Platinum(II) Compounds Containing Cyclometalated Tridentate Ligands: Synthesis, Luminescence Studies, and a Selective Fluoro for Methoxy Substitution

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ABSTRACT

Two series of potentially tridentate ligands of formula ArCH=N(CH2)2NMe2 and
ArCH=N(CH2)3NMe2 (Ar = C6H5, 2-FC6H4, 4-FC6H4, 2,3,4-F3C6H2) were used to prepare
[C,N,N′]-cyclometalated platinum compounds containing either a chloro or a methyl ancillary ligand.
The synthesis of the compounds [PtCl{Me2N(CH2)xN=CHR}] (3a−h), via the corresponding
compounds [PtCl2{Me2N(CH2)xN=CHAr}] (2), requires drastic conditions and proceeds more easily
for ligands derived from N,N-dimethylpropylenediamine (x = 3). Along the process, an unexpected
selective nucleophilic substitution of a fluoro for a methoxy substituent took place at the aryl ring for
ligands 2,3,4-F3C6H2CH=N(CH2)xNMe2. The syntheses of compounds
[PtMe{Me2N(CH2)xN=CHR}] (4a−h) using [Pt2Me4(μ-SMe2)2] as a precursor took place for all
ligands under relatively mild conditions. All compounds were fully characterized, including molecular
structure determination for [PtCl{Me2N(CH2)3N=CH(4-FC6H3)}] (3b) and [PtCl{Me2N-
(CH2)3N=CH(2-OMe,3,4-F2C6H)}] (3g). The absorption and emission spectra were also studied for the
[C,N,N′]-cyclometalated platinum(II) compounds, and all of the compounds were emissive in the solid
state and in dichloromethane solution at room temperature (compounds 3) or at 77 K (compounds 4).
The size of the [N,N′]-chelate ring and the number and position of the substituents in the aryl ring
modulate the intensity and the energy of the emission.

X = Cl, Me

Me2

n = 1 or 2

C6H4; 2-FC6H3; 4-FC6H3; 2,3,4-F3C6H
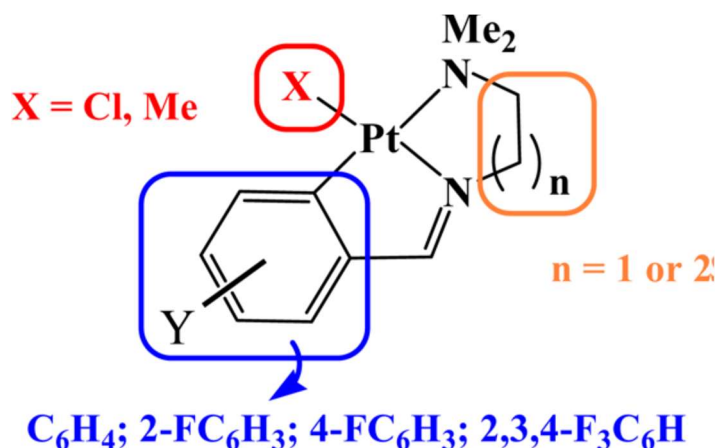
INTRODUCTION

In the last years significant research effort has focused on the photophysical properties of luminescent square-planar platinum complexes. The aim of this research is to provide an understanding of the factors that govern the luminescence efficiencies of platinum(II) complexes as well as to apply these compounds in organic light emitting diodes (OLEDs) and in other devices.[1]

Many cyclometalated platinum complexes have proved to be luminescent in solution at ambient temperature, because [C,N] ligands increase the energies of metal-centered excited states in comparison to analogous [N,N] ligands.[1] In addition, rigidity generally favors luminescence over nonradiative decay pathways, and therefore tridentate [N,N,C], [N,C,N], and [C,N,C] ligands generally based on substituted pyridines and polypyridines may offer an advantage over bidentate [C,N] ligands.[2] Moreover, systematic studies carried out for several of these systems indicate that the emission may be tuned by structural modification of the ligands; in particular, the nature and the position of the substituents might influence the photophysics of the platinum complexes.[1,3]

In spite of the great number of cycloplatinated compounds for which the luminescence properties have been studied so far, those containing aldimine or ketimine ligands have been less explored.[4] In this work we report the preparation and luminescence properties of cyclometalated platinum compounds containing tridentate [C,N,N′] imine ligands with fluoro substituents (compounds 3 and 4 shown in Chart 1). This study should allow us to compare the behavior of these compounds in relation with (a) the size of the [N,N′] chelate ring (five- versus six-membered), (b) the number and position of the fluoro substituents in the ring, and (c) the nature of the ancillary ligands (methyl or chloro) coordinated to the platinum. These effects will also be analyzed in relation to the choice and success of the preparation procedure.

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RESULTS AND DISCUSSION

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84   Two series of potentially tridentate ligands of formula ArCH=N(CH2)2NMe2 and
85   ArCH=N(CH2)3NMe2 (Ar = C6H5, 2-FC6H4, 4-FC6H4, 2,3,4-F3C6H2) derived from N,N-
86   dimethylethylenediamine and N,N-dimethylpropylenediamine, respectively, were used in the present
87   work. As stated above, the ligands were selected in order to compare the results between those derived
88   from propylene or ethylenediamine, as well as to analyze the effect of fluorine substituents. In particular,
89   the position of a single fluoro substituent in an ortho or para position as well as the increased
90   fluorination will be studied.

91   **Synthesis of Compounds [PtCl{Me2N(CH2)xN=CHR}](3a−h).** The syntheses of compounds
92   [PtCl{Me2N(CH2)3N=CHC6H5}] (3e)5 and [PtCl{Me2N(CH2)2N=CHC6H5}] (3f)6 have been
93   previously reported from the corresponding ligands, cis-[PtCl2(dmso)2] as metalating agent, methanol
94   as solvent, and sodium acetate as an external base. However, a systematic comparison of the reactivities
95   of both series of ligands containing either an ethylene or a propylene moiety linking the two nitrogen
96   atoms and different substituents in the aryl ring has not been carried out so far. With this purpose, in this
97   work we planned to follow the general synthetic procedure shown in Scheme 1 for both series of imines.

98   Initially, several reaction conditions were tested for ligand 1a, including either one-pot procedures or
99   prior isolation of the corresponding [N,N′]-chelate complex 2a. As previously reported for similar
100   systems,5−7 the best results were obtained when [N,N′] coordination compounds (compounds 2) were
101   previously isolated and such complexes, when refluxed for several hours in a donor solvent in the
102   presence of sodium acetate, further reacted to yield cycloplatinated derivatives via C−H activation. The
103   best results for the latter step were obtained when an equivalent amount of sodium acetate was used and
104   the reaction time in refluxing methanol was 48−72 h, since the use of larger amounts of added base,
105   prolonged reaction times, or the use of mixtures of toluene and methanol as solvents led to partial
106   decomposition with formation of metallic platinum. Therefore, these optimal reaction conditions were
107   followed in the synthesis of compounds 3, which requires previous isolation of the corresponding
108   compounds 2.

109   The reaction of the imines 1a−g with cis-[PtCl2(dmso)2] in refluxing methanol gave the corresponding
110   coordination compounds [PtCl2{Me2N(CH2)xN=CHAr}] (2). For ligands derived from N,N-
111   dimethylpropanediamine a mixture of two isomers corresponding to the two possible conformations (Z
112   and E) around the C=N bond was obtained. Generally, the Z isomer was the most abundant, or even the
113   only one which was isolated and characterized, as for 2b. However, for ligands derived from N,N-
114   dimethylethylenediamine, the corresponding coordination compounds were isolated exclusively as the
115   less sterically crowded E isomer. The different behavior might arise from the higher flexibility of the
116   six- versus the five-membered [N,N′]-chelate rings, which minimizes the steric crowding around the
117   platinum in the Z isomer. As previously reported,5,8 these isomers display striking differences in their
118   spectral features. In particular, the imine proton of the E isomers is strongly deshielded (δ ca. 9.30−9.60
119   ppm) due to the proximity to platinum and displays lower J(H−Pt) values (48−60 Hz) in comparison to
120   those for the Z isomers (115−120 Hz). In addition, for the Z isomer both the methylene and NMe2
121   protons are nonequivalent. The number of signals observed in the 19F NMR spectra was in all cases
122   consistent with the presence of one or two isomers, as well as with the number of fluorine substituents in
123   the imine. Formation of the [N,N′]-chelate compounds [PtCl{Me2N(CH2)xN=CHAr}] (2) was
124   confirmed by ESI(+) mass spectra and elemental analyses.

125   The tridentate [C,N,N′] cyclometalated compounds 3a−d were obtained from the equimolar reaction of
126   the coordination compounds and sodium acetate in refluxing methanol. The process involves the
127   activation of a C(aryl)−H bond and the formal release of HCl, which is promoted in the presence of a
128   base. For compounds 2c,d, the C−H bond activation should be preceded by an isomerization step from

129   an unreactive E to the adequate Z conformation. In contrast, compounds 2a,b, containing the more
130   flexible propylene moiety, were obtained as a mixture of Z and E conformers (2a) or as the Z conformer
131   exclusively (2b), thus facilitating the cyclometalation process. The yields of the cyclometalation
132   reactions were in all cases moderate; however, slightly higher yields in the range 36−40% were obtained
133   for propylene derivatives 3a,b after 48 h in comparison to those for the corresponding ethylene
134   derivatives 3c,d, for which yields in the range 29−32% were obtained after 72 h. These results confirm
135   that the higher flexibility of the propylene versus the ethylene moieties facilitates the cyclometalation
136   reaction, leading to [C,N,N′]-cycloplatinated compounds. In all cases, 1H NMR spectra confirmed the
137   formation of the expected fused [6,5,6]- or [6,5,5]-tricyclic system. As reported for analogous
138   systems,5,6,8 J(H−Pt) values for the imine proton (141−144 Hz) are higher than those observed for
139   compounds 2. The 19F NMR spectra show only one signal, for which coupling to platinum was only
140   observed for compound 3a. For 3b, 13C NMR and 1H−13C-HSQC spectra were also taken and confirm
141   the cyclometalation process, since only three resonances corresponding to aromatic C−H were observed.
142   All compounds were characterized by ESI(+) mass spectra and elemental analyses, and 3b was also
143   characterized crystallographically.

