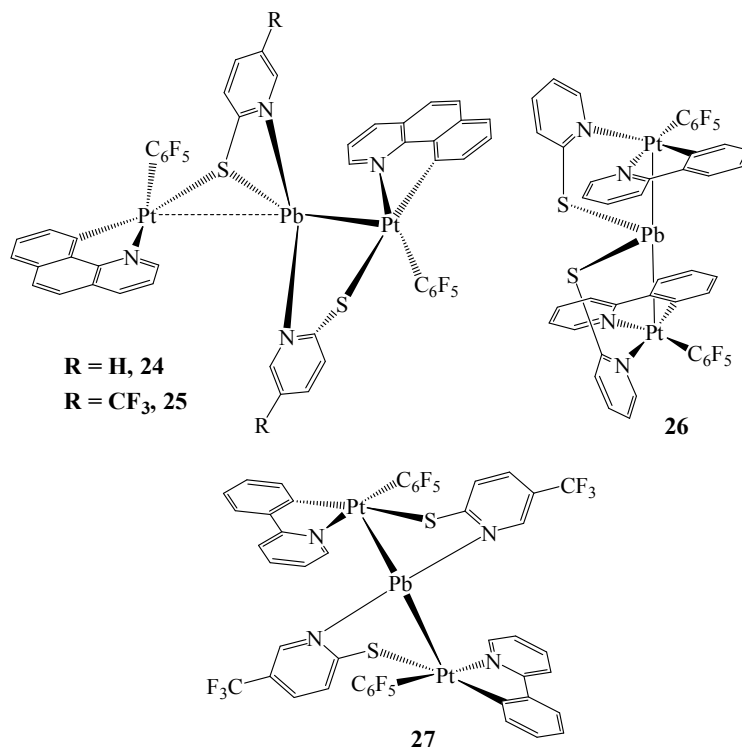


Fig. 8. Molecular structures of 22 (left) and 23 (right). Photographic images of the luminescence color change upon sorption of acetone vapor under UV light irradiation (365 nm). Adapted with permission from Ref. [111]. Copyright 2013 The Royal Society of Chemistry.

character in the excited state. Similarly, excluding 17, all the complexes are rather good emitters in their CH_2Cl_2 solutions. The weak emission of 17 in its CH_2Cl_2 solution is likely related to molecular motions in the solution. On the

other hand, the frozen molecule at 77 K gives a yellow emission with structured band and ${}^3\text{ILCT}/{}^3\text{MLCT}$ character. The importance of Pt...Pt interaction becomes more prominent when the monomers are completely non-emissive



Scheme 8. The structures of 24-27

unlike their corresponding binuclear forms. In total, 20 and 21 show the highest quantum efficiencies. The complex 21 is the only complex that shows a dual emission band at 298 and 77 K having mixed ³ILCT/³MLCT and ³MMLCT characters (Fig. 7b) and its emission color is not purely red like the other derivatives [109].

Aryl-Cycloplatinated(II) Complexes

A several aryl cyclometalated platinum(II) complexes were described by us as unique starting materials for producing of novel emissive cycloplatinated complexes. The treatment of precursor complex [Pt(C₆F₅)(bzq)(acetone)], H [8], with [Pb(Spy)₂] led to formation a novel cluster [{Pt(C₆F₅)(bzq)}₂Pb(Spy)₂], 22. The cluster 22, interestingly can be converted to [{Pt(C₆F₅)(bzq)}₂Pb(Spy)₂(acetone)], 23, by capturing the acetone vapor (Fig. 8). This observation confirmed that 22 can be involved in a reversible vapoluminescence process. Upon photoexcitation, the solid-state emission color of 22 changed from orange-red (620 nm) to yellow-orange

(580 nm) in a few minutes (~10 min). In total, this reversible vapoluminescence happened for 22 in the presence of other donor organic solvents such as MeCN, MeOH and THF. It is assumed that the connection of donor solvents to the Pb(II) center makes a change in the local environment. According to the X-ray and DFT studies, the change in emission color of 22 in the presence of VOCs initially arises from a difference in the distortion of the geometry around the lead center upon photoexcitation [111].

Other clusters containing Pt₂Pb luminescent core [Pt(C₆F₅)(C[^]N)}₂Pb(μ-Spy-5-R)₂], C[^]N = bzq, R = H, 24; C[^]N = bzq, R = CF₃, 25; C[^]N = ppy, R = H, 26; C[^]N = ppy, R = CF₃, 27, were prepared (Scheme 8) by the reaction of the precursors H and [Pt(C₆F₅)(ppy)(dmsol)], I [112] with [Pb(Spy)₂] or [Pb(Spy-5-CF₃)₂]. The Pb environment and its stereochemical activity of 6s² lone pair affects their photophysical properties. Excluding 26, all of them are sensible to external stimuli depending on the solvent (24 and 25, Fig. 9) and crystallization conditions (27). For 27

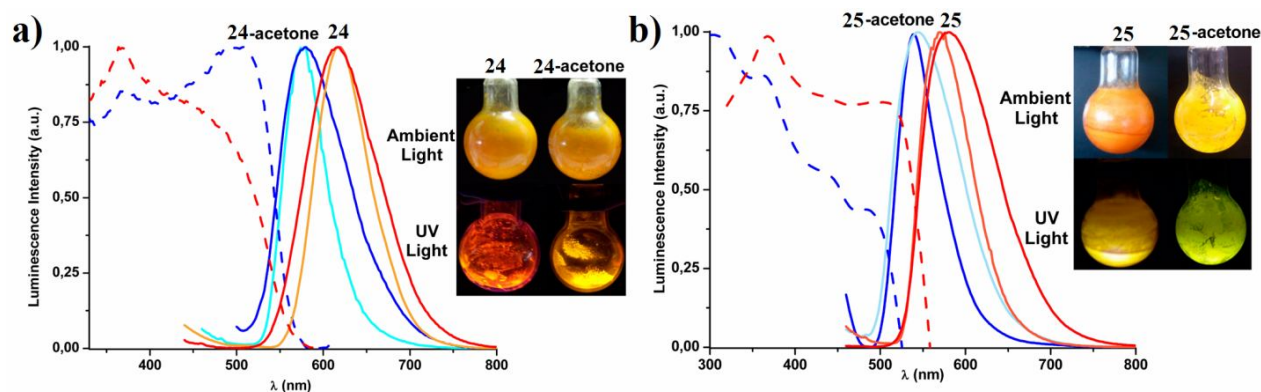
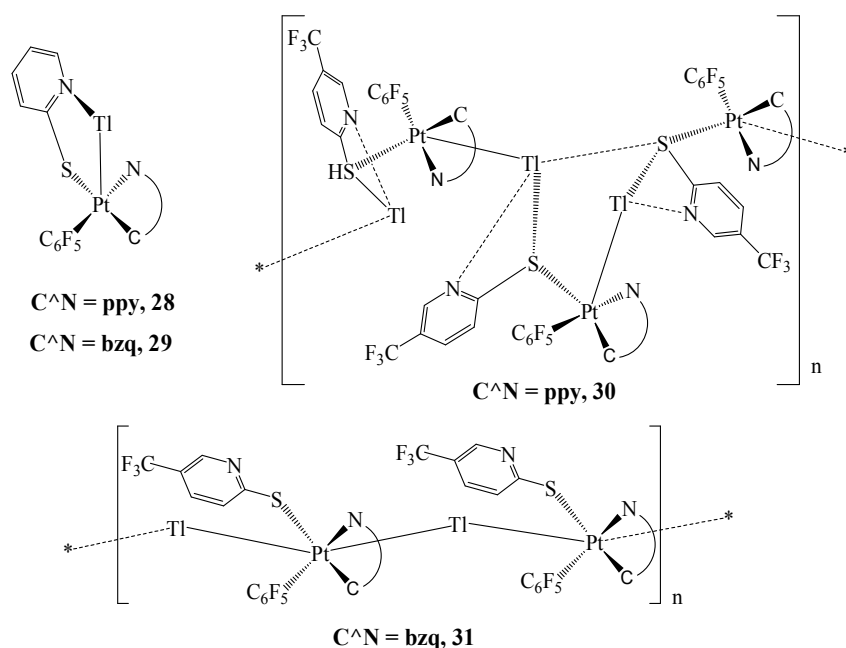


Fig. 9. a) Normalized excitation (dotted lines) and emission (solid lines) of 24 and 24-acetone in the solid state at 298 K (red and deep blue) and at 77 K (orange and light blue). Photographs show the color and luminescence changes of 24 after addition of one drop of acetone. b) Normalized excitation (dotted lines) and emission (solid lines) spectra of 25 and 25-acetone (powders) at 298 K (red and deep blue) and at 77 K (orange and light blue). Photographs show the color and luminescence changes of 25 after addition of one drop of acetone. Adapted with permission from Ref. [112]. Copyright 2014 American Chemical Society.



