Dalton Transactions

PAPER



Cite this: Dalton Trans., 2016, 45, 10599

Received 2nd May 2016, Accepted 24th May 2016 DOI: 10.1039/c6dt01722c

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Introduction

A deep understanding of the behaviour of photoexcited chemical species is crucial for the development of new technologies that take advantage of light as a sustainable source of energy.¹ In this context, the study of the photophysical and photochemical properties of transition metal complexes has been a very active research field for several decades, owing to their versatility and manifold applications. The strong spin-orbit coupling (SOC) induced by second- and third-row transition metal ions enables an efficient population of long-lived triplet excited states via rapid intersystem crossing (ISC) from singlet excited states.² Such triplet states are highly desirable for important photonic applications, including bioimaging,³ photocatalysis,⁴ photodynamic chemotherapy⁵ or the development of electroluminescent devices.⁶ In particular, $Ru(\pi)$,⁷ $Ir(\pi)^8$ and $Pt(\pi)^9$ complexes with heteroaromatic ligands have been extensively studied for their phosphorescence, which generally arises from metal-to-ligand charge transfer (MLCT), ligand-centred (LC) or mixed LC/MLCT excited states. For many of the applications of these transition-metal complexes, high phosphorescence quantum yields $(\Phi_{\rm P})$ are advantageous, which depend on the

Spotlight on the ligand: luminescent

fluorenyl moiety*

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cyclometalated Pt(IV) complexes containing a

The synthesis, electrochemistry and photophysical properties of a family of Pt(Iv) complexes with cyclometalated 2-(9,9-dimethylfluoren-2-yl)pyridine (flpy) are reported. Homoleptic and heteroleptic triscyclometalated complexes with a meridional configuration, $mer-[Pt(C^N)_2(flpy)]OTf$, with $C^N = flpy$ or cyclometalated 2-phenylpyridine (ppy), were prepared by reacting the bis-cyclometalated precursors $[Pt(C^N)_2Cl_2]$ with flpyH in the presence of two equivalents of AgOTf. The corresponding facial isomers were obtained by photoisomerization. The Pt(Iv) complexes with flpy display intense absorptions in the near-visible region and yellow phosphorescence in fluid solutions at 298 K, with quantum yields in the range 0.06–0.28 and lifetimes of hundreds of microseconds. The emissions arise from essentially ³LC

> quantum yield of intersystem crossing (Φ_{ISC}) and the radiative and nonradiative rate constants of the phosphorescing state (k_r and k_{nr} , respectively), according to the following equation:

$$\Phi_{\mathrm{P}} = \Phi_{\mathrm{ISC}} \frac{k_{\mathrm{r}}}{k_{\mathrm{r}} + k_{\mathrm{n}}}$$

In general, the ISC event is very fast in these complexes and $\Phi_{\rm ISC}$ usually approaches unity. Thus, the strategies to obtain high $\Phi_{\rm P}$ values are based on increasing $k_{\rm r}$ and/or reducing k_{nr} .^{8a} Phosphorescence is a spin-forbidden transition ($T_n \rightarrow S_0$) and therefore the associated k_r values are generally lower compared to those of fluorescent emissions $(S_n \rightarrow S_0)$. However, the SOC induced by heavy transition metals causes a mixing of states of different spin multiplicities, leading to less pure spin states and higher k_r values.² Accordingly, a decrease in metal orbital contribution to the emitting excited state, which is usually associated with a lower MLCT character, causes a reduction in $k_{\rm r}$.¹⁰ This is especially important in metal complexes that emit from essentially ³LC states, in which obtaining modest k_r values is crucial to achieve significant quantum yields. Alternatively, highly efficient emissions can be obtained by hindering nonradiative processes. Aside from bimolecular quenching, transition metal complexes typically display two main intramolecular nonradiative deactivation channels: thermal population of low-lying quenching states and vibrational coupling to the ground state. The first one involves non-emissive states that are close in energy to the emitting

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[†]Electronic supplementary information (ESI) available: Additional spectroscopic and computational data. See DOI: 10.1039/c6dt01722c

⁽flpy) states in all cases, with little metal-orbital contribution. However, computational calculations and experimental data demonstrate that subtle variations in the contribution of metal orbitals to the emitting state have a profound impact on quantum yields, while nonradiative deactivation through the thermal population of deactivating LMCT states does not have a significant influence.

state. Frequently, these quenching states result from the population of metal $d\sigma^*$ orbitals, *i.e.* metal-centred (MC)¹¹ or ligand-to-metal charge transfer (LMCT)¹² states, leading to important geometry distortions, dissociation of ligands or even reduction of the metal center.¹³ The use of strong-field ligands such as carbenes or cyclometalated scaffolds has proven to raise the energy of these states, thereby reducing quenching.9b,14 Vibrational coupling to the ground state is especially important in emitting states that lie at low energies or display distorted structures with respect to the ground state. In order to prevent distortions in the excited state, rigid complexes have been prepared by using pincer¹⁵ or tetradentate¹⁶ ligands as well as assembling dendrimeric structures¹⁷ or extending π -conjugation in the ligands.¹⁸ In particular, the use of cyclometalated ligands bearing a fluorenyl instead of a phenyl moiety has been notably successful in improving the emission properties of transition metal complexes. In fact, strongly emissive Ir(III),^{11*a*,19} Pt(II),²⁰ Pd(II)²¹ and Au(III)²² complexes have been reported with this type of ligands, which show lower k_{nr} values in comparison with the phenyl derivatives in most cases.