144   With the aim of obtaining the corresponding tridentate [C,N,N′]-cyclometalated compounds the
145   reactions of the coordination compounds 2g,h with an equimolar amount of sodium acetate in refluxing
146   methanol were also carried out. However, for these ligands the reaction (shown in Scheme 2) was more
147   complex and involved a selective nucleophilic substitution of the fluorine substituent adjacent to the
148   imine group for a methoxy group, leading eventually to the compounds [PtCl{Me2N(CH2)xN=CH(2-
149   OMe,3,4-F2C6H)}] (3g for x = 3 and 3h for x = 2). Selective platinum-catalyzed activation and
150   subsequent functionalization of aryl C−F bonds to produce arylmethyl ethers in a process involving
151   platinum(IV)/platinum(II) species has been reported. 9 The involvement of platinum(IV) species is ruled
152   out in the present case, since previous results indicate that intramolecular C−F bond activation takes
153   place at electron-rich platinum substrates such as [Pt2Me4(μ-SMe2)2] but not at cis- [PtCl2(dmso)2].10
154   On the other hand, ligands 1g,h were recovered unaltered after 72 h of reflux in methanol in the presence
155   of an equimolar amount of sodium acetate. Moreover, the fluoro for methoxy substitution was not
156   observed along the syntheses of compounds 3a−d, for which only one fluoro substituent is present.
157   Therefore, it is likely that the combined effects of coordination of the imine ligand to platinum and the
158   presence of several fluorine substituents are able to activate the fluoroaryl group toward nucleophilic
159   aromatic substitution in a way similar to that for recently reported examples in which acetylenes are
160   used as electron-withdrawing groups promoting nucleophilic aromatic substitution.11 The presence of
161   sodium acetate in the reaction media is also required, since the fluoro for methoxy substitution process
162   was not observed in the preparation of compounds 2g,h. It is interesting to point out that fluorine for
163   alkoxy nucleophilic substitution has been reported as a strategy leading to blue-emitting cyclometalated
164   iridium(III) complexes with increased solubility.12

165   In both cases, the 1H NMR spectra confirmed formation of the [C,N,N′]-cycloplatinated compounds and
166   the J(H−Pt) values for the imine proton are similar to those obtained for compounds 3a−d. Only one
167   resonance corresponding to an aromatic proton was observed, and a doublet at ca. 4 ppm was assigned
168   to the methoxy hydrogen atoms which are coupled to the adjacent fluorine. The 19F NMR spectra show
169   only two signals, whose multiplicities and coupling constants are in good agreement with the proposed
170   structures.13 The characterization of these compounds was completed with ESI(+) mass spectra,
171   elemental analyses, and the determination of the molecular structure of 3g.

172   **Crystal Structures of Compounds 3b,g**. Suitable crystals of compounds 3b,g (Figures 1 and 2,
173   respectively) were grown from dichloromethane−methanol solution. For 3b, the asymmetric unit
174   contains eight molecules (Figures S1 and S2, Supporting Information) that are spaced between 5 and 8
175   Å: i.e., the distances are too long to be able to establish weak intermolecular interactions. The crystal
176   structure of 3g is constituted by two different molecules distributed in antiparallel positions (Figure S3,
177   Supporting Information) which are connected by H bonds between the O atom of the methoxy units and

178 one hydrogen atom of the central methylene of the diamine of a second molecule. The 3D packing of the
179 complex is constituted by different dimers, as shown in the unit cell (Figure S4, Supporting
180 Information).

181 The compounds consist of a fused [6,5,6]-tricyclic system containing an ortho-metalated phenyl group, a
182 five-membered metallacycle and a six-membered chelate ring with two nitrogen atoms coordinated to
183 platinum. The square-planar coordination around the platinum is completed with a chlorine atom. For
184 3g, the molecular structure provides conclusive evidence of the presence of a methoxy group in the
185 position adjacent to the imine moiety, as deduced from NMR spectra. Bond lengths and angles are well
186 within the range of values obtained for analogous compounds.[5−8] The Pt−amine distances are greater
187 than Pt−imine distances in agreement with both the weaker ligating ability of amines for platinum and
188 the greater trans influence of the aryl versus the chloro ligand.[8c] Most bond angles at platinum are close
189 to the ideal value of 90°, and the smallest angle corresponds in each case to the metallacycle (80.3(4)°
190 (3b) and 80.76(15)° (3g)). As previously observed for related compounds,[5] the six-membered chelate
191 ring presents a strong deviation from planarity and the chelate angles N(1)−Pt−N(2) (97.2(4)° (3b) and
192 96.78(13)° (3g)) are in both cases greater than for analogous compounds with a fivemembered chelate
193 ring. In each case, the metallacycle is nearly coplanar with the coordination plane, the dihedral angle
194 between the mean planes being 2.3(4)° for 3b and 3.22(15)° for 3g.

195 **Synthesis of Compounds [PtMe{Me2N(CH2)xNCH=R}](4a−h).** The synthesis of compounds
196 [PtMe{Me2N-(CH2)xN=CHR}] (4a−h) was carried out following the previously reported procedures
197 for compounds 4c,f,h, which consist of the reaction of [Pt2Me4(μ-SMe2)2] with the corresponding
198 imine.[14] The mechanism of these reactions has been thoroughly studied, and it is assumed that prior
199 coordination of the ligand produces [N,N′]-chelate complexes that further react to produce
200 cyclometalated compounds with loss of methane.[14] These compounds have been generally prepared
201 under mild conditions, for instance in acetone at room temperature, and the bidentate imines used so far
202 are derived from N,N-dimethylethylenediamines. In this work, as shown in Scheme 3, the reactions
203 were carried out in refluxing toluene and were completed within 1 h for both imines derived from
204 ethylene and propylenediamines. In this case, no further reaction was observed for the trifluorinated
205 imines 1g,h, which can be related to the greater electron density of the platinum in these compounds, as
206 well as to the absence of methanol in the reaction mixtures. As a whole, this method appear to be a
207 convenient one-pot procedure that does not require previous isolation of the corresponding coordination
208 compounds to give the cyclometalated compounds with good yields. In all cases, 1H NMR spectra
209 confirmed formation of the expected [C,N,N′] cycloplatinated compounds, in which a methyl ligand
210 completes the coordination sphere around the platinum. The methyl ligand, the imine, and the NMe2 are
211 coupled to platinum, and the J(H−Pt) values for the imine proton (ca. 60 Hz) are lower than those
212 obtained for compounds 3, which is consistent with the presence of a methyl instead of a chloro ligand
213 trans to the imine.[8a,b] The 19F NMR spectra are consistent with the proposed structures: in particular,
214 the presence of three signals for 4g,h confirms the presence of the three fluoro atoms.

215 **Absorption and Emission Spectroscopy**. Both absorption and emission spectra have been recorded in
216 aerated dichloromethane solutions, and emission spectra were also recorded in the solid state for
217 cyclometalated platinum compounds 3 and 4. The resulting data are shown in Table 1 with
218 representative absorption and emission spectra shown in Figures 3−6.

219 The absorption spectra of 10−4 M dichloromethane solution of compounds 3 in solution at 298 K show
220 several bands in the UV−visible range with moderate ε values. The lowest energy band in the range
221 376−400 nm with extinction coefficients between 2200 and 5100 M−1 cm−1 is attributable to Pt(5d) →
222 π*(L) metal-to-ligand charge transfer (MLCT) mixed with intraligand (IL) transitions.[15] Compounds 3
223 emit in the visible region at 298 K when excited at the wavelength corresponding in each case to the
224 lowest energy band. The emission spectra of all compounds 3 follow a similar pattern and display three
225 maxima (one displayed as shoulder) in the range 575−700 nm. The observation of vibronically

226 structured bands with progressional spacings at ca. 1200 cm−1, typical of ν(C=C) and ν(C=N) stretching
227 frequencies in the excited state, demonstrates the involvement of ligand character in their emission
228 origin. Solid emission spectra were also recorded upon excitation of the samples at the corresponding
229 lowest energy absorption band. In all cases, the same profile (well vibronically structured band) as
230 recorded in solution is observed (Table 1 and Figures S5 and S6 (Supporting Information)). No
231 excimeric emission bands that usually present broad emission bands were recorded in any case.
232 Emission spectra were also recorded at different concentrations in order to check if possible aggregate
233 formation was obtained in solution. As can be seen in Figure S8 (Supporting Information), the emission
234 profile when going from 1×10^{-4} to 3×10^{-5} M is similar and the contribution of aggregates on the
235 spectra does not seem to be very certain. Nevertheless, it cannot be ruled out definitively, due to the
236 small increase of the longer wavelength emission at higher concentrations. This is in agreement with the
237 fact that no π−π stacking interactions are observed in the crystal packing of the molecules (Figures
238 S1−S4, Supporting Information).

239 In all cases, the excitation spectra match the absorption spectra in solution at room temperature. The
240 large red shift observed for the emission is characteristic of phosphorescence emission, as expected from
241 a triplet state typical for platinum complexes due to strong spin−orbit coupling favored by the well-
242 known heavy-atom effect. This is in agreement with the high luminescence lifetime values estimated on
243 the order of 1 μs when we record the spectra of the complexes in the presence and in the absence of
244 oxygen.

245 Although the differences in emission energies are very small, it was found that the presence of a fluoro
246 substituent in position 2 produces a small red shift (ca. 5 nm) and a blue shift (10−15 nm) for the
247 substituent in position 4 for both series of compounds derived from ethylenediamine (3f,c,d) or from
248 propylenediamine (3e,a,b). The apparently controversial effect of fluoro substituents can be rationalized
249 by taking into account the inductive electron-withdrawing and the mesomeric electron-donating effects
250 of fluorine, which might result in an decreased or an increased electron density on platinum.3
251 Compounds 3g,h, which contain a methoxy group at the 2-position together with fluoro substituents at
252 the 3- and 4- positions, also display a small red shift in comparison with the unsubstituted analogues
253 3e,f. Similar effects in the emission wavelengths due to the presence of fluoro or methoxy substituents
254 have been previously reported.3,16

255 The calculated quantum yields are modest (ca. 10−3) and are in agreement with the fact that the
256 strongest emission is recorded for 3d. For each pair of compounds with the same substituents, the
257 emission is more intense for the compounds derived from ethylenediamine than for those derived from
258 propylenediamine (3c > 3a, 3d > 3b, 3f > 3e, and 3h > 3g). Although the differences are small, this trend
259 is consistent with the fact that the greater rigidity associated with the five- versus the six-membered
260 chelates favors luminescence over nonradiative decay pathways. Attempts to improve the photophysical
261 properties by modifying the [N,C,N] ligand, in particular the size of the chelate rings, have been recently
262 reported.17

263 Studies carried out for compounds 4 indicate absorption spectra similar to those obtained for compounds
264 3, with the lowest energy band in the range 391−415 nm. The lower energy of these bands in
265 comparison to those of compounds 3 (in the range 376−400 nm) can be related to the higher electron
266 density at the metal center expected for compounds 4. Compounds 4, when excited at the lowest energy
267 absorption band were nearly nonemissive in solution at room temperature. This could be due to the
268 presence of a high-energy oscillator (C−H) in their first coordination sphere, which could provide an
269 efficient pathway for multiphonon relaxation. On the other hand, at 77 K deactivation processes are
270 minimized and emission was observed. The obtained spectra were similar to those corresponding to
271 compounds 3. In particular, for both series of ligands derived from either ethylene or propylenediamine,
272 a small red shift is observed when a fluoro substituent is present in position 2 (4c versus 4f or 4a versus
273 4e), while the presence of a fluoro substituent in position 4 produces a small blue shift (4d versus 4f or

274   4b versus 4e). The most strongly emissive compound of this series is 4b, as shown in Figure 6, where
275   the emission spectra of the complexes are normalized with respect to 4b.

276   Finally, a comparison of compounds 3 and 4 which only differ in the ancillary ligand (chloro versus
277   methyl) suggests that the chloro derivatives are best suited for photophysical properties, since they are
278   luminescent in solution at room temperature while methyl analogues only display this behaviour at low
279   temperature. This result supports the fact that the identity of the remaining ligand in tridentate
280   cycloplatinated compounds is also crucial in determining whether or not the compounds are emissive.[1b]
281   Although C-donor ligands such as cyanide and acetylide which are able to increase the ligand field
282   strength have been shown to give good results,[1b] the methyl ligand is not such a good choice since, as
283   stated above, it can provide an efficient pathway for multiphonon relaxation.