Scheme 9. The structures of 28-31

(ppy/Spy-5-CF₃), different emissions were found with different environments around the Pb(II) ion. Two asymmetrical forms with a relatively short Pt-Pb bond (pale orange 27.acetone and orange 27-o) and also a symmetrical

yellow form (27-y), were observed for their emissions. It should be noted that, slow crystallization and low concentration cause the thermodynamically yellow product, but fast crystallization favors orange solids with an

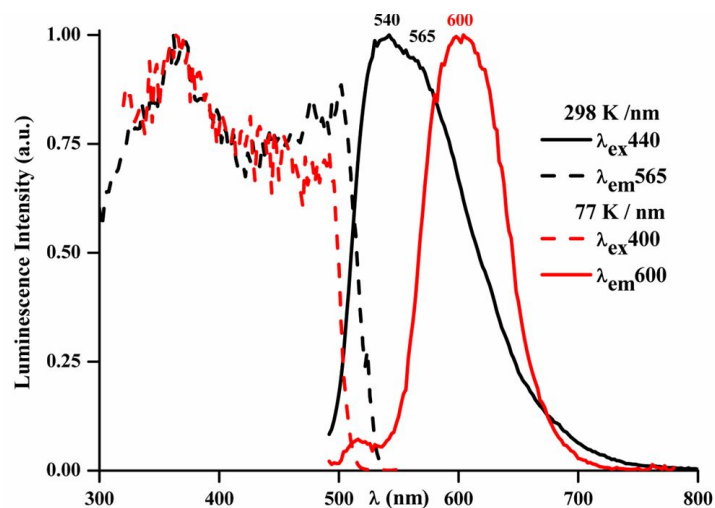


Fig. 10. Normalized excitation and emission spectra of 31 in the solid state at 298 and 77 K. Adapted with permission from Ref. [88]. Copyright 2016 American Chemical Society.

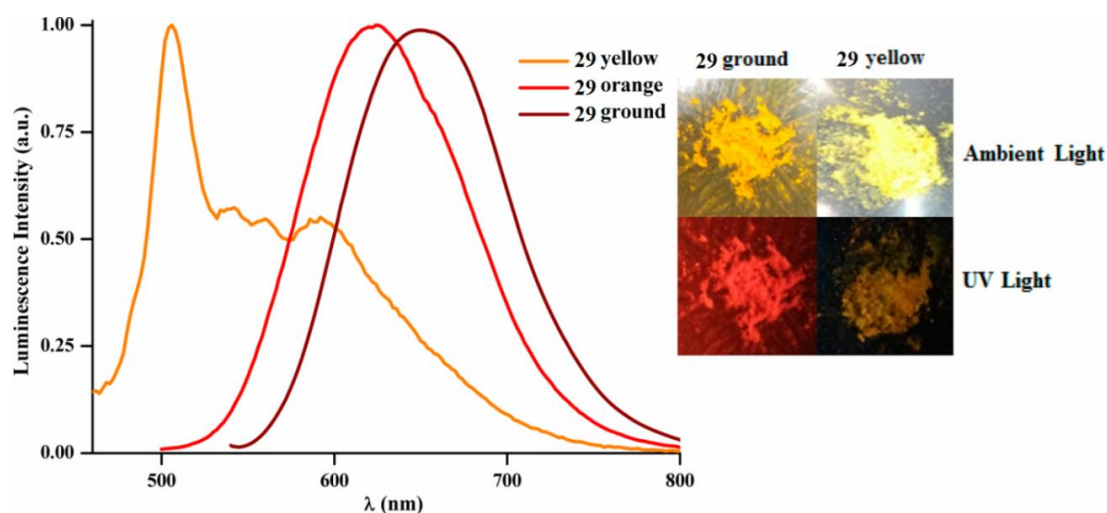


Fig. 11. Normalized emission spectra of solid samples of 29 in yellow, orange and brown colors at 298 K. Photographs show the color and luminescence changes of yellow form after grinding. Adapted with permission from Ref. [88]. Copyright 2016 American Chemical Society.

outstanding red shift of emission. Interestingly, reversible mechanochromic color and luminescence changes were observed for 27 [112].

In addition to the above-mentioned investigations, the precursor complexes H and I as two precursors with C_6F_5 ligand were reacted with $[Ti(Spy)]$ which resulted in the

complexes $[Pt(C_6F_5)(C^N)Ti(Spy)]$, $C^N = ppy$, 28; bzq, 29. In the same condition, treatment of H and I with $[Ti(Spy-5-CF_3)]$ yield the complexes $[Pt(C_6F_5)(C^N)Ti(Spy-5-CF_3)]_n$, $C^N = ppy$, 30; bzq, 31 (Scheme 9). The factors that influence structures and luminescence properties are the donor characteristics of the

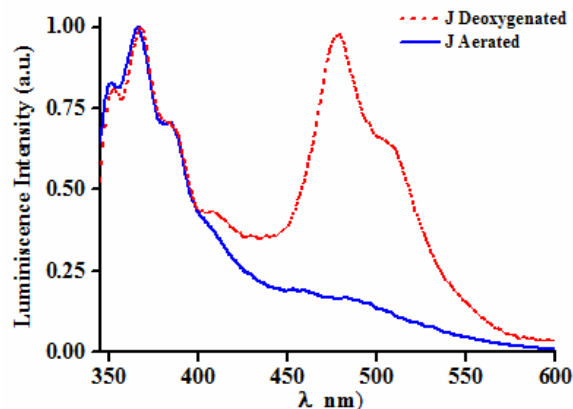
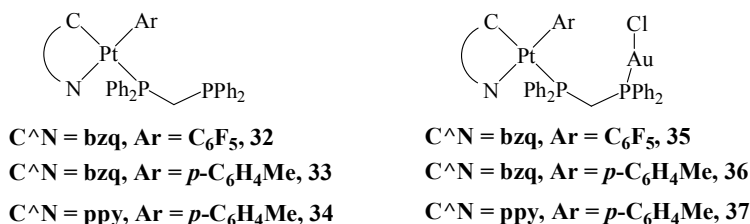


Fig. 12. Normalized emission spectra of J in CH₂Cl₂ solution (5×10^{-5} M) at 298 K in deoxygenated and aerated solutions. ($\lambda_{\text{ex}} < 320$ nm). Adapted with permission from Ref. [54]. Copyright 2015 The Royal Society of Chemistry.



Scheme 10. The structures of 32-37

pyridine-2-thiolate ancillary ligands and the cyclometalated groups. All the complexes show emission in the solid state (298 and 77 K) and in glassy solutions (CH₂Cl₂ and acetone). In the solid state, 28 and 30 show dual emission bands; structured high energy and unstructured low-energy bands which originate from monomer units and ³ππ* excimeric emission, respectively. The ³ππ*-stacking transition is dominated at 77 K. For 29, based on the type of isolation conditions (fast and slow crystallization), different colors and emissions (orange and yellow) were observed. Extended chain in 31 only exhibits a high energy band at ambient temperature, arising from ³L'LCT (SpyCF₃ → bzq) excited state with a minor contribution of ³MLCT/³MM'CT (M = Pt; M' = Tl). At 77 K, the ππ*-stacking emission in 31 is dominated (Fig. 10). Interestingly, reversible luminescent mechanochromic was observed for 29 with yellow color (Fig. 11) [88].

The *p*-MeC₆H₄-containing precursor complexes of [Pt(*p*-MeC₆H₄)(C[^]N)(SMe₂)] [113], C[^]N = bzq, J; ppy, K

(Scheme 1) are luminescent in solution and solid states at different temperatures. In order to confirm the photophysical data, DFT and TD-DFT studies were also carried out. Due to the extended π conjugation in cyclometalated moiety of J compared to K, their emission spectra showed red-shifted in relation to K. The emission spectra of both complexes exhibited a mixed ³IL/³MLCT/³L'LCT (L = C[^]N and L' = aryl ligands) character. Furthermore, J displayed fluorescence in addition to its phosphorescence profile in diluted solution by appearing a dual emission spectrum. It can be confirmed by vanishing the low energy emission band (phosphorescence) when molecular oxygen is added to the solution (Fig. 12) [54].