Recently, we prepared the first family of meridional (*mer*) and facial (*fac*) homoleptic tris-cyclometalated Pt(IV) complexes *mer/fac*-[Pt(C^N)₃]⁺, with C^N = cyclometalated 2-phenyl-pyridine (ppy), 2-(*p*-tolyl)pyridine (tpy), 2-(2,4-difluorophenyl) pyridine (dfppy), or 1-phenylpyrazole (ppz); the *fac* isomers display blue emissions from essentially ³LC states with quantum yields up to 0.49 in fluid solution at 298 K and lifetimes of hundreds of microseconds.²³ In order to examine the colour tunability of this class of complexes, we later addressed the introduction of cyclometalated ligands of lower π - π * transition energies and prepared heteroleptic derivatives

mer- $[Pt(C^N)_2(C'^N)]^+$, with $C^N = ppy$ or dfppy and $C'^N = ppy$ cyclometalated 2-(2-thienyl)pyridine (thpy) or 1-phenylisoquinoline (piq), which showed yellow or orange phosphorescent emissions arising from ³LC states localized on the thpy or pig ligands, respectively, but lower efficiencies.²⁴ The attempts to obtain heteroleptic $fac-[Pt(C^N)_2(C'^N')]^+$ or homoleptic mer- $[Pt(C'^N')_3]^+$ complexes with $C'^N' =$ they or piq were unsuccessful because they led to reduction to $Pt(\pi)$.²⁴ In the light of these results, we set out to obtain more stable and rigid derivatives using a cyclometalated ligand incorporating a fluorenyl moiety. In a recent article, we reported a family of neutral complexes of the type [Pt(C^N)₂(Me)Cl], including one example with cyclometalated 2-(9,9-dimethylfluoren-2-yl)pyridine (flpy), that displays yellow phosphorescence with a good emission efficiency, long lifetime and high absorptivity.²⁵ Herein, we present the preparation, photophysical characterization and electrochemistry of homoleptic and heteroleptic tris-cyclometalated complexes containing flpy as the chromophoric ligand, together with a neutral bis-cyclometalated derivative, which display long-lived yellow phosphorescence in all cases and reach quantum yields up to 0.28.

Results and discussion

Synthesis

The synthetic routes to the Pt(IV) complexes with the flpy ligand are outlined in Scheme 1. We first explored the preparation of heteroleptic tris-cyclometalated complexes containing two ppy as supporting ligands and one flpy as the chromophoric ligand by following a similar procedure to that reported for other heteroleptic complexes.²⁴ Thus, the reaction of



Scheme 1 Synthetic routes to tris-cyclometalated Pt(v) complexes with flpy. Reagents and conditions: (a) K₂PtCl₄, EtOCH₂CH₂OH/H₂O (3:1), 80 °C, 2 days; (b) PhICl₂, CH₂Cl₂, 25 °C, 1 h; (c) flpyH, 2 AgOTf, 1,2-dichloroethane, 90 °C, 2 days; (d) $h\nu$, MeCN, 3 h.

 $[Pt(ppy)_2Cl_2]$ (2a)²⁶ with flpyH in the presence of 2 equiv. of AgOTf in 1,2-dichloroethane at 90 °C afforded mer-[Pt(ppy)₂(flpy)]OTf (mer-3ab) in moderate yield. Irradiation of a MeCN solution of the latter satisfactorily resulted in photoisomerization to the facial isomer, fac-[Pt(ppy)2(flpy)]OTf (fac-3ab). Encouraged by these results, we next addressed the synthesis of homoleptic flpy derivatives using a similar route. The first step required the preparation of [Pt(flpy)(flpyH)Cl] (1b) from K₂PtCl₄ by using the procedure reported for other derivatives with ppy-based ligands.²⁷ Oxidation of this compound with PhICl₂ led to the cyclometalation of the pendant (9,9-dimethylfluoren-2-yl) moiety of the flpyH ligand and the introduction of a second chloride to give $[Pt(flpy)_2Cl_2]$ (2b) in nearly quantitative yield. The introduction of the third flpy ligand to give mer-[Pt(flpy)₃]OTf (mer-3b) and the subsequent photoisomerization to fac-[Pt(flpy)3]OTf (fac-3b) succeeded following the method employed for the heteroleptic derivatives. Complexes fac-3ab and mer/fac-3b are the first fac-heteroleptic and mer/fac-homoleptic tris-cyclometalated Pt(IV) complexes bearing a cyclometalated ligand of a relatively low $\pi - \pi^*$ transition energy. Their successful synthesis contrasts with the results obtained previously with thpy and piq ligands.