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CONCLUSIONS

The cyclometalated compounds [PtMe{Me2N(CH2)xN=CHR}] (4a−h) with R = C6H4, 2-FC6H3, 4-FC6H3, 2,3,4-F3C6H were easily obtained from the reaction of [Pt2Me4(μ-SMe2)2] with the corresponding ligands derived from either N,N-dimethylpropylene or N,N-dimethylethylenediamine. In contrast, the synthesis of the corresponding chloro analogues [PtCl{Me2N(CH2)xN=CHR}] (3a−h), carried out from the corresponding precursors [PtCl2{Me2N(CH2)xN=CHAr}] (2), was found to be more favored for six-membered than for five-membered [N,N′]-chelates. This result is related to the fact that for the latter the bidentate ligand adopts the E conformation and consequently an E−Z isomerization should precede the cyclometalation step. In addition, for the ligands 2,3,4-F3C6H2CHN(CH2)xNMe2 an unexpected nucleophilic substitution of a fluoro for a methoxy substituent took place along the cyclometalation process, leading to the compounds [PtCl{Me2N(CH2)xN=CH(2-OMe,3,4-F2C6H)}] (3g for x = 3 and 3h for x = 2). Further work aimed at analyzing the scope of this process is currently in progress.

Cycloplatinated compounds 3a−g are luminescent in the solid state and in solution at room temperature, and those containing a [6,5,5]-tricyclic system display higher quantum yields in comparison to those containing a [6,5,6]-tricyclic system. Cycloplatinated compounds 4a−g are luminescent in the solid state and in solution at low temperature. For both series of cyclometalated platinum compounds, the emission energies can be tuned by varying the aryl substituents.

EXPERIMENTAL SECTION

309

310 **General Considerations.** Microanalyses were performed at the Centres Cientifı́cs i Tecnoloġics
311 (Universitat de Barcelona).18 Mass spectra were performed at the Unitat d'Espectrometria de Masses
312 (Universitat de Barcelona) in a LC/MSD-TOF spectrometer using 1/1 H2O/CH3CN to introduce the
313 sample (ESI-MS) or in a ThermoFinnigan TRACE DSQ spectrometer (CI-MS). NMR spectra were
314 performed at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using a Mercury-400 (1H,
315 400 MHz; 1H−13C HSQC; 13C, 100.6 MHz; 19F, 376.5 MHz) spectrometer and referenced to SiMe4
316 (1H, 13C) or CFCl3 (19F). δ values are given in ppm and J values in Hz. Abbreviations used: s, singlet;
317 d, doublet; t, triplet; q, quadruplet; qi, quintuplet; m, multiplet; br, broad. UV−visible spectra of CH2Cl2
318 solutions of compounds 1, 3, and 4 were recorded at 298 K with a Cary 100 scan 388 Varian UV
319 spectrometer, and the emission and excitation spectra of aerated solutions of compounds 3a−h and 4a−h
320 were obtained on a Horiba Jobin-Yvon SPEX Nanolog-TM spectrofluorimeter at 298 K or at 77 K.
321 Deoxygenated solutions of the compounds have been also used for the estimation of luminescence
322 lifetimes. This experiments have been done bubbling N2(g) previously saturated with dichloromethane
323 in order to minimize the concentration of the sample. Total luminescence quantum yields were measured
324 at 298 K relative to [Ru(bipy)3]Cl2 in water (ϕ = 0.042) as a standard reference.19 The corresponding
325 absorption of the complexes used for these measurements is lower than 0.1.

326 Numbering scheme for NMR data:

327
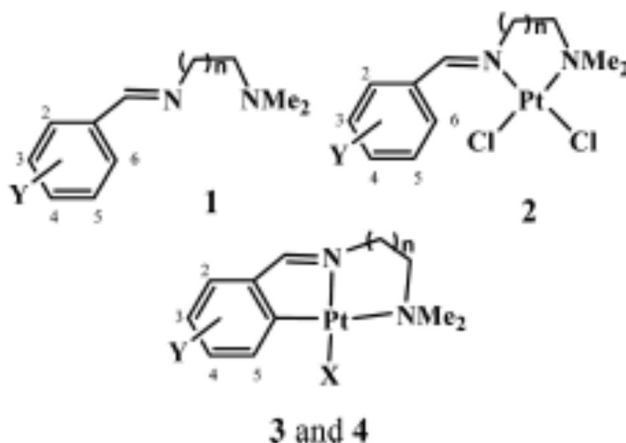
3 and 4

328

329

330 **Preparation of the Complexes**. The compounds cis-[PtCl2(dmso)2]20 and [Pt2Me4(μ-SMe2)2],21
331 ligands 1c,f,h13 and 1e,5 and compounds 2e and 3e,5 2f and 3f,6 and 4c,f,h14 were prepared as reported
332 elsewhere.

333 2-FC6H4CH⊕N(CH2)3NMe2 (1a). This compound was obtained from the reaction of 0.500 g (4.9
334 mmol) of 3-dimethylamino-1-propanamine with 0.610 g (4.9 mmol) of 2-fluorobenzaldehyde in 20 mL
335 of toluene. The reaction mixture was stirred at room temperature for 2 h, sodium sulfate was added and
336 filtered off, and the solvent was removed under vacuum to give a yellow oil. Yield: 0.969 g (95%). 1H
337 NMR (400 MHz, CDCl3): δ 8.25 [s, 1H, CHN]; 7.96 [dd, 1H, 3J(H−H) = 2.0, 3J(H−H) = 7.6, H6]; 7.38
338 [m, 1H, H5]; 7.17 [t, 1H, 3J(H−H) = 7.6, H4]; 7.07 [ddd, 1H, 4J(H−H) = 1.2, 3J(H−H) = 8.4, 3J(F−H) =
339 10.4, H3]; 3.68 [td, 2H, 4J(H−H) = 1.6, 3J(H−H) = 7.2, NCH2]; 2.37 [t, 2H, 3J(H−H) = 7.2,
340 CH2NMe2]; 2.26 [s, 6H, NMe2]; 1.89 [qi, 2H, 3J(H−H) = 7.0, CH2CH2CH2]. 19F NMR (376,5 MHz,
341 CDCl3): δ −122.09 [m, 1F]. CI-MS: 208.9 [M + H]+ .

4-FC6H4CH=N(CH2)3NMe2 (1b). This compound was prepared as a yellow oil by following the same method from 0.510 g (5.0 mmol) of 3-dimethylamino-1-propanamine and 0.620 g (5.0 mmol) of 4-fluorobenzaldehyde. Yield: 0.912 g (88%). 1H NMR (400 MHz, CDCl3): δ 8.25 [s, 1H, CHN]; 7.72 [m, 2H, H2,6]; 7.09 [dd, 2H, 4J(H−H) = 2.4, 3J(F−H) = 8.8, H3, 5]; 3.63 [td, 2H, 4J(H−H) = 1.2, 3J(H−H) = 7.2, NCH2]; 2.36 [t, 2H, 3J(H−H) = 7.2, CH2NMe2]; 2.24 [s, 6H, NMe2]; 1.87 [qi, 2H, 3J(H−H) = 7.2, CH2CH2CH2]. 19F NMR (376.5 MHz, CDCl3): δ −109.92 [m, 1F]. CI-MS: 208.9 [M + H]+.

4-FC6H4CH=N(CH2)2NMe2 (1d). This compound was prepared as a pale yellow oil by following the same method from 0.580 g (6.3 mmol) of 2-dimethylamino-1-ethanamine and 0.880 g (7.1 mmol) of 4-fluorobenzaldehyde. Yield: 1.119 g (92%). 1H NMR (400 MHz, CDCl3): δ 8.26 [s, 1H, CHN]; 7.71 [dd, 2H, 4J(F−H) = 5.6, 3J(H−H) = 8.8, H2,6]; 7.06 [t, 2H, 3J(H−F) = 3J(H−H) = 8.8, H3,5]; 3.71 [t, 2H, 3J(H−H) = 6.8, NCH2]; 2.62 [t, 2H, 3J(H−H) = 6.8, CH2NMe2]; 2.30 [s, 6H, NMe2]. 19F NMR (376,5 MHz, CDCl3): δ −109.79 [m, 1F]. CI-MS: 194.9 [M + H]+.

2,3,4-F3C6H2CH=N(CH2)3NMe2 (1g). This compound was prepared as a yellow oil following the same method from 0.638 g (6.24 mmol) of 3-dimethylamino-1-propanamine and 1.0 g (6.24 mmol) of 2,3,4-trifluorobenzaldehyde. Yield: 0.838 g (55%). 1H NMR (400 MHz, CDCl3): δ 8.49 [s, 1H, CHN]; 7.71 [dd, 1H, 3J(H−H) = 8.0, 4J(H−F) = 4.0, H6]; 7.01 [m, 1H, H5]; 3.67 [t, 2H, 3J(H−H) = 6.8, NCH2]; 2.34 [t, 2H, 3J(H−H) = 7.2, CH2NMe2]; 2.24 [s, 6H, NMe2]; 1.86 [qi, 2H, 3J (H−H) = 7.2, CH2CH2CH2]. 19F NMR (376,5 MHz, CDCl3): δ −131.08 [m, F2]; - 143.07 [dtd, 3J(F−F) = 18.8, 4J(F−F) = 3J(H−F) = 7.5, 4J(F−H) = 3.8, F4]; −160.90 [tdd, 3J(F−F) = 18.8, 4J(F−H) = 7.5, 5J(F−H) = 2.2, F3]. CI-MS: 244.7 [M + H]+.

[PtCl2{Me2N(CH2)3N=CH(2-FC6H4)}] (2a). A mixture formed by 0.303 g (0.72 mmol) of cis-[PtCl2(dmso)2] and 0.153 g (0.73 mmol) of imine 1a was treated with dry methanol and heated at 65 °C for 4 h with continuous stirring. The mixture was filtered; the solvent was evaporated to half volume, allowing crystallization at room temperature. Yield (white solid; mixture of E and Z isomers): 0.223 g (65%). 1H NMR (400 MHz, CDCl3): Z isomer δ 10.96 [t, 1H, 3J(H−H) = 8.0, H6]; 8.89 [s, 1H, 3J(Pt−H) = 118.4, CHN]; 7.68 [m, 1H, H4]; 7.46 [t, 1H, 3J(H−H) = 8.0, H5]; {5.00 [m, 1H]; 4.21 [m, 1H], CH2N}; 3.20 [m, 1H, CH2NMe2]; {2.99 [s, 3H]; 2.86 [s, 3H], NMe2}; {2.41 [m, 1H]; 1.97 [m, 1H], CH2CH2CH2}. 1H NMR (400 MHz, CDCl3): E isomer δ 9.35 [s, 1H, 3J(Pt−H) = 60.0, CHN]; 7.56 [m, 1H, H4]; 7.37 [t, 1H, 3J(H−H) = 7.2, H5]; 4.02 [t, 2H, 3J(H−H) = 6.8, CH2N]; 3.01 [s, 6H, NMe2]; 2.72 [m, 2H, CH2NMe2]; 2.21 [m, 2H, CH2CH2CH2]. 19F NMR (376.5 MHz, CDCl3): δ −110.7 [m, Z isomer]; − 115.75 [m, E isomer]. ESI (+)-MS: 492.07 [M + NH4]+ ; 439.07 [M − Cl]+; 497.03 [M + Na]+. Anal. Found (calcd for C12H17Cl2FN2Pt): C, 29.7 (30.39); H, 3.5 (3.62); N, 5.7 (5.92).