Following the application of aryl-based cycloplatinated(II) complex in the construction of luminescent compounds, the reaction of the precursors H, J and K with 1 equivalent of dppm gave the complexes [PtAr(C[^]N)(dppm)], Ar = C₆F₅, C[^]N = bzq, **32**; Ar = *p*-

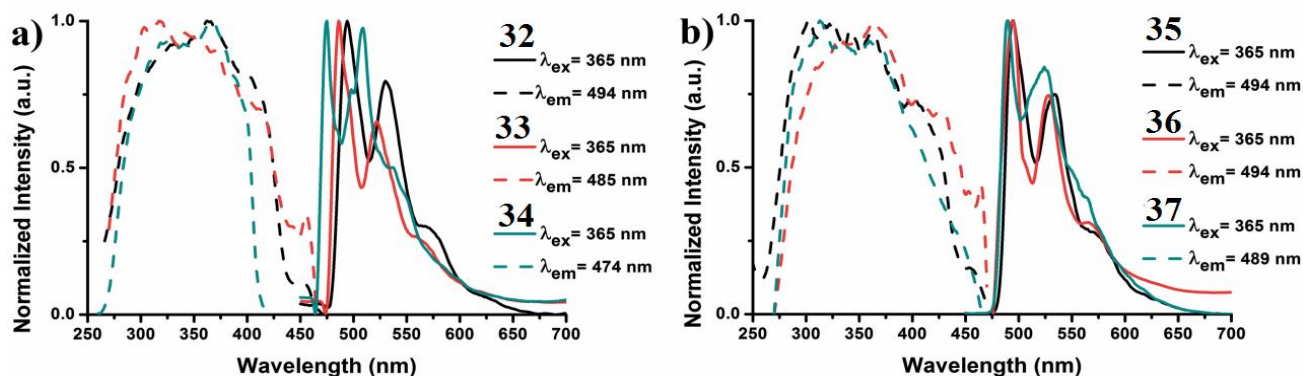
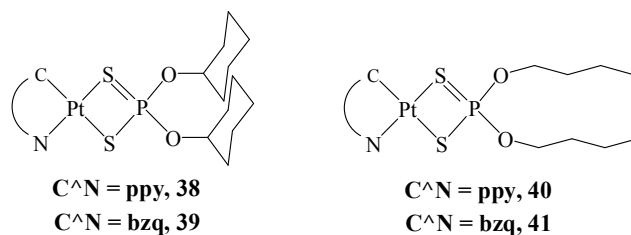


Fig. 13. Normalized emission (solid lines) and excitation (dashed lines) spectra in the solid state for a) 32-34 and b) 35-37 at 77 K. Adapted with permission from Ref. [114]. Copyright 2019 Wiley-VCH.



Scheme 11. The structures of 38-41

MeC_6H_4 , $\text{C}^{\wedge}\text{N} = \text{bzq}$, 33 [113]; $\text{Ar} = p\text{-MeC}_6\text{H}_4$, $\text{C}^{\wedge}\text{N} = \text{ppy}$ 34 [113], respectively. The free phosphine head of monodentate dppm in 32-34 can be connected to Au center of $[\text{AuCl}(\text{SMe}_2)]$ [108] to give the heterobimetallic complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{Ar})(\mu\text{-dppm})\text{AuCl}]$, $\text{Ar} = \text{C}_6\text{F}_5$, $\text{C}^{\wedge}\text{N} = \text{bzq}$ 35; $\text{Ar} = p\text{-MeC}_6\text{H}_4$, $\text{C}^{\wedge}\text{N} = \text{bzq}$ 36; $\text{Ar} = p\text{-MeC}_6\text{H}_4$, $\text{C}^{\wedge}\text{N} = \text{ppy}$ 37, respectively (Scheme 10). The crystal structures of these heterobimetallic complexes exhibited no Pt(II)-Au(I) interaction and dppm ligand was located as a bridging ligand between two metal centers. Their photophysical investigations showed that these complexes emit only in rigid media. Notably by addition of Au(I), no remarkable changes were observed in the electronic structures and emission spectra at 298 or 77 K (Fig. 13 for the spectra at 77 K). In all the conditions, the emission spectra exhibited the structured emission bands with the large amount of $^3\text{ILCT}$ ($\text{L} = \text{C}^{\wedge}\text{N}$ ligand) in the emissive state. It can be due to the absence of Pt(II)-Au(I) bond as mentioned in these Pt(II)-Au(I) complexes. DFT and TD-DFT calculations on

35 and 36 supported the absence of metal-metal bond interaction and photophysical data [114].

Cl-Cycloplatinated(II) Complexes

Mononuclear cycloplatinated(II) complexes with a Cl ligand constitute an important family of luminescent Pt(II) complexes. In an effort to preparation of luminescent cycloplatinated complexes featuring the Pt($\text{C}^{\wedge}\text{N}$) chromophoric fragment, the complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{S}^{\wedge}\text{S})]$, $\text{C}^{\wedge}\text{N} = \text{ppy}$, $\text{S}^{\wedge}\text{S} = \text{ctp}$, 38; $\text{C}^{\wedge}\text{N} = \text{bzq}$, $\text{S}^{\wedge}\text{S} = \text{ctp}$, 39, $\text{S}^{\wedge}\text{S} = \text{btp}$, 40; $\text{C}^{\wedge}\text{N} = \text{bzq}$, $\text{S}^{\wedge}\text{S} = \text{btp}$, 41, were prepared *via* the reaction of the Cl-containing precursor complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{dmsO})\text{Cl}]$ [63], $\text{C}^{\wedge}\text{N} = \text{bzq}$, $\text{L} = \text{ppy}$, with two potentially anionic $\text{S}^{\wedge}\text{S}$ chelates ctp and btp (Scheme 11). Inspiring the UV-Vis spectra in solution, the absorptions have been affected by $\text{C}^{\wedge}\text{N}$ cyclometalated moiety, not depending on the nature of alkyl groups in the structures of $\text{S}^{\wedge}\text{S}$ ligands. The similarity observed between the UV-Vis spectra in solution and solid is an evidence for the lack of

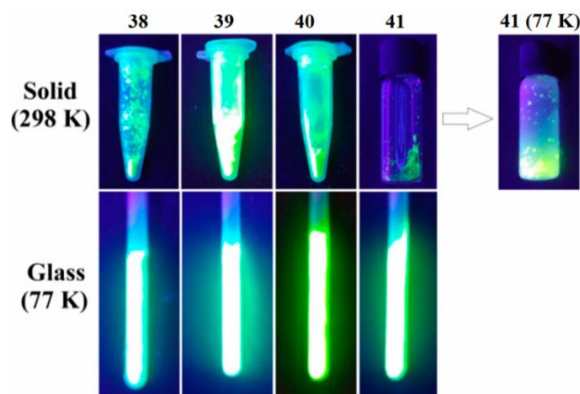


Fig. 14. Photographic images of 38-41 under UV light in solid and glass states. Adapted with permission from Ref. [60]. Copyright 2017 American Chemical Society.

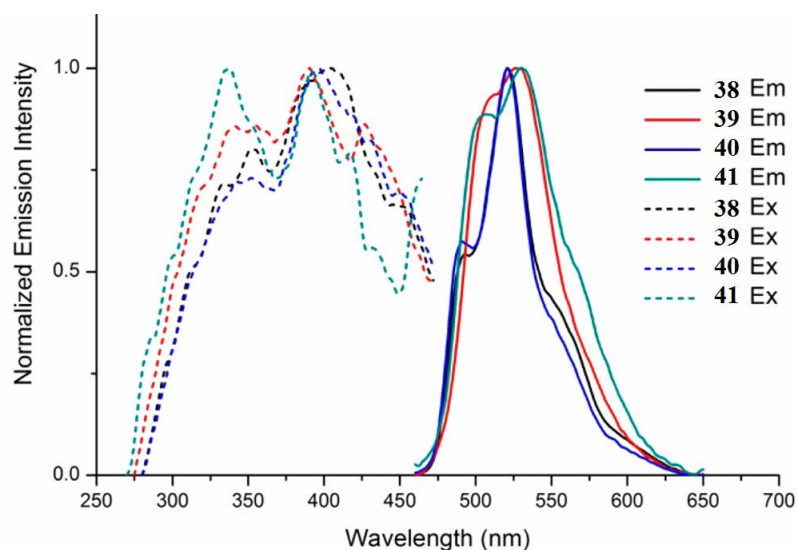
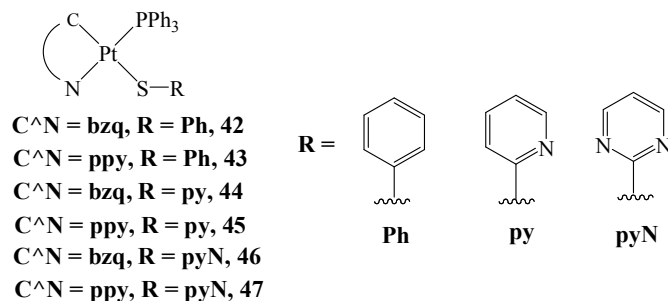


Fig. 15. Normalized emission (solid lines) and excitation spectra (dashed lines) for 38-41 in solid state at 298 K. Adapted with permission from Ref. [60]. Copyright 2017 American Chemical Society.

Pt-Pt or excimeric π - π interactions. All the complexes except 41, being a good emitter only at 77 K, are strong green emitters at room temperature and 77 K (Fig. 14) whereas negligible emissions have been detected in CH_2Cl_2 solution at room temperature. The emission spectra of all the complexes in solid state (298 and 77K) and CH_2Cl_2 glassy state indicate structured emission bands, originating from $^3\text{ILCT}$ transition ($\text{L} = \text{C}^{\wedge}\text{N}$ ligand) with small amount of $^3\text{MLCT}$ transition. The emission spectra of showed that

the S $^{\wedge}$ S ligands do not affect the emission profiles. Only the R groups affected the structural rigidity and consequently the quantum yield values of complexes. The energy of UV-Vis spectra and emission bands of containing bzq are slightly red-shifted in relation to ppy complexes due to extending the π -conjugation system (Fig. 15) [60].

Furthermore, the starting complexes L and M were treated with PPh_3 to give the complex $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{PPh}_3)\text{Cl}]$, $\text{C}^{\wedge}\text{N} = \text{bzq}$, N [115]; ppy, O [116], respectively. These



Scheme 12. The structures of 42-47

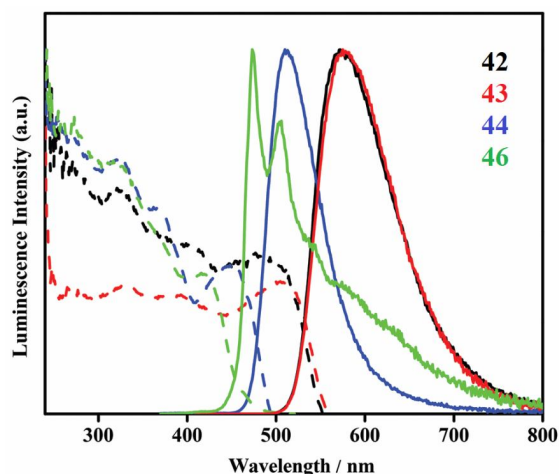


Fig. 16. Normalized excitation (dashed lines) and emission (solid lines) spectra of 42-44 and 46 in the solid state at 298 K. Adapted with permission from Ref. [117]. Copyright 2017 The Royal Society of Chemistry.

phosphine complexes were reacted through facile salt metathesis by the replacement of chloride ligand with various thiolate ligands to make the luminescent products $[Pt(C^{\wedge}N)(PPh_3)(\kappa^1-S-SR)]$, $C^{\wedge}N = \text{bzq}$, $R = \text{SPh}$, 42; $C^{\wedge}N = \text{ppy}$, $R = \text{SPh}$, 43; $C^{\wedge}N = \text{bzq}$, $R = \text{Spy}$, 44; $C^{\wedge}N = \text{ppy}$, $R = \text{Spy}$, 45; $C^{\wedge}N = \text{bzq}$, $R = \text{SpyN}$, 46; $C^{\wedge}N = \text{ppy}$, $R = \text{SpyN}$, 47 (Scheme 12). All the complexes were emissive at 298 K in the solid state except 45 and 47 which are emissive only at 77 K. In the solid state at 298 K (Fig. 16), 42 and 43 showed broad orange emissions. Their emission spectra were almost similar to each other, coming from $d_{Pt}/\pi_{SR} \rightarrow \pi^*_{C^{\wedge}N}$ transition. 44 indicated unstructured green emission band whereas 46 had a green-blue emission with a structured band, originating from ${}^3\text{ILCT}/{}^3\text{MLCT}$

($M = \text{Pt}$, $L = \text{bzq}$) excited state. In the bzq containing complexes, the trend of $\text{SPh} > \text{Spy} > \text{SpyN}$ were observed for the quantum yield and the decay time values. As mentioned above, 45 and 47 were non-emissive at room temperature. The DFT-optimized geometries of 45 and 47 in T_1 state clearly showed the reason of such observation. Theoretically, a large distortion occurs in the square planar geometry (S_0) to a distorted tetrahedral geometry (T_1) which is not practical in reality (Fig. 17). In the other emissive complexes, rigid structures are probably induced by $\pi \cdots \pi$ interactions between the R group of SR and one phenyl group of the PPh_3 ligand. All thiolate complexes were not emissive in solution at 298 K, due to the geometrical distortions that occur upon excitation in a non-rigid

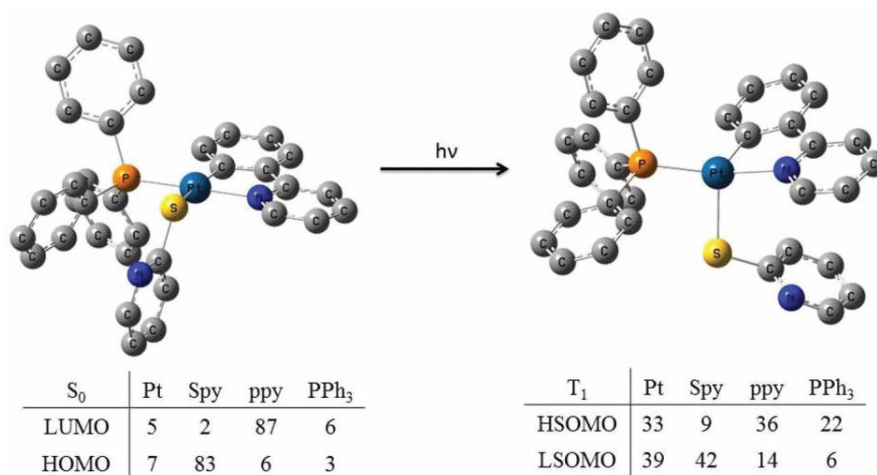
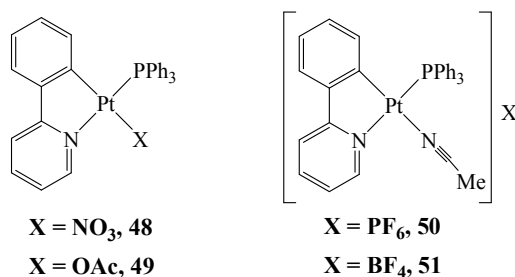


Fig. 17. DFT optimized S₀ (left) and T₁ (right) geometries of 45 with the corresponding contribution of different fragments in frontier molecular orbitals (H atoms are omitted for clarity of presentation). Adapted with permission from Ref. [117]. Copyright 2017 the Royal Society of Chemistry.



Scheme 13. The structures of 48-51

environment [117].