[PtCl2{Me2N(CH2)3N=CH(4-FC6H4)}] (2b). This compound was prepared by following the same procedure from 0.302 g (0.72 mmol) of cis-[PtCl2(dmso)2] and 0.153 g (0.73 mmol) of imine 1b. Yield (offwhite solid; Z isomer): 0.165 g (49%). 1H NMR (400 MHz, CDCl3): δ 9.34 [m, 2H, H2,6]; 8.47 [s, 1H, 3J(Pt−H) = 115.6, CHN]; 7.27 [t, 2H, 3J(H−F) = 3J(H−F) = 8.0, H3,5]; {4.93 [m, 1H]; 4.13 [m, 1H], CH2N}; {3.20 [m, 1H]; 2.72 [m, 1H], CH2NMe2}; {2.97 [s, 3H]; 2.84 [s, 3H], NMe2}; {2.50 [m, 1H]; 1.97 [m, 1H], CH2CH2CH2}. 19F NMR (376.5 MHz, CDCl3): δ −101.64 [m]. ESI (+)-MS: 492.08 [M + NH4]+ ; 971.01 [2 M + Na]+. Anal. Found (calcd for C12H17Cl2FN2Pt): C, 31.1 (30.39); H, 3.6 (3.62); N, 5.5 (5.92).

[PtCl2{Me2N(CH2)2N=CH(2-FC6H4)}] (2c). This compound was prepared by following the same procedure from 0.301 g (0.71 mmol) of cis-[PtCl2(dmso)2] and 0.160 g (0.82 mmol) of imine 1c. Yield (yellow solid; E isomer): 0.149 g (45%). 1H NMR (400 MHz, CDCl3): δ 9.60 [s, 1H, 3J(Pt−H) = 57.6, CHN]; 7.60 [m, 1H, H4]; 7.44 [d, 1H, 3J(H−H) = 7.6, H6]; 7.30 [td, 1H, 4J(H−H) = 1.2, 3J(H−H) = 7.6, H5]; 7.19 [t, 1H, 3J(F−H) = 9.2, H3]; 3.82 [t, 2H, 3J(H−H) = 6.0, CH2N]; 3.12 [s, 6H, 3J(Pt−H) = 33.2, NMe2]; 2.67 [t, 2H, 3J(H−H) = 6.0, CH2NMe2]. 19F NMR (376.5 MHz, CDCl3): δ −108.32 [m]. ESI

389 (+)-MS: 478.06 [M + NH4]+ ; 483.01 [M + Na]+ . Anal. Found (calcd) for C11H15Cl2FN2Pt): C 28.4
390 (28.71); H 2.9 (3.29); N 6.3 (6.10).

391 [PtCl2{Me2N(CH2)2N=CH(4-FC6H4)}] (2d). This compound was prepared by following the same
392 procedure from 0.302 g (0.71 mmol) of cis-[PtCl2(dmso)2] and 0.150 g (0.82 mmol) of imine 1d. Yield
393 (yellow solid; E isomer): 0.131 g (43%). 1H NMR (400 MHz, CDCl3): δ 9.47 [s, 1H, 3J(Pt−H) = 54.4,
394 CHN]; 7.58 [dd, 2H, 4J(F−H) = 5.6, 3J(H−H) = 8.0, H2,6]; 7.19 [t, 2H, 3J(H−F) = 3J(H−H) = 8.4,
395 H3,5]; 4.04 [t, 2H, 3J(H−H) = 6.0, CH2N]; 3.13 [s, 6H, NMe2]; 2.69 [t, 2H, 3J(H−H) = 6.0, H7]. 19F-
396 NMR (376,5 MHz, CDCl3): δ −104.40 [m]. ESI (+)-MS: 478.06 [M + NH4]+ ; 483.02 [M + Na]+.
397 Anal. Found18 (calcd for C11H15Cl2FN2Pt): C, 28.5 (28.71); H, 3.1 (3.29); N, 6.1 (6.10).

398 [PtCl2{Me2N(CH2)3N=CH(2,3,4-F3C6H)}] (2g). This compound was prepared by following the same
399 procedure from 0.319 g (0.71 mmol) of cis-[PtCl2(dmso)2] and 0.173 g (0.71 mmol) of imine 1g. Yield
400 (offwhite solid; mixture of E and Z isomers): 0.265 g (73%). 1H NMR (400 MHz, CDCl3): Z isomer δ
401 10.75 [m, 1H]; 9.04 [s, 1H, 3J(Pt−H) = 120.0, CHN]; 7.29 [m, 1H]; {5.00 [m, 1H]; 4.26 [ddd, 1H,
402 J(H−H) = 11.2, 6.8, 2.0], CH2N}; {2.97 [s, 3H]; 2.86 [s, 3H], NMe2}; 2.73 [m, 2H,CH2NMe2]; {2.48
403 [m, 1H]; 2.01 [m, 1H], CH2CH2CH2}. 1H NMR (400 MHz, CDCl3): E isomer δ 9.33 [s, 1H, 3J(Pt−H)
404 = 56.0, CHN]; 7.18−7.14 [m, 2H]; 4.03 [t, 2H, 3J(H−H) = 6.8, CH2N]; 3.00 [s, 6H, NMe2]; 2.73 [m,
405 2H, CH2NMe2]; 2.24 [m, 2H, CH2CH2CH2]. 19F NMR (376,5 MHz, CDCl3): Z isomer δ −122.53 [m,
406 1F, F2]; − 135.92 [dddd, 1F, 3J(F−F) = 22.6, 4J(F−F) = 15.2, 3J(F−H) = 7.6, 3J(F−H) = 3.8, F4]; −
407 158.97 [tdd, 1F, 3J(F−F) = 22.5, 4J(F−H) = 7.6, 5J(F−H) = 3.8, F3]. 19F NMR (376,5 MHz, CDCl3): E
408 isomer: δ −125.98 [m, 1F]; − 130.76 [m, 1F]; − 157.03 [tdd, 1F, 3J(F−F) = 18.8, 4J(F−H) = 7.6,
409 5J(F−H) = 3.8, F3]. ESI (+)-MS: 528.06 [M + NH4]+; 475.05 [M − Cl]. Anal. Found (calcd) for
410 C12H15Cl2F3N2Pt: C, 28.0 (28.29); H, 3.0 (2.97); N, 5.7 (5.50).

411 [PtCl2{Me2N(CH2)2N=CH(2,3,4-F3C6H)}] (2h). This compound was prepared by following the same
412 procedure from 0.300 g (0.71 mmol) of cis-[PtCl2(dmso)2] and 0.163 g (0.71 mmol) of imine 1h. Yield
413 (yellow solid; E isomer): 0.250 g (71%). 1H NMR (400 MHz, CDCl3): δ 9.59 [s, 1H, 3J(Pt−H) = 48.0,
414 CHN]; 7.34 [m, 1H]; 7.16 [m, 1H]; 3.87 [t, 2H, 3J(H−H) = 6.0, CH2N]; 3.13 [s, 6H, NMe2]; 2.71 [t, 2H,
415 3J(H−H) = 6.0, H7]. 19F NMR (376,5 MHz, CDCl3): δ −125.34 [dddd, 1F, 3J(F−F) = 18.8, 4J(F−F) =
416 15.0, 3J(F−H) = 7.5, 4J(F−H) = 3.8, F4]; − 128.91 [m, 1F, F2]; − 156.80 [tdd, 1F, 3J(F−F) = 18.8,
417 4J(F−H) = 7.5, 5J(F−H) = 3.8, F3]. ESI (+)-MS: 514.04 [M + NH4]+. Anal. Found (calcd for
418 C11H13Cl2F3N2Pt): C, 26.0 (26.66); H, 3.2 (2.65); N, 5.3 (5.66).

419 [PtCl{Me2N(CH2)3N=CH(2-FC6H3)}] (3a). This compound was obtained using method 1: a mixture
420 of 0.250 g (0.59 mmol) of cis-[PtCl2(dmso)2], 0.128 g (0.61 mmol) of imine 1a, and 0.050 g (0.61
421 mmol) of sodium acetate in 20 mL of dry methanol was refluxed for 48 h. Upon evaporation of the
422 solvent to 10 mL, small amounts of compound 2a and metallic platinum were filtered off, and the
423 solution was kept at 5 °C until crystallization was completed. The solid was recrystallized in CH2Cl2/
424 MeOH to produce orange crystals. Yield: 22 mg (9%). Alternatively, compound 3a was prepared using
425 method 2: a mixture of 0.150 g (0.316 mmol) of compound 2a and 0.026 g (0.316 mmol) of sodium
426 acetate in 20 mL of dry methanol was heated under reflux for 48 h, and the solvent was evaporated to
427 produce an oily residue that was extracted with 5 mL of CH2Cl2. Methanol was added, and the solution
428 was kept at 5 °C until crystallization was completed. Yield (orange solid): 60 mg (43.3%). 1H NMR
429 (400 MHz, CDCl3): δ 8.67 [t, 1H, 4J(H−H) = 1.6, 3J(Pt−H) = 142.4, CHN]; 7.80 [d, 1H, 3J(H−H) = 8.0,
430 3J(H−Pt) = 40.0, H5]; 7.20 [m, 1H, H4]; 6.64 [ddd, 1H, 4J(H−H) = 0.8, 3J(H−H) = 8.0, 3J(F−H) = 10.0,
431 H3]; 3.92 [m, 2H, NCH2]; 2.86 [m, 2H, CH2NMe2]; 2.85 [s, 6H, NMe2]; 2.04 [qi, 2H, 3J(H−H) = 5.2,
432 CH2CH2CH2]. 19F NMR (376.5 MHz, CDCl3): δ − 115.00 [dd, 3J(F−H) = 9.8, 4J(F−H) = 6.0,
433 4J(Pt−F) = 56.5]. ESI (+)-MS: 438.08 [M + H]+ ; 461.06 [M + Na]+. Anal. Found18 (calcd for
434 C12H16ClFN2Pt): C, 33.1 (32.92); H, 3.7 (3.68); N, 6.1 (6.40).

435

436 [PtCl{Me2N(CH2)3N=CH(4-FC6H3)}] (3b). This compound was prepared by following method 2 from
437 0.150 g of 2b and an equimolar amount of sodium acetate. Yield (orange solid): 50 mg (36.0%). 1H
438 NMR (400 MHz, CDCl3): δ 8.32 [t, 1H, 4J(H−H) = 1.6, 3J(Pt−H) = 141.6, CHN]; 7.72 [dd, 1H,
439 3J(H−Pt) = 40.0, 3J(F−H) = 10.0, 4J(H− H) = 2.4, H5]; 7.24 [dd, 1H, 3J(H−H) = 8.0, 4J(H−F) = 4.0,
440 H2]; 6.70 [td, 1H, 3J(F−H) = 3J(H−H) = 8.5, 4J(H−H) = 2.4, H3]; 3.86 [m, 3J(H−Pt) = 36.0, 2H,
441 NCH2]; 2.85 [m, 8H, NMe2 + CH2NMe2]; 2.02 [qi, 2H, 3J(H−H) = 5.3, CH2CH2CH2]. 19F NMR
442 (376.5 MHz, CDCl3): δ −104.07 [m, 1F]. 13C NMR (100.6 MHz, CDCl3): δ 27.23 [3J(C−Pt) = 31.0,
443 CH2CH2CH2]; 50.19 [NMe2]; 57.50 [2J(C−Pt) = 38.0, NCH2]; 64.12 [CH2NMe2]; 110.37 [d, 2J(C−F)
444 = 24.1, C3]; 121.17 [d, 2J(C−F) = 20.1, C5]; 129.01 [d, 3J(C−F) = 10.1, C2]; 141.00 [d, 4J(C−F) = 2.0,
445 C1]; 146.00 [d, 3J(C−F) = 7.0, C6]; 163.54 [d, 1J(C−F) = 257.5, C4]; 175.13 [2J(C−Pt) = 96.6, CHN].
446 ESI (+)-MS: 439.07 [M + H]+ ; 456.10 [M + NH4]+ . Anal. Found18 (calcd for C12H16ClFN2Pt): C,
447 32.0 (32.92); H, 3.7 (3.68); N, 6.3 (6.40).