Based on the coordination ability of the anion in the AgX salts (X = NO₃, OAc, PF₆, BF₄), they were reacted with O and produce neutral complexes [Pt(ppy)(PPh₃)X], X = NO₃, 48; OAc, 49, or cationic complexes [Pt(ppy)(PPh₃)(CH₃CN)X], X = PF₆, 50; BF₄, 51 (Scheme 13). With the exception of 51, all the complexes were strong green emitters in solid state at 298 K. By lowering the temperature at 77 K, in solid state and solution (glassy state) due to the rigidochromism, the emission of all the cases became sharper. The emitter complexes had lifetime values in the microsecond range, displaying the phosphorescence character of the emissions. The complexes 48 and 49

displayed the same emission bands in solid and solution states (298 and 77 K) and the role of the anions (NO₃, OAc) did not appear in the emission band. On the basis of the band shapes, emissive state is originated from ³ILCT (L = ppy) with small amount of ³MLCT and no intermolecular interactions (Pt...Pt or π...π stacking) were observed in the emission bands. On the other hand, 50 and 51 with the same cationic part and different counteranions, indicated completely different emission bands and colors (Fig. 18), although they had similar UV-Vis spectra. The emission band for 51 in the solid state (298 and 77 K) was containing two emission bands centered at 488 nm (green area) and a more intense unstructured band at 562 nm

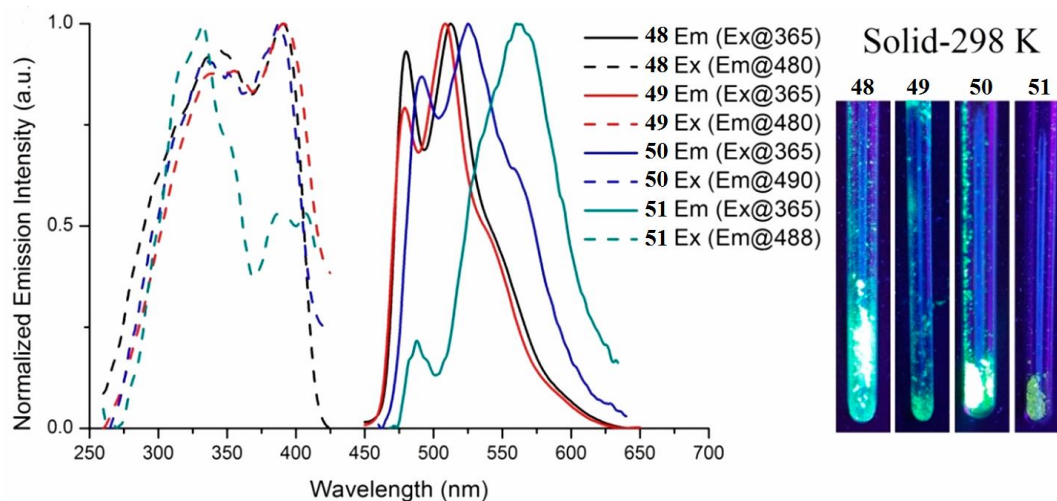
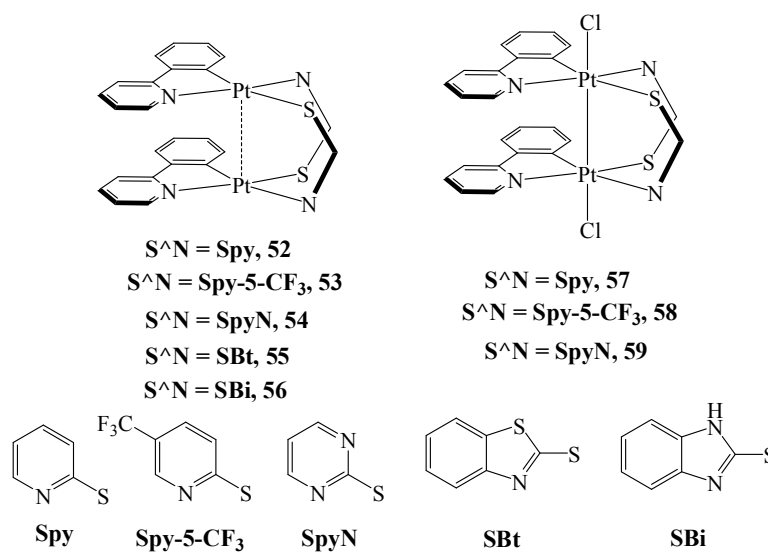


Fig. 18. Normalized emission and excitation spectra together with photographic images for 48-51 in the solid state at 298 K. Adapted with permission from Ref. [118]. Copyright 2018 American Chemical Society.



Scheme 14. The structures of 52-59

(yellow area) which arise from intramolecular transitions and intermolecular short contacts, respectively. The nature of counteranions (PF_6^- and BF_4^-) affected through the short contacts between counteranion and the cationic complex. The photoluminescence and UV-Vis data for the complexes were supported by DFT and TD-DFT calculations [118].

In an interesting work, the precursor complex **M** was able to make several half-lantern cycloplatinated(II)

complexes $[\{\text{Pt}(\text{ppy})(\mu\text{-S}^{\wedge}\text{N})\}_2]$, $S^{\wedge}N = \text{Spy}, 52$; $\text{Spy-5-CF}_3, 53$; $\text{SpyN}, 54$; $\text{SBt}, 55$; $\text{SBi}, 56$, in the reaction with different potentially bridging heterocyclic thionate ligands (Scheme 14). Some of these complexes, 52-54, can be easily oxidized in CHCl_3 or CH_2Cl_2 result in binuclear complexes $[\{\text{Pt}(\text{ppy})(\mu\text{-S}^{\wedge}\text{N})\text{Cl}\}_2]$, $S^{\wedge}N = \text{Spy}, 57$; $\text{Spy-5-CF}_3, 58$; $\text{SpyN}, 59$ (Scheme 14). The UV-Vis absorption spectra of all the derivatives (52-56) in the

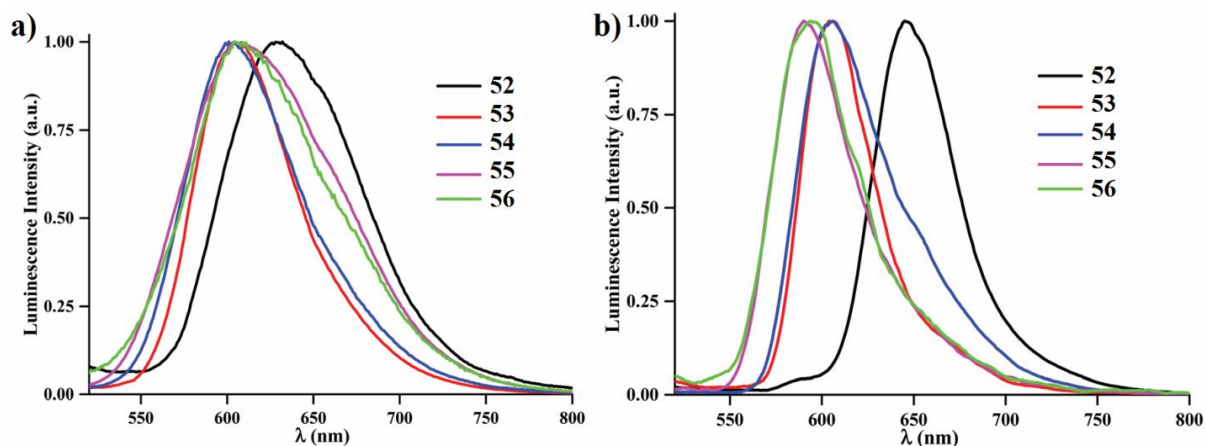


Fig. 19. Normalized emission spectra of 52-56 in the solid state at a) 298 K and b) 77 K ($\lambda_{\text{ex}} = 440$ nm). Adapted with permission from Ref. [119]. Copyright 2019 The Royal Society of Chemistry.

solution, were indicated a weak absorption around 489-500 nm that did not present in their precursor M. According to the previous TD-DFT calculations on similar molecules, the lowest energy absorption band was originated from the short Pt...Pt interaction. The UV-Vis spectra of 52-56 in the solid state were similar to those for the solutions with a slight red shift. This red shift was observed in absorption bands at lower energies in the solid state compared with solution state which was due to the shortening Pt...Pt distance in the solid state. Because of short Pt...Pt interactions in 52-56, they were strong red emitters both in CH_2Cl_2 solution and solid state (298 and 77 K). The emission profile of these complexes were originated from this Pt...Pt interaction ($^3\text{MMLCT}$, $L = \text{ppy}$; Fig. 19). For 52-56, this trend was observed for the emission wavelength maximum in CH_2Cl_2 : 660 ($\mu\text{-Spy}$) > 645 ($\mu\text{-Spy-5-CF}_3$) ~ 640 ($\mu\text{-SBt}$) > 635 ($\mu\text{-SpyN}$) > 630 nm ($\mu\text{-SBi}$). According to the quantum yield measurements, 53 was the most emissive compound in both solid and solution states. The presence of the sterically demanding CF_3 group prevents intermolecular quenching, as a non-radiative deactivation pathway [119]. However, 57-59 were not emissive as expected for $d^7\text{-}d^7$ complexes.