448 [PtCl{Me2N(CH2)2N=CH(2-FC6H3)}] (3c). This compound was prepared by following method 2 from
449 0.150 g of 2c and an equimolar amount of sodium acetate and increasing the reaction time to 72 h. Yield
450 (orange solid): 44 mg (32%). 1H NMR (400 MHz, CDCl3): δ 8.62 [t, 1H, 4J(H−H) = 1.2, 3J(Pt−H) =
451 144.4, CHN]; 7.29 [m, 1H, H3]; 7.23 [t, 3J(H−H) = 7.8, 1H, H4]; 6.47 [d, 1H, 3J(H−H) = 8.1, H5]; 4.03
452 [td, 2H, 3J(H−H) = 6.0, 4J(H−H) = 1.2, 3J(H−Pt) = 34.4, NCH2]; 3.10 [t, 2H, 3J(H−H) = 6.0,
453 CH2NMe2]; 2.89 [s, 3J(H−Pt) = 14.8, 6H, NMe2]. 19F NMR (376.5 MHz, CDCl3): δ −108.14 [m, 1F].
454 ESI (+)-MS: 423.06 [M + H]+. Anal. Found18 (calcd for C11H14ClFN2Pt): C, 31.9 (31.20); H, 4.0
455 (3.33); N, 6.1 (6.62).

456 [PtCl{Me2N(CH2)2N=CH(4-FC6H3)}] (3d). This compound was prepared by following method 2 from
457 0.150 g of 2d and the equimolar amount of sodium acetate and increasing the reaction time to 72 h.
458 Yield (orange solid): 40 mg (29%). 1H NMR (400 MHz, CDCl3): δ 8.26 [s, 1H, 3J(Pt−H) = 141.2,
459 CHN]; 7.41 [dd, 1H, 3J(F−H) = 9.5, 4J(H−H) = 2.8, 3J(H−Pt) = 50.8, H5]; 7.24 [dd, 1H, 3J(H−H) = 8.0,
460 4J(H−F) = 5.6, H2]; 6.69 [td, 1H, 3J(F−H) = 3J(H−H) = 8.8, 4J(H−H) = 2.8, H3]; 4.06 [t, 2H, 3J(H−H)
461 = 6.0, NCH2]; 3.11 [t, 2H, 3J(H−H) = 6.0, CH2NMe2]; 2.90 [s, 6H, NMe2]. 19F NMR (376.5 MHz,
462 CDCl3): δ −102.92 [m, 1F]. ESI (+)-MS: 442.08 [M + NH4]+. Anal. Found (calcd for
463 C11H14ClFN2Pt): C, 30.7 (31.20); H, 3.4 (3.33); N, 6.7 (6.62).

464 [PtCl{Me2N(CH2)3N=CH(2-OMe,3,4-F2C6H)}] (3g). This compound was prepared following method
465 2 from 0.150 g of 2g and an equimolar amount of sodium acetate and increasing the reaction time to 72
466 h. Yield (orange solid): 40 mg (28%). 1H NMR (400 MHz, CDCl3): δ 8.59 [s, 1H, 3J(Pt−H) = 144.0,
467 CHN]; 7.48 [dd, 1H, 3J(F−H) = 11.5, 4J(H−F) = 7.5, H5]; 4.01 [d, 3H, 5J(H−F) = 4.0, OMe]; 3.86 [t,
468 2H, 3J(H−H) = 4.0, NCH2]; 2.83 [m, 8H, NMe2 + CH2NMe2]; 2.01 [m, 2H, CH2CH2CH2]. 19F NMR
469 (376.5 MHz, CDCl3): δ −127.20 [dd, 1F, 3J(F−F) = 18.8, 3J(H−F) = 11.3, 4J(H−Pt) = 45.2, F4]; −
470 163.15 [ddq, 1F, 3J(F−F) = 18.8, 4J(H−F) = 7.5, 5J(H−F) = 3.8, F3]. HRESI(+)- MS: m/z 486.0705,
471 calcd for C13H18F2ClN2OPt [M + H]+ 486.0718; 450.0937, calcd for C13H17F2N2OPt [M − Cl]+
472 450.0951. Anal. Found (calcd for C13H17F2ClN2OPt): C, 31.7 (32.16); H, 3.5 (3.53); N, 5.6 (5.77).

473 [PtCl{Me2N(CH2)2N=CH(2-OMe,3,4-F2C6H)}] (3h). This compound was prepared by following
474 method 2 from 0.150 g of 2h and an equimolar amount of sodium acetate and increasing the reaction
475 time to 72 h. Yield (orange solid): 42 mg (29%). 1H NMR (400 MHz, CDCl3): δ 8.56 [s, 1H, 3J(Pt−H)
476 = 140.0, CHN]; 7.17 [dd, 1H, 3J(F−H) = 11.5, 4J(H−F) = 7.5, H5]; 4.06 [t, 2H, 3J(H−H) = 6.0, NCH2];
477 4.02 [d, 3H, 5J(H−F) = 3.2, OMe]; 3.01 [t, 2H, 3J(H−H) = 6.0, CH2NMe2]; 2.89 [s, 6H, 3J(Pt−H) =
478 15.2, NMe2]. 19F NMR (376.5 MHz, CDCl3): δ −126.14 [dd, 1F, 3J(F−F) = 18.8, 3J(H−F) = 12.0, F4];
479 − 163.00 [ddq, 1F, 3J(F−F) = 18.8, 4J(H−F) = 7.5, 5J(H−F) = 3.8, F3]. ESI (+)-MS: 472.05 [M + H]+.
480 Anal. Found (calcd for C12H15F2ClN2OPt): C, 30.4 (30.57); H, 3.4 (3.21); N, 5.8 (5.94).

481 [PtMe{Me2N(CH2)3N=CH(2-FC6H3)}] (4a). This compound was obtained using the following
482 procedure: 0.100 g (0.17 mmol) of [Pt2Me4(μ-SMe2)2] and 0.072 g (0.34 mmol) of imine 1a were
483 dissolved in 20 mL of toluene, and the obtained solution was refluxed for 1 h. The solvent was removed,

484 and the residue was treated with diethyl ether to give a red solid. Yield: 115 mg (79%). 1H NMR (400
485 MHz, CDCl3): δ 8.91 [s, 1H, 3J(Pt−H) = 60.4, CHN]; 7.44 [d, 1H, 3J(Pt−H) = 64.0, 3J(H−H) = 8.0,
486 H5]; 7.17 [td, 1H, 3J(H−H) = 8.0, 4J(H−F) = 6.4, H4]; 6.61 [ddd, 1H, 3J(F−H) = 10.4, 3J(H−H) = 8.0,
487 4J(H−H) = 0.8, H3]; 3.89 [m, 2H, NCH2]; 2.91 [m, 2H, CH2NMe2]; 2.73 [s, 6H, 3J(Pt−H) = 24.0,
488 NMe2]; 2.03 [qi, 2H, 3J(H−H) = 5.6, CH2CH2CH2]; 1.02 [s, 3H, 2J(Pt−H) = 80.0, Me-Pt]. 19F NMR
489 (376.5 MHz, CDCl3): δ −117.53 [dd, 1F, 3J(F−H) = 11.3, 4J(F−H) = 7.5, 4J(Pt−F) = 56.5]. ESI (+)-MS:
490 443.12 [M − H + CH3CN]+. Anal. Found (calcd for C13H19FN2Pt): C, 37.8 (37.41); H, 4.8 (4.59); N,
491 6.3 (6.71).

492 [PtMe{Me2N(CH2)3N=CH(4-FC6H3)}] (4b). This compound was obtained by using the same
493 procedure from 0.100 g (0.17 mmol) of [Pt2Me4(μ-SMe2)2] and 0.078 g (0.35 mmol) of imine 1b.
494 Yield (red solid): 105 mg (72%). 1H NMR (400 MHz, d6-acetone): δ 8.66 [s, 1H, 3J(Pt−H) = 62.8,
495 CHN]; 7.32 [m, 1H, H2]; 7.21 [dd, 1H, 3J(H−F) = 11.2, 4J(H−H) = 2.5, 3J(Pt−H) = 35.6, H5]; 6.60
496 [ddd, 1H, 3J(F−H) = 9.1, 3J(H−H) = 8.0, 4J(H−H) = 2.0, H3]; 3.85 [t, 2H, J(H−H) = 5.0, NCH2]; 2.87
497 [m, 2H, CH2NMe2]; 2.66 [s, 6H, 3J(Pt−H) = 23.3, NMe2]; 1.99 [m, 2H, CH2CH2CH2]; 0.81 [s, 3H,
498 2J(Pt−H) = 81.7, Me-Pt]. 19F-NMR (376.5 MHz, CDCl3): δ −107.58 [ddd, 1F, 3J(F−H) = 11.3,
499 3J(F−H) = 7.5, 4J(F−H) = 3.7, 4J(F−Pt) = 71.5]. ESI (+)-MS: 443.12 [M − H + CH3CN]+. Anal. Found
500 (calcd for C13H19FN2Pt·2H2O): C, 34.5 (34.44); H, 4.8 (5.11); N, 6.0 (6.17).

501 [PtMe{Me2N(CH2)2N=CH(4-FC6H3)}] (4d). This compound was obtained by using the same
502 procedure from 0.100 g (0.17 mmol) of [Pt2Me4(μ-SMe2)2] and 0.068 g (0.35 mmol) of imine 1d.
503 Yield (red solid): 109 mg (77%). 1H NMR (400 MHz, d6-acetone): δ 8.71 [s, 1H, 3J(Pt−H) = 61.0,
504 CHN]; 7.30 [dd, 3J(H−H) = 8.0, 4J(H−F) = 6.0, 4J(H−Pt) = 27.0, 1H, H2]; 7.10 [dd, 1H, 3J(H−F) =
505 10.4, 4J(H−H) = 2.6, 3J(Pt−H) = 85.0, H5]; 6.57 [ddd, 1H, 3J(F−H) = 9.2, 3J(H−H) = 8.0, 4J(H−H) =
506 2.6, H3]; 4.11 [t, 2H, 3J(H−H) = 6.0, NCH2]; 3.18 [t, 2H, 3J(H−H) = 6.0, CH2NMe2]; 2.77 [s, 6H,
507 3J(Pt−H) = 21.0, NMe2]; 0.77 [s, 3H, 2J(Pt−H) = 79.0, Me-Pt]. 19F NMR (376.5 MHz, CDCl3): δ
508 −106.64 [td, 1F, 3J(F−H) = 9.5, 4J(F−H) = 5.9, 4J(F−Pt) = 88.0]. ESI (+)-MS: 429.10 [M - H +
509 CH3CN]+; 401.09 [M - Me + CH3CN]+. Anal. Found18 (calcd for C12H17FN2Pt): C, 34.5 (35.72); H,
510 4.2 (4.25); N, 6.7 (6.95).