CONCLUSIONS

In this review contribution, we presented our last decade

published works in the field of photophysics of cycloplatinated(II) complexes. Based on the ancillary ligands of Me, aryl and Cl, we divided our works into three main categories. The precursor cycloplatinated(II) complexes A-M (Scheme 1) were shown to be talented to make luminescent products by replacing their labile leaving groups (SMe_2 , dmsO, acetone, Cl) with appropriate strong-field ligands. In the case of Me- and aryl-based cycloplatinated(II) complexes, the strong Pt-Me or Pt-aryl bonds can be preserved during the reaction with the other ligands like phosphines and therefore they were present in the product. Based on our experiences, the simple mononuclear cycloplatinated(II) complexes exhibited strong green to yellow emissions at room or low temperature; however, there are some methods which can be used in order to create orange to red emissions in these complexes. For the Me-cycloplatinated(II) complexes, metal-metal bonds can be established between two Pt(II) centers and it makes a deep red emission in these binuclear complexes. The presence of such Pt-Pt bond was not detectable in the similar aryl-based complexes [120]. Moreover, Me- and aryl-cycloplatinated(II) precursors can also be employed for the synthesis of heterobimetallic or heteropolymetallic complexes. Definitely, the emissions of these heteronuclear complexes are very different from their mononuclear (only Pt(II)) derivatives. On the other hand, Cl-cycloplatinated(II) precursors presented a different chemistry to make different

luminescent complexes. Because in their structures two labile ligands (anionic (Cl) and neutral (dmsO)) were available. For example, cycloplatinated(II) complexes having L⁺L or L⁺X (L = neutral, X = anionic) chelates can be generated applying a Cl-cycloplatinated(II) precursor. Also, the very important class of emissive binuclear cycloplatinated(II) complexes *i.e.* half-lanterns can be made by these Cl-containing precursors.

Certainly, there are still many open questions or many complexes that should be synthesized in this field of research. In the future, we will try to conduct our research pathway toward making new heterobimetallic or heteropolymetallic cycloplatinated(II) complexes by embedding the metal centers such as Re(I), Ru(II), Rh(III), Ir(III), Au(I) into the structures of these complexes. This is the way to go for synthesizing the strong emissive complexes with different emission behavior. In addition to the strong emissions at low energies, these new complexes should be biocompatible in order to be applied for bio-imaging purposes.

ACKNOWLEDGMENTS

The Institute for Advanced Studies in Basic Sciences (IASBS) Research Council (G2020IASBS32629) and the Iran National Science Foundation (Grant no. 97007977) are also gratefully acknowledged. Authors thank all their present and past co-workers involved in the luminescent cycloplatinated system projects for their contribution. Sincere appreciation to Prof. Dr. Elena Lalinde, Prof. Dr. M. Teresa Moreno and their research group for their continuous scientific and personal support.

Abbreviations

HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; DFT, density functional theory; TD-DFT, time-dependent density functional theory.

MLCT, metal to ligand charge transfer; ILCT, intra ligand charge transfer; LLCT, ligand to ligand charge transfer; MMLCT, metal-metal to ligand charge transfer; VOCs, volatile organic chemicals;

ppy, 2-phenylpyridine; bzq, 7,8-benzoquinoline; Vpy, 2-vinylpyridine; O-bpy, 2,2'-bipyridine *N*-oxide; bpy, 2,2'-

bipyridine; ptpy, 2-(*p*-tolyl)pyridine; bppy, 2-(3-bromophenyl)pyridine; dfppy, 2-(2,4-difluorophenyl)pyridine.

B(C₆F₅)₃, tris(pentafluorophenyl)borane.

dppy, 2-(diphenylphosphino)pyridine; PPh₂Me, methyl diphenylphosphine;

allyl diphenylphosphine; PPh₃, triphenylphosphine; dpmp, (bis(diphenylphosphino)methane); dp₂a, (*N,N*-bis(diphenylphosphino)amine).

ctp, *O,O'*-di(cyclohexyl)dithiophosphate; btp, *O,O'*-di(butyl)dithiophosphate.

SPh, thiophenol; Spy, pyridine-2-thiol; Spy-5-CF₃, 5-(trifluoromethyl)pyridine-2-thiol; SpyN, pyrimidine-2-thiol; SBt, benzothiazole-2-thiol; SBi, benzimidazole-2-thiol.

REFERENCES

- [1] L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura and F. Barigelletti, in *Photochemistry and Photophysics of Coordination Compounds II*, Springer, 2007, pp. 143-203.
- [2] J.G. Williams, in *Photochemistry and Photophysics of Coordination Compounds II*, Springer, 2007, pp. 205-268.
- [3] Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* 39 (2010) 638.
- [4] J.G. Williams, A.J. Wilkinson, V.L. Whittle, *Dalton Trans.* (2008) 2081.
- [5] P.J.G. Saris, M.E. Thompson, *Org. Lett.* 18 (2016) 3960.
- [6] A. Bossi, A.F. Rausch, M.J. Leitzl, R. Czerwiec, M.T. Whited, P.I. Djurovich, H. Yersin, M.E. Thompson, *Inorg. Chem.* 52 (2013) 12403.
- [7] A.F. Rausch, L. Murphy, J.A.G. Williams, H. Yersin, *Inorg. Chem.* 51 (2012) 312.
- [8] J.R. Berenguer, E. Lalinde, M.T. Moreno, S. Sánchez, J. Torroba, *Inorg. Chem.* 51 (2012) 11665.
- [9] S. Fuertes, A.J. Chueca, L. Arnal, A. Martín, U. Giovanella, C. Botta, V. Sicilia, *Inorg. Chem.* 56 (2017) 4829.
- [10] S. Fuertes, A.J. Chueca, M. Perálvarez, P. Borja, M. Torrell, J. Carreras, V. Sicilia, *ACS Appl. Mater. Interfaces* 8 (2016) 16160.
- [11] M. Micksch, M. Tenne, T. Strassner, *Organometallics* 33 (2014) 3464.

- [12] A. Tronnier, S. Metz, G. Wagenblast, I. Muenster, T. Strassner, *Dalton Trans.* 43 (2014) 3297.
- [13] S. Fuertes, H. García, M. Perálvarez, W. Hertog, J. Carreras, V. Sicilia, *Chem. Eur. J.* 21 (2015) 1620.
- [14] R.B. Aghakhanpour, S.M. Nabavizadeh, M. Rashidi, M. Kubicki, *Dalton Trans.* 44 (2015) 15829.
- [15] M.H.-Y. Chan, H.-L. Wong, V.W.-W. Yam, *Inorg. Chem.* 55 (2016) 5570.
- [16] A. Chakraborty, J.E. Yarnell, R.D. Sommer, S. Roy, F.N. Castellano, *Inorg. Chem.* 57 (2018) 1298.
- [17] D. Zhao, J.A. Krause, W.B. Connick, *Inorg. Chem.* 54 (2015) 8339.
- [18] J. Moussa, A. Loch, L.-M. Chamoreau, A. Degli Esposti, E. Bandini, A. Barbieri, H. Amouri, *Inorg. Chem.* 56 (2017) 2050.
- [19] J. Moussa, G.R. Freeman, J.G. Williams, L.M. Chamoreau, P. Herson, H. Amouri, *Eur. J. Inorg. Chem.* (2016) 761.
- [20] O.S. Wenger, *Chem. Rev.* 113 (2013) 3686.
- [21] J.R. Berenguer, E. Lalinde, M.T. Moreno, *Coord. Chem. Rev.* 366 (2018) 69.
- [22] W. Lu, B.-X. Mi, M.C. Chan, Z. Hui, C.-M. Che, N. Zhu, S.-T. Lee, *J. Am. Chem. Soc.* 126 (2004) 4958.
- [23] A.F. Rausch, H.H. Homeier, H. Yersin, in *Photophysics of Organometallics*, Springer, 2010, pp. 193-235.
- [24] L. Murphy, J.G. Williams, in *Molecular Organometallic Materials for Optics*, Springer, 2010, pp. 75-111.
- [25] H. Yersin, *Highly efficient OLEDs with Phosphorescent Materials*, John Wiley & Sons, 2008.
- [26] B. Pashaei, H. Shahroosvand, M. Graetzel, M.K. Nazeeruddin, *Chem. Rev.* 116 (2016) 9485.
- [27] V.W.W. Yam, R.P.L. Tang, K.M.C. Wong, X.X. Lu, K.K. Cheung, N. Zhu, *Chem. Eur. J.* 8 (2002) 4066.
- [28] P.-H. Lanoë, H. Le Bozec, J.G. Williams, J.-L. Fillaut, V. Guerschais, *Dalton Trans.* 39 (2010) 707.
- [29] P.K. Siu, S.W. Lai, W. Lu, N. Zhu, C.M. Che, *Eur. J. Inorg. Chem.* (2003) 2749.
- [30] N.M. Shavaleev, H. Adams, J. Best, R. Edge, S. Navaratnam, J.A. Weinstein, *Inorg. Chem.* 45 (2006) 9410.
- [31] J. Liu, C.-H. Leung, A.L.-F. Chow, R.W.-Y. Sun, S.-C. Yan, C.-M. Che, *Chem. Commun.* 47 (2011) 719.
- [32] W.-Y. Wong, C.-L. Ho, *J. Mater. Chem.* 19 (2009) 4457.
- [33] F. Niedermair, O. Kwon, K. Zojer, S. Kappaun, G. Trimmel, K. Mereiter, C. Slugovc, *Dalton Trans.* (2008) 4006.
- [34] B. Yin, F. Niemeyer, J.G. Williams, J. Jiang, A. Boucekkine, L. Toupet, H. Le Bozec, V. Guerschais, *Inorg. Chem.* 45 (2006) 8584.
- [35] A. Valore, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, F. De Angelis, S. Fantacci, *Chem. Commun.* 46 (2010) 2414.
- [36] M. Ghedini, T. Pugliese, M. La Deda, N. Godbert, I. Aiello, M. Amati, S. Belviso, F. Lelj, G. Accorsi, F. Barigelletti, *Dalton Trans.* (2008) 4303.
- [37] J. Liu, C.-J. Yang, Q.-Y. Cao, M. Xu, J. Wang, H.-N. Peng, W.-F. Tan, X.-X. Lü, X.-C. Gao, *Inorg. Chim. Acta* 362 (2009) 575.
- [38] A.L. Díez, J. Forniés, C. Larraz, E. Lalinde, J.A. López, A. Martín, M.T. Moreno, V. Sicilia, *Inorg. Chem.* 49 (2010) 3239.
- [39] J.R. Berenguer, Á. Díez, E. Lalinde, M.T. Moreno, S. Ruiz, S. Sánchez, *Organometallics* 30 (2011) 5776.
- [40] J.R. Berenguer, Á. Díez, A. García, E. Lalinde, M.T. Moreno, S. Sánchez, J. Torroba, *Organometallics* 30 (2011) 1646.
- [41] A. Díez, J. Forniés, A. García, E. Lalinde, M.T. Moreno, *Inorg. Chem.* 44 (2005) 2443.
- [42] Á. Díez, J. Forniés, S. Fuertes, E. Lalinde, C. Larraz, J.A. López, A. Martín, M.T. Moreno, V. Sicilia, *Organometallics* 28 (2009) 1705.
- [43] S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukaide, J. Kamatani, S. Igawa, A. Tsuboyama and T. Takiguchi, *Dalton Trans.* (2005) 1583.
- [44] B.X. Mi, P.F. Wang, Z.Q. Gao, C.S. Lee, S.T. Lee, H.L. Hong, X.M. Chen, M.S. Wong, P.F. Xia, K.W. Cheah, *Adv. Mater.* 21 (2009) 339.
- [45] F.-M. Hwang, H.-Y. Chen, P.-S. Chen, C.-S. Liu, Y. Chi, C.-F. Shu, F.-I. Wu, P.-T. Chou, S.-M. Peng, G.-H. Lee, *Inorg. Chem.* 44 (2005) 1344.
- [46] G. Zhou, C.L. Ho, W.Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T.B. Marder, A. Beeby, *Adv. Funct. Mater.* 18 (2008) 499.
- [47] G. Zhou, Q. Wang, C.L. Ho, W.Y. Wong, D. Ma, L.

- Wang, Z. Lin, *Chem. -Asian J.* 3 (2008) 1830.
- [48] F. De Angelis, S. Fantacci, N. Evans, C. Klein, S.M. Zakeeruddin, J.-E. Moser, K. Kalyanasundaram, H.J. Bolink, M. Grätzel, M.K. Nazeeruddin, *Inorg. Chem.* 46 (2007) 5989.
- [49] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M.E. Thompson, *Inorg. Chem.* 40 (2001) 1704.
- [50] L.-L. Wu, C.-H. Yang, I.-W. Sun, S.-Y. Chu, P.-C. Kao, H.-H. Huang, *Organometallics* 26 (2007) 2017.
- [51] J. Brooks, Y. Babayan, S. Lamansky, P.I. Djurovich, I. Tsyba, R. Bau, M.E. Thompson, *Inorg. Chem.* 41 (2002) 3055.
- [52] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, *J. Am. Chem. Soc.* 125 (2003) 7377.
- [53] Y.H. Song, Y.C. Chiu, Y. Chi, Y.M. Cheng, C.H. Lai, P.T. Chou, K.T. Wong, M.H. Tsai, C.C. Wu, *Chem. Eur. J.* 14 (2008) 5423.
- [54] M. Jamshidi, S.M. Nabavizadeh, H.R. Shahsavari, M. Rashidi, *RSC Adv.* 5 (2015) 57581.
- [55] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, *J. Am. Chem. Soc.* 123 (2001) 4304.
- [56] C.-C. Cheng, W.-S. Yu, P.-T. Chou, S.-M. Peng, G.-H. Lee, P.-C. Wu, Y.-H. Song, Y. Chi, *Chem. Commun.* (2003) 2628.
- [57] P.-C. Wu, J.-K. Yu, Y.-H. Song, Y. Chi, P.-T. Chou, S.-M. Peng, G.-H. Lee, *Organometallics* 22 (2003) 4938.
- [58] C. Di Pietro, S. Serroni, S. Campagna, M.T. Gandolfi, R. Ballardini, S. Fanni, W.R. Browne, J.G. Vos, *Inorg. Chem.* 41 (2002) 2871.
- [59] J.G. Vos, J.M. Kelly, *Dalton Trans.* (2006) 4869.
- [60] M. Fereidoonzhad, B. Kaboudin, T. Mirzaee, R. Babadi Aghakhanpour, M. Golbon Haghghi, Z. Faghhih, Z. Faghhih, Z. Ahmadipour, B. Notash, H.R. Shahsavari, *Organometallics* 36 (2017) 1707.
- [61] F. Niedermair, K. Waich, S. Kappaun, T. Mayr, G. Trimmel, K. Mereiter, C. Slugovc, *Inorg. Chim. Acta* 360 (2007) 2767.
- [62] J. DePriest, G.Y. Zheng, C. Woods, D.P. Rillema, N.A. Mikirova, M.E. Zandler, *Inorg. Chim. Acta* 264 (1997) 287.
- [63] N. Godbert, T. Pugliese, I. Aiello, A. Bellusci, A. Crispini, M. Ghedini, *Eur. J. Inorg. Chem.* (2007) 5105.
- [64] H.R. Shahsavari, R.B. Aghakhanpour, M. Babaghasabha, M.G. Haghghi, S.M. Nabavizadeh, B. Notash, *New J. Chem.* 41 (2017) 3798.
- [65] H.R. Shahsavari, R.B. Aghakhanpour, M. Hossein-Abadi, M.G. Haghghi, B. Notash, M. Fereidoonzhad, *New J. Chem.* 41 (2017) 15347.
- [66] S. Pazireh, R. Babadi Aghakhanpour, M. Rashidi, S. M. Nabavizadeh, *New J. Chem.* 42 (2018) 1337.
- [67] S. Pazireh, R. Babadi Aghakhanpour, S. Fuertes, V. Sicilia, F. Niroomand Hosseini, S.M. Nabavizadeh, *Dalton Trans.* 48 (2019) 5713.
- [68] C. Ezquerro, A. Sepúlveda, A. Grau-Atienza, E. Serrano, E. Lalinde, J.R. Berenguer, J. Garcia-Martinez, *J. Mater. Chem. C* 5 (2017) 9721.
- [69] Á. Díez, E. Lalinde, M.T. Moreno, S. Ruiz, *Organometallics* 35 (2016) 1735.
- [70] J. Forniés, N. Giménez, S. Ibáñez, E. Lalinde, A. Martín, M.T. Moreno, *Inorg. Chem.* 54 (2015) 4351.
- [71] S. Pazireh, V. Sicilia, I. Ara, A. Martín, S. Fuertes, *Organometallics* 38 (2019) 3804.
- [72] J.A. Gareth Williams, S. Develay, D.L. Rochester and L. Murphy, *Coord. Chem. Rev.* 252 (2008) 2596.
- [73] H. Yersin, A.F. Rausch, R. Czerwieniec, T. Hofbeck, T. Fischer, *Coord. Chem. Rev.* 255 (2011) 2622.
- [74] M. Fereidoonzhad, H.R. Shahsavari, S. Abedanzadeh, B. Behchenari, M. Hossein-Abadi, Z. Faghhih, M.H. Beyzavi, *New J. Chem.* 42 (2018) 2385.
- [75] W. Lu, M.C. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* 126 (2004) 7639.
- [76] J. Ding, D. Pan, C.-H. Tung, L.-Z. Wu, *Inorg. Chem.* 47 (2008) 5099.
- [77] A. Poater, S. Moradell, E. Pinilla, J. Poater, M. Solà, M.Á. Martínez, A. Llobet, *Dalton Trans.* (2006) 1188.
- [78] V.W.W. Yam, K.H.Y. Chan, K.M.C. Wong, N. Zhu, *Chem. Eur. J.* 11 (2005) 4535.
- [79] A.Y.-Y. Tam, K.M.-C. Wong, G. Wang, V.W.-W. Yam, *Chem. Commun.* (2007) 2028.
- [80] V.W.-W. Yam, K.M.-C. Wong, N. Zhu, *J. Am. Chem. Soc.* 124 (2002) 6506.
- [81] C.-M. Che, L.Y. He, C.K. Poon, T.C. Mak, *Inorg.*