511 [PtMe{Me2N(CH2)3N=CHC6H4}] (4e). This compound was obtained by using the same procedure
512 from 0.100 g (0.17 mmol) of [Pt2Me4(μ-SMe2)2] and 0.065 g (0.35 mmol) of imine 1e. Yield (red
513 solid): 95 mg (69%). 1H NMR (400 MHz, d6-acetone): δ 8.49 [s, 1H, 3J(Pt−H) = 60.0, CHN]; 7.61 [d,
514 3J(H−H) = 7.6, 3J(H−Pt) = 64.0, 1H, H5]; 7.20 [m, 1H]; 7.07 [t, 1H, 3J(H−H) = 8.2, H4]; 6.88 [t, 1H,
515 3J(H−H) = 7.4, H3]; 3.78 [t, 2H, 3J(H−H) = 4.8, NCH2]; 2.84 [m, 2H, CH2NMe2]; 2.66 [s, 6H,
516 3J(Pt−H) = 22.4, NMe2]; 1.95 [qi, 2H, 3J(H−H) = 5.5, CH2CH2CH2]; 0.93 [s, 3H, 2J(Pt−H) = 81.0,
517 Me-Pt]. ESI (+)-MS: 425.13 [M − H + CH3CN]+; 383.10 [M − Me]+. Anal. Found (calcd for
518 C13H20N2Pt·H2O): C, 37.1 (37.41); H, 5.0 (5.31); N, 6.1 (6.71).

519 [PtMe{Me2N(CH2)3N=CH(2,3,4-F3C6H)}] (4g). This compound was obtained by using the same
520 procedure from 0.100 g (0.17 mmol) of [Pt2Me4(μ-SMe2)2] and 0.085 g (0.36 mmol) of imine 1g.
521 Yield (red solid): 102 mg (65%). 1H NMR (400 MHz, d6-acetone): δ 8.85 [s, 1H, 3J(Pt−H) = 60.0,
522 CHN]; 7.21 [ddd, 1H, 3J(H−F) = 9.0, 4J(H−F) = 7.2, 5J(H−F) = 2.0, H5]; 3.89 [t, 2H, J(H−H) = 4.0,
523 NCH2]; 2.91 [m, 2H, CH2NMe2]; 2.73 [s, 6H, 3J(Pt−H) = 24.0, NMe2]; 2.03 [qi, 2H, 3J(H−H) = 5.5,
524 CH2CH2CH2]; 0.95 [s, 3H, 2J(Pt−H) = 80.0, Me- Pt]. 19F NMR (376.5 MHz, CDCl3): δ −129.20 [ddd,
525 1F, 3J(F−F) = 19.4, 3J(F−H) = 10.7, 4J(F−F) = 7.5, F4]; − 139.23 [dd, 1F, 3J(F−F) = 19.4, 4J(F−F) =
526 7.5, F2]; − 170.41 [td, 1F, 3J(F−F) = 19.4, 4J(F−H) = 7.5, F3];. ESI (+)-MS: 437.07 [M − Me]+; 479.10
527 [M − Me + CH3CN]+; 891.2 [2 M − Me]+. Anal. Found (calcd for C13H17F3N2Pt· H2O): C, 33.5
528 (33.11); H, 4.1 (4.06); N, 5.8 (5.94).

529 **X-ray Diffraction**. Suitable crystals were grown in dichloromethane−methanol at room temperature. X-
530 ray intensity data were measured on a D8 VENTURE system equipped with a multilayer
531 monochromator and a Mo high brilliance microfocus source (λ = 0.71073 Å) at 100 K. For 3b, the

532 integration of the data using a monoclinic unit cell yielded a total of 197137 reflections to a maximum θ
533 angle of 25.11° (0.84 Å resolution), 18361 of which were independent and 16383 were greater than
534 $2\sigma(F2)$. Data were corrected for absorption effects using the multiscan method. For 3g, the integration of
535 the data using a monoclinic unit cell yielded a total of 14556 reflections to a maximum θ angle of 30.54°
536 (0.70 Å resolution), 3778 of which were independent and 3142 were greater than $2\sigma(F2)$. The structures
537 were solved and refined using the Bruker SHELXTL software package.[22] Further information is given
538 in Table S1 (Supporting Information).

539

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541

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545

546   **Notes**

547   The authors declare no competing financial interests.

548

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550

553

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619   analytical purity and are provided to illustrate the best values obtained to date. NMR spectra of

620   these compounds are provided as Supporting Information.

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629 ..

630   **Legends to figures**

631

632   **Scheme 1.** Synthesis of Compounds 3

633

634   **Scheme 2.** Synthesis of Compounds 3g,h with Fluoro for Methoxy Substitution

635

636   **Figure 1.** Molecular structure of compound 3b (molecule a). Selected bond lengths (Å) and angles (deg)

637   with estimated standard deviations: Pt(1a)−N(1a), 1.986(9); Pt(1a)−C(1a), 1.998(10); Pt(1a)−N(2a),

638   2.174(8); Pt(1a)−Cl(1a), 2.297(3); N(2a)−C(10a), 1.483(15); C(10a)−C(9a), 1.53(2); C(9a)−C(8a),

639   1.53(2); C(8a)−N(1a), 1.467(15); N(1a)−C(7a), 1.293(15); C(7a)−C(6a), 1.430(18); C(6a)−C(1a),

640   1.383(15); N(2a)−Pt(1a)−N(1a), 97.2(4); N(1a)−Pt(1a)−C(1a), 80.3(4); C(1a)−Pt(1a)−Cl(1a), 93.1(3);

641   N(2a)−Pt(1a)−Cl(1a), 89.5(3).

642

643   **Figure 2**. Molecular structure of compound 3g. Selected bond lengths (Å) and angles (deg) with

644   estimated standard deviations: Pt(1)−N(1), 1.997(4); Pt(1)−C(1), 2.000(3); Pt(1)−N(2), 2.174(3);

645   Pt(1)−Cl(1), 2.3093(11); N(2)−C(10), 1.498(5); C(10)−C(9), 1.521(6); C(9)−C(8), 1.514(6); C(8)−N(1),

646   1.483(5); N(1)−C(7), 1.301(5); C(7)−C(6), 1.442(6); C(6)−C(1), 1.408(6); N(2)−Pt(1)−N(1), 96.78(13);

647   N(1)−Pt(1)−C(1), 80.76(15); C(1)−Pt(1)−Cl(1), 92.85(13); N(2)−Pt(1)−Cl(1), 89.61(10).

648

649   **Scheme 3.** Synthesis of Compounds 4

650

651   **Figure 3.** Absorption spectra of compounds 3 in dichloromethane solution at 298 K at 10^{-4} M

652   concentration.

653

654   **Figure 4.** Emission spectra of compounds 3 in dichloromethane solution at 298 K: λexc 388 (3a), 376

655   (3b), 400 (3c), 391 (3d), 383 (3e), 391 (3f), 383 (3g), 391 nm (3h); concentration 10^{-4} M; three slits.

656   Emission spectra are normalized with respect to the strongest recorded emission maximum for

657   comparison purposes.

658

659   **Figure 5.** Absorption spectra of compounds 4 in dichloromethane solution at 298 K at 10^{-4} M
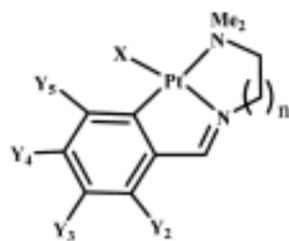
660   concentration.

661

662   **Figure 6**. Emission spectra of compounds 4 in dichloromethane solution at 77 K: λexc 405 (4a), 390

663   (4b), 415 (4c), 400 (4d), 400 (4e), 409 (4f), 402 (4g), 410 nm (4h); concentration 10^{-4} M; three slits.

664   Emission spectra are normalized with respect to the strongest recorded emission maximum for

665   comparison purposes.

666

CHART 1

667

668

669

	X	Y₂	Y₃	Y₄	Y₅	n		X	Y₂	Y₃	Y₄	Y₅	n
3a	Cl	F	H	H	H	2	4a	Me	F	H	H	H	2
3b	Cl	H	H	F	H	2	4b	Me	H	H	F	H	2
3c	Cl	F	H	H	H	1	4c	Me	F	H	H	H	1
3d	Cl	H	H	F	H	1	4d	Me	H	H	F	H	1
3e	Cl	H	H	H	H	2	4e	Me	H	H	H	H	2
3f	Cl	H	H	H	H	1	4f	Me	H	H	H	H	1
3g	Cl	OMe	F	F	H	2	4g	Me	F	F	F	H	2
3h	Cl	OMe	F	F	H	1	4h	Me	F	F	F	H	1

670

671

672   **SCHEME 1**
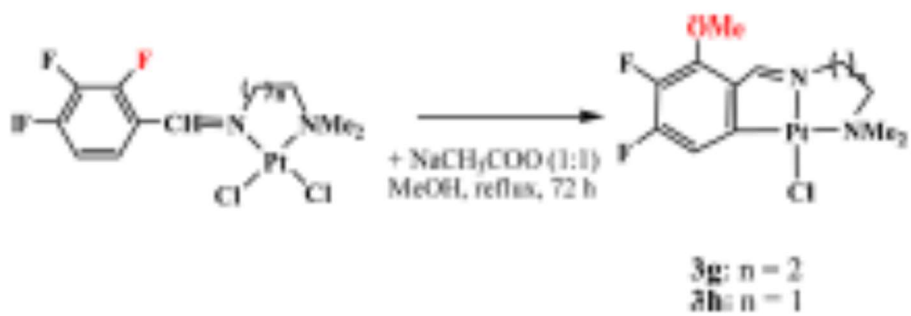
673

674

675

676

677

678

SCHEME 2

3g: n = 2
3h: n = 1

FIGURE 1

FIGURE 2

SCHEME 3

$$0.5 \quad [Pt_2Me_4(\mu\text{-}SMe_2)_2] \quad + \quad \text{(structure 1)} \quad \xrightarrow{\text{toluene, reflux, 1h}} \quad \text{(structure 4)} \quad + \quad MeH$$