- Chem. 28 (1989) 3081.
- [82] T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* 123 (2001) 743.
- [83] D.E. Janzen, L.F. Mehne, D.G. VanDerveer, G.J. Grant, *Inorg. Chem.* 44 (2005) 8182.
- [84] J. Forniés, S. Ibáñez, A. Martín, M. Sanz, J.R. Berenguer, E. Lalinde, J. Torroba, *Organometallics* 25 (2006) 4331.
- [85] S. Jamali, Z. Mazloomi, S.M. Nabavizadeh, D. Milić, R. Kia, M. Rashidi, *Inorg. Chem.* 49 (2010) 2721.
- [86] S. Fuertes, A.J. Chueca, A. Martín, V. Sicilia, *Cryst. Growth Des.* 17 (2017) 4336.
- [87] S. Fuertes, C.H. Woodall, P.R. Raithby, V. Sicilia, *Organometallics* 31 (2012) 4228.
- [88] J.R. Berenguer, E. Lalinde, A. Martín, M.T. Moreno, S. Sánchez, H.R. Shahsavari, *Inorg. Chem.* 55 (2016) 7866.
- [89] M.J. Karimi, S. Jamali, *J. Organomet. Chem.* 786 (2015) 14.
- [90] S. Horiuchi, S. Moon, E. Sakuda, A. Ito, Y. Arikawa, K. Umakoshi, *Dalton Trans.* 47 (2018) 7113.
- [91] H. Molaee, S.M. Nabavizadeh, M. Jamshidi, M. Vilsmeier, A. Pfitzner, M. Samandar Sangari, *Dalton Trans.* 46 (2017) 16077.
- [92] R. Muñoz-Rodríguez, E. Buñuel, N. Fuentes, J.G. Williams, D.J. Cárdenas, *Dalton Trans.* 44 (2015) 8394.
- [93] R. Packheiser, P. Ecorchard, B. Walfort, H. Lang, *J. Organomet. Chem.* 693 (2008) 933.
- [94] C.H. Shin, J.O. Huh, S.J. Baek, S.K. Kim, M.H. Lee, Y. Do, *Eur. J. Inorg. Chem.* (2010) 3642.
- [95] J. Forniés, S. Fuertes, A. Martín, V. Sicilia, E. Lalinde, M.T. Moreno, *Chem. Eur. J.* 12 (2006) 8253.
- [96] S. Back, R.A. Gossage, M. Lutz, I. del Río, A.L. Spek, H. Lang, G. van Koten, *Organometallics* 19 (2000) 3296.
- [97] S. Yamaguchi, H. Shinokubo, A. Osuka, *Inorg. Chem.* 48 (2009) 795.
- [98] H. Sesolis, C.K.-M. Chan, G. Gontard, H.L.-K. Fu, V.W.-W. Yam, H. Amouri, *Organometallics* 36 (2017) 4794.
- [99] G. Ferraro, G. Petruk, L. Maiore, F. Pane, A. Amoresano, M.A. Cinellu, D.M. Monti, A. Merlino, *Int. J. Biol. Macromol.* 115 (2018) 1116.
- [100] M. Golbon Haghghi, M. Rashidi, S.M. Nabavizadeh, S. Jamali, R.J. Puddephatt, *Dalton Trans.* 39 (2010) 11396.
- [101] S. Jamali, R. Ghazfar, E. Lalinde, Z. Jamshidi, H. Samouei, H.R. Shahsavari, M.T. Moreno, E. Escudero-Adán, J. Benet-Buchholz, D. Milic, *Dalton Trans.* 43 (2014) 1105.
- [102] A. Zucca, L. Maidich, V. Carta, G.L. Petretto, S. Stoccoro, M. Agostina Cinellu, M.I. Pilo, G.J. Clarkson, *Eur. J. Inorg. Chem.* (2014) 2278.
- [103] M. Niazi, H.R. Shahsavari, *J. Organomet. Chem.* 803 (2016) 82.
- [104] C. Anderson, M. Crespo, J. Morris, J.M. Tanski, *J. Organomet. Chem.* 691 (2006) 5635.
- [105] M.E. Moustafa, P.D. Boyle, R.J. Puddephatt, *Organometallics* 33 (2014) 5402.
- [106] A. Zucca, G.L. Petretto, S. Stoccoro, M.A. Cinellu, M. Manassero, C. Manassero, G. Minghetti, *Organometallics* 28 (2009) 2150.
- [107] S. Rajabi, S. Jamali, S. Naseri, A. Jamjah, R. Kia, H. Samouei, P. Mastroilli, H.R. Shahsavari, P.R. Raithby, *Organometallics* 38 (2019) 1709.
- [108] M.-C. Brandys, M.C. Jennings, R.J. Puddephatt, *J. Chem. Soc., Dalton Trans.* (2000) 4601.
- [109] M. Nazari, H.R. Shahsavari, *Appl. Organomet. Chem.* 33 (2019) e5020.
- [110] F. Juliá, P. González-Herrero, *J. Am. Chem. Soc.* 138 (2016) 5276.
- [111] J.R. Berenguer, E. Lalinde, A. Martín, M.T. Moreno, S. Ruiz, S. Sánchez, H.R. Shahsavari, *Chem. Commun.* 49 (2013) 5067.
- [112] J.s.R. Berenguer, E. Lalinde, A. Martín, M.T. Moreno, S. Ruiz, S. Sánchez, H.R. Shahsavari, *Inorg. Chem.* 53 (2014) 8770.
- [113] S. M. Nabavizadeh, M. Golbon Haghghi, A.R. Esmaeilbeig, F. Raoof, Z. Mandegani, S. Jamali, M. Rashidi, R.J. Puddephatt, *Organometallics* 29 (2010) 4893.
- [114] H.R. Shahsavari, N. Giménez, E. Lalinde, M.T. Moreno, M. Fereidoonzhad, R. Babadi Aghakhanpour, M. Khatami, F. Kalantari, Z. Jamshidi, M. Mohammadpour, *Eur. J. Inorg. Chem.* (2019) 1360.
- [115] P.S. Pregosin, F. Wombacher, A. Albinati, F. Lianza,

- J. Organomet. Chem. 418 (1991) 249.
- [116] H. Samouei, M. Rashidi, F.W. Heinemann, J. Iran Chem. Soc. 11 (2014) 1207.
- [117] M. Jamshidi, M. Babaghasabha, H.R. Shamsavari and S.M. Nabavizadeh, Dalton Trans. 46 (2017) 15919.
- [118] H.R. Shamsavari, R. Babadi Aghakhanpour, M. Nikravesh, J. Ozdemir, M. Golbon Haghghi, B. Notash, M.H. Beyzavi, Organometallics 37 (2018) 2890.
- [119] H.R. Shamsavari, E. Lalinde, M.T. Moreno, M. Niazi, S.H. Kazemi, S. Abedanzadeh, M. Barazandeh, M.R. Halvagar, New J. Chem. 43 (2019) 7716.
- [120] M.S. Sangari, M.G. Haghghi, S.M. Nabavizadeh, M. Kubicki, M. Rashidi, New J. Chem. 41 (2017) 13293.