n = 1 or 2
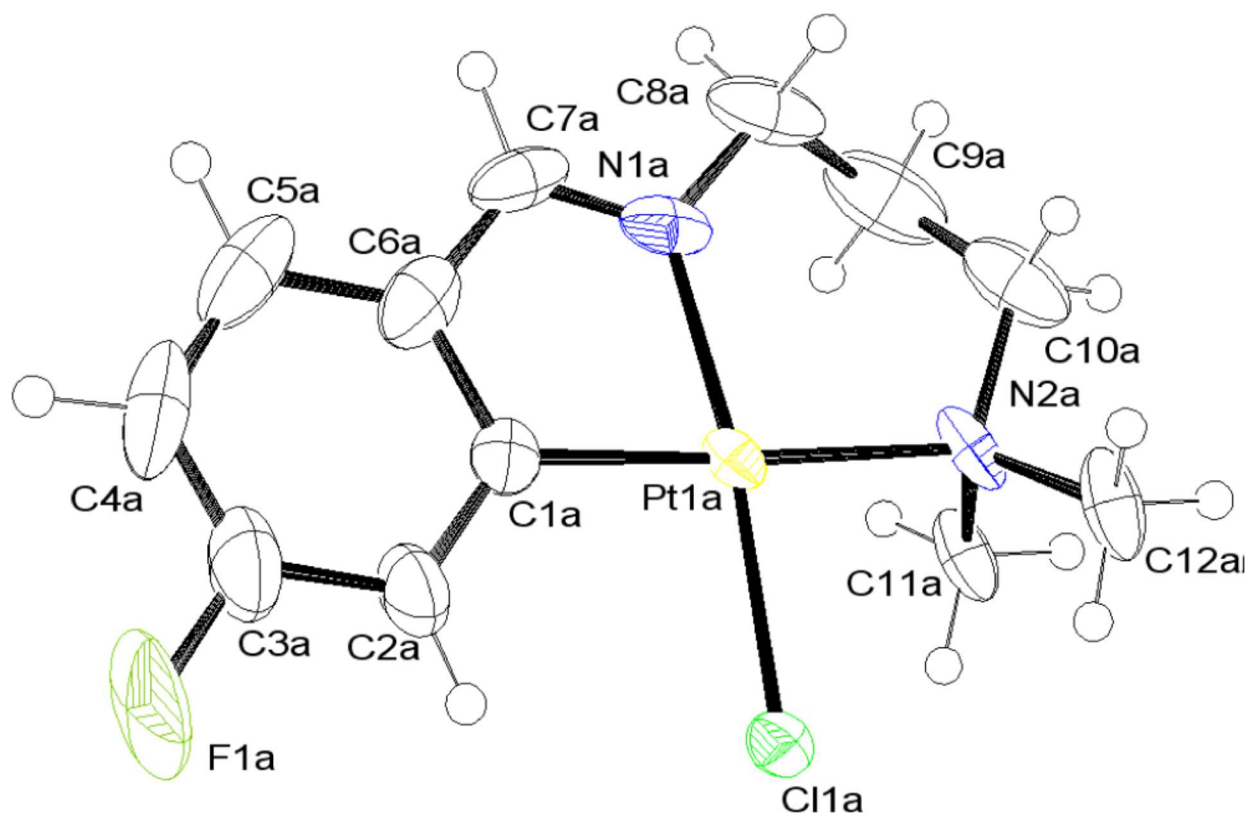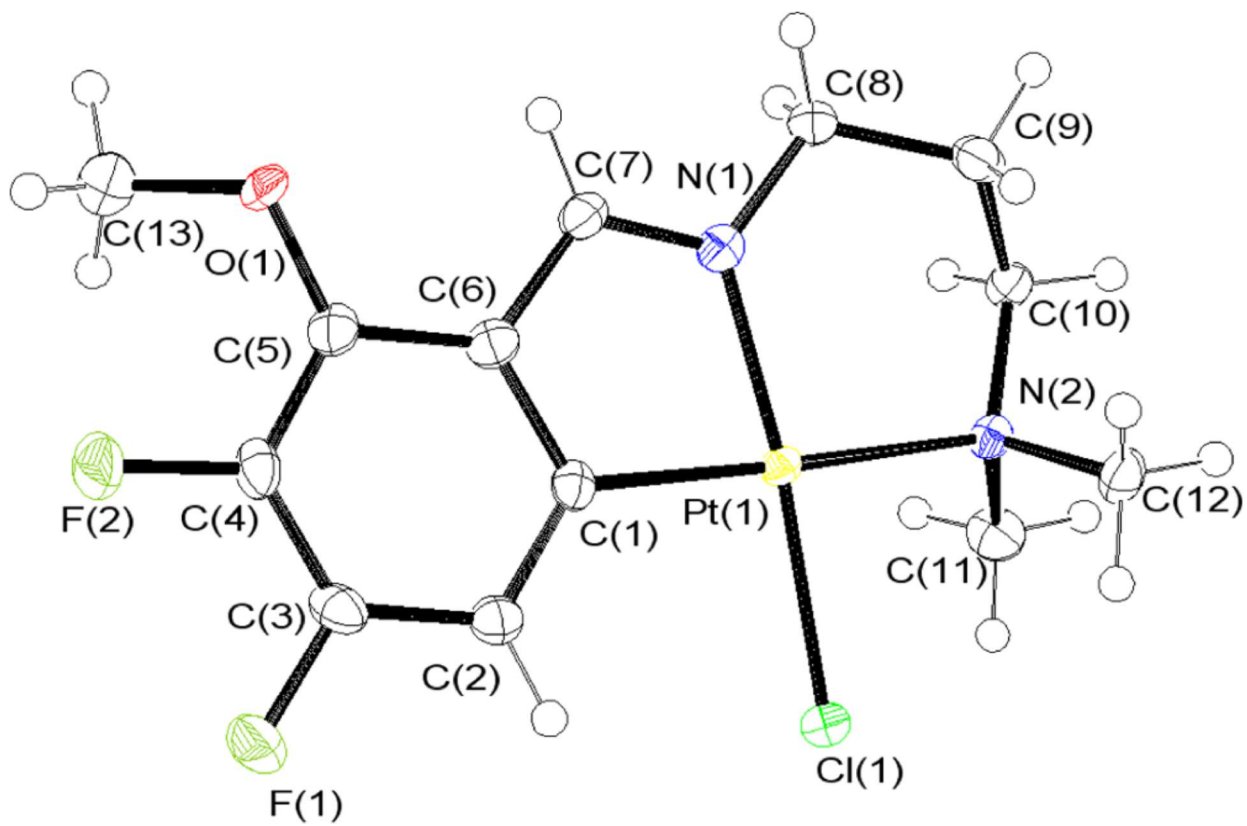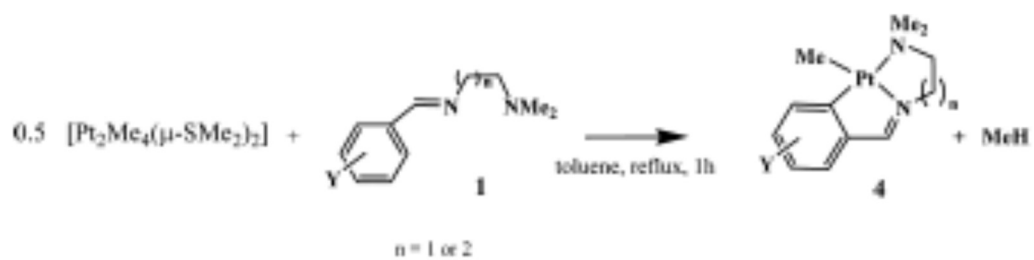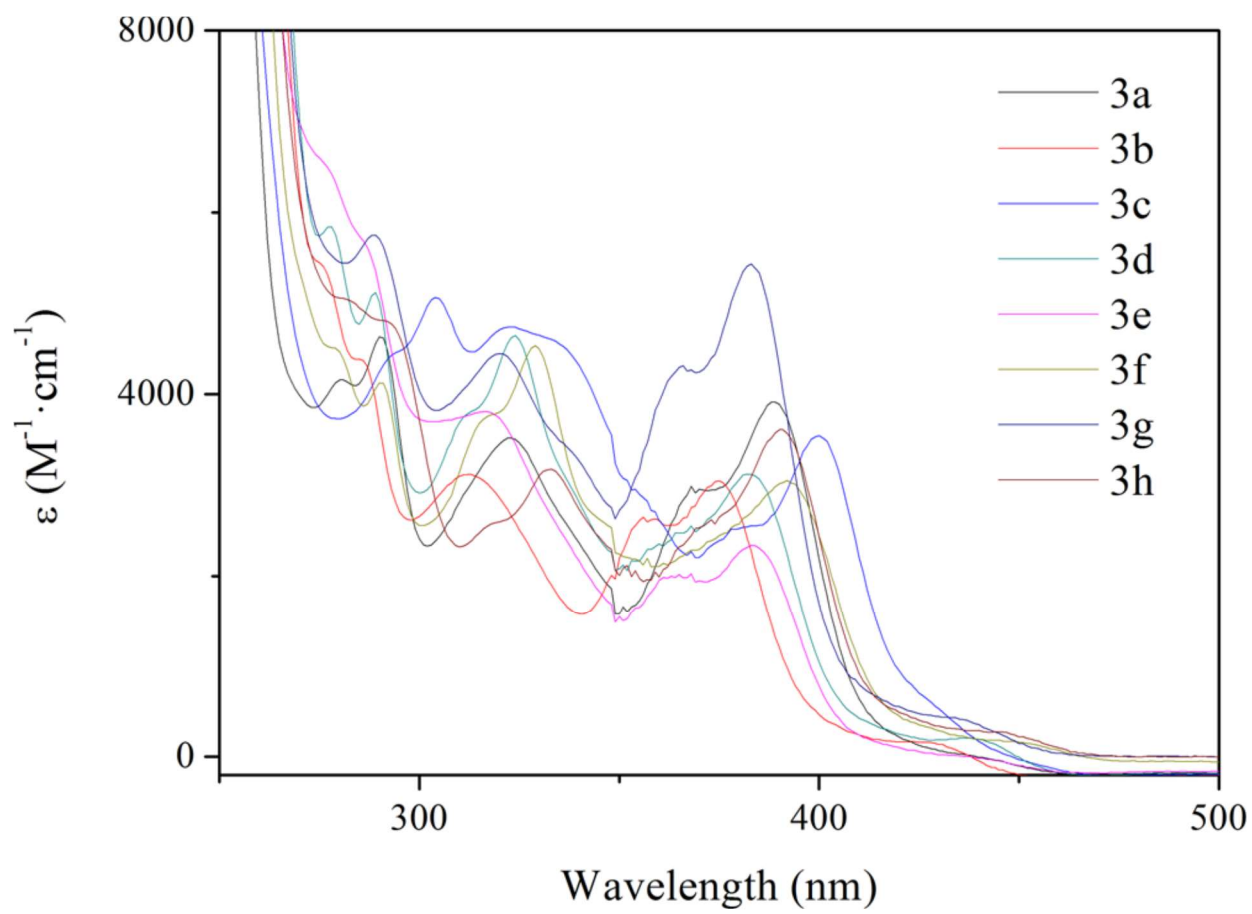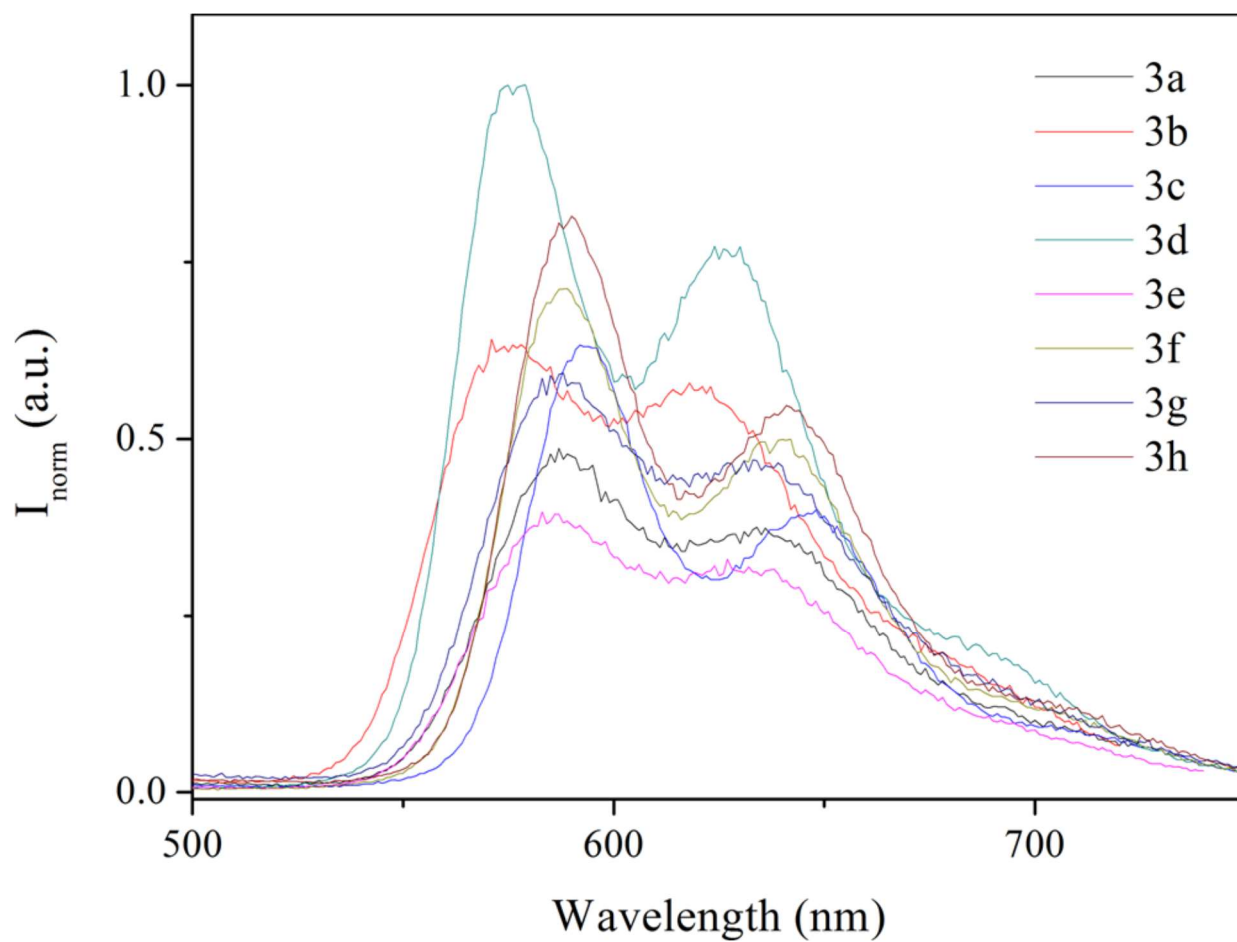
FIGURE 3

FIGURE 4

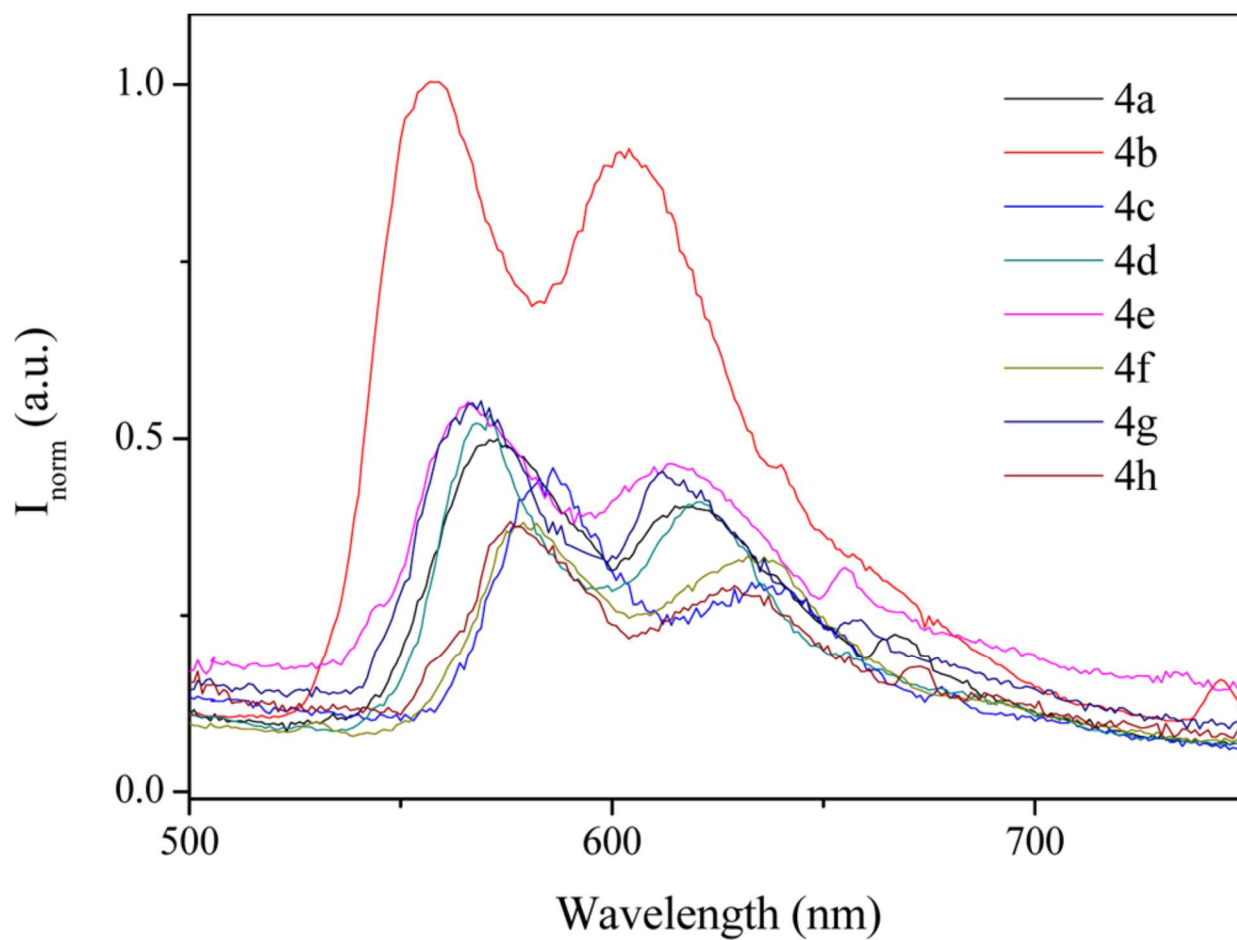## FIGURE 5

710

711

712

Wavelength (nm)

713

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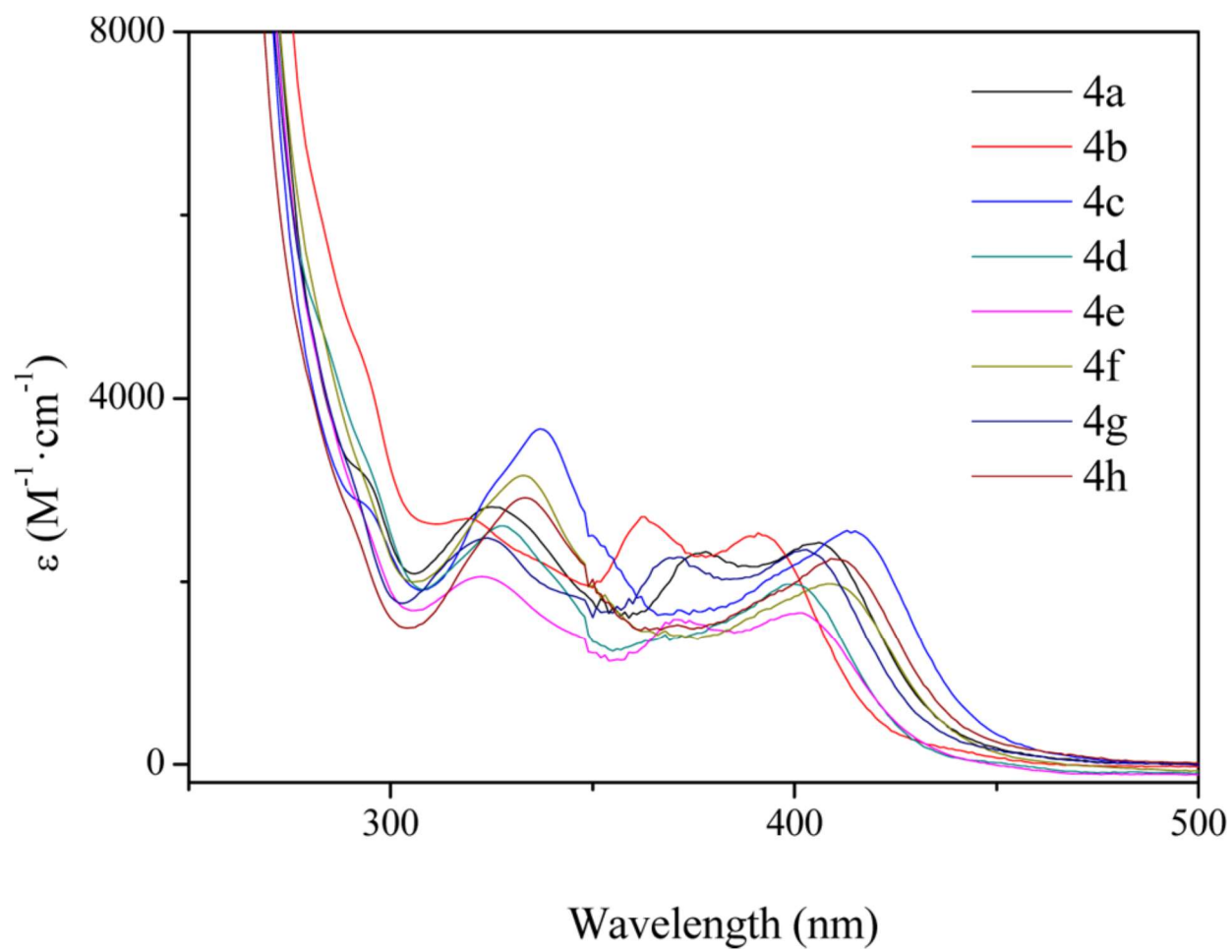
FIGURE 6

720 **Table 1.** Absorption and Emission Properties of Cyclometalated Platinum Compounds 3 and 4 in
721 CH2Cl2 Solution and in the Solid State[a]

722
723

complex	absorption λ_{max}/nm (ε/M^{-1} cm^{-1})	emission in solution λ_{max}/nm	emission in solid λ_{max}/nm	ϕ^b	temp/K
3a	290 (4631), 323 (3517), 388 (3914)	588, 639, 707	589, 641, 710	0.0025	298
3b	311 (3114), 376 (3022)	577, 622, 680	575, 616, 675	0.0038	298
3c	304 (4917), 330 (4513), 400 (3489)	593, 644, 715	595, 644, 712	0.0028	298
3d	327 (3870), 381 (2753)	575, 626, 690	567, 616, 678	0.0048	298
3e	316 (3663), 383 (2250)	586, 633, 701	577, 625, 690	0.0032	298
3f	329 (4359), 391 (2911)	588, 641, 704	580, 638, 702	0.0036	298
3g	323 (4155), 383 (5074)	590, 642, 698	590, 642, 702	0.0028	298
3h	332 (3250), 391 (3701)	590, 634, 700	575, 625, 690	0.0035	298
4a	325 (2734), 378 (2283), 408 (2324)	575, 618, 673	586, 630, 680	c	77
4b	319 (2446), 362 (2464), 391 (2298)	557, 604, 664	573, 618, 658	c	77
4c	337 (3240), 415 (2287)	585, 637, 685	589, 640, 680	c	77
4d	328 (2462), 399 (1853)	568, 621, 681	569, 619, 678	c	77
4e	322 (2053), 401 (1657)	566, 615, 665	585, 632, 679	c	77
4f	332 (2986), 408 (1876)	580, 636, 685	583, 638, 685	c	77
4g	324 (2343), 372 (2145), 403 (2222)	567, 620, 675	587, 630, 680	c	77
4h	333 (3053), 409 (2359)	578, 633, 684	580, 634, 689	c	77

[a]Emission spectra were recorded upon excitation at the lowest energy absorption band. [b]Quantum yields for emission in solution referred to
724 [Ru(bipy)$_3$]Cl$_2$ in H$_2$O. [c]Not observed.