Photophysical properties

The absorption spectra of complexes 2b, mer/fac-3ab and mer/ fac-3b were recorded in CH_2Cl_2 (ca. 1×10^{-5} M) at 298 K (Fig. 1, Table 1). All complexes give rise to intense and struc-



Fig. 1 Absorption and emission spectra of the studied compounds in CH₂Cl₂ at 298 K.

| Table 1 | Electronic | absorption | data | for | the | studied | complexes | ir |
|-----------------------------------|--------------|-------------------------|------|-----|-----|---------|-----------|----|
| CH ₂ Cl ₂ s | olution (ca. | 1×10^{-5} M) a | | | | | | |

| Complex | $\lambda/\mathrm{nm} \left(\varepsilon \times 10^{-3}/\mathrm{M}^{-1} \mathrm{~cm}^{-1} \right)$ |
|---------|---|
| mer-3ab | 260 (32.2), 307 (30.2), 348 (31.8), 371 (30.2) |
| fac-3ab | 262 (27.9), 306 (27.0), 319 (24.0), 331 (22.5, sh), 356 (23.1, sh), 370 (24.8) |
| 2b | 251 (22.5, sh), 297 (26.8, sh), 305 (28.1), 360 (41.2, sh), 373 (47.3) |
| mer-3b | 257 (33.7), 305 (35.6), 362 (62.6, sh), 374 (65.0) |
| fac-3b | 261 (33.1), 295 (34.8, sh), 303 (35.6), 356 (68.5), 369 (70.0) |

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tured absorptions in the range of 250-400 nm that can be ascribed predominantly to ¹LC (π - π *) transitions within the cyclometalated ligands. The lowest-energy band is very similar in shape and energy in all derivatives, which indicates that it arises from the flpy ligand; this is further supported by the fact that its molar absorptivity increases with the number of flpy ligands and can reach 70000 M^{-1} cm⁻¹; such highly intense absorptions in the near-visible range are particularly desirable for applications in the fields of photocatalysis or bioimaging. The heteroleptic complexes mer-3ab and fac-3ab exhibit additional bands in the range 310-350 nm. Thus, the facial isomer shows structured bands in the range 310-335 nm that resemble those of fac-[Pt(ppy)₃]OTf, which arise from π - π^* transitions within the ppy ligands; the same assignment is plausible for these absorptions in fac-3ab. The absorption spectrum of mer-3ab displays a broad band centred at \sim 350 nm, probably resulting from mixed LLCT/LC(ppy) transitions. These assignments are in agreement with the results obtained by TDDFT calculations (see the ESI[†]).

The excitation and emission spectra of complexes 2b, mer/ fac-3ab and mer/fac-3b were registered in CH₂Cl₂ solution at 298 K and in butyronitrile (PrCN) frozen glasses at 77 K. The emission data are summarized in Table 2 and emission spectra at 298 K are depicted in Fig. 1. Excitation spectra at 298 K and emission spectra at 77 K are given in the ESI† (Fig. S7 and S8[†]). All the studied compounds are luminescent in fluid solution at 298 K, displaying the same structured emission band, with small variations in energy, and radiative lifetimes in the order of hundreds of microseconds. The corresponding excitation spectra match the absorption profiles in all cases (Fig. S10, ESI†), thus confirming that the emissions do not arise from possible photodecomposition products. This is especially significant in the case of mer-3b because the emissions of all the previously reported mer isomers of homoleptic tris-cyclometalated Pt(IV) complexes in fluid solutions were found to arise from small amounts of the photochemically generated fac counterparts.^{23,24} At 77 K, the emissions are slightly blue-shifted, indicating a very small rigidochromic effect, and their structure becomes better resolved. In addition, lifetimes increase as a result of the partial suppression of nonradiative processes. These features are indicative of

Table 2 Emission data of the studied compounds

| | 298 K ^a | 77 K ^b | | | | | |
|----------------|-----------------------------------|-------------------|----------------|---|--|-----------------------------------|----------------|
| Complex | $\lambda_{\rm em}^{\ c}/{\rm nm}$ | Φ^d | $\tau^e/\mu s$ | $k_{\rm r}^{f} \times 10^{-3}/{\rm s}^{-1}$ | $\frac{k_{\rm nr}{}^g \times}{10^{-3}/{\rm s}^{-1}}$ | $\lambda_{\rm em}^{\ c}/{\rm nm}$ | $\tau^e/\mu s$ |
| mer-3ab | 517 | 0.06 | 252 | 0.24 | 3.73 | 508 | 1152 |
| fac-3ab | 516 | 0.13 | 218 | 0.60 | 3.99 | 507 | 708 |
| 2b | 518 | 0.28 | 231 | 1.21 | 3.12 | 510 | 504 |
| mer-3b | 520 | 0.08 | 154 | 0.52 | 5.97 | 511 | 660 |
| fac-3 b | 516 | 0.17 | 209 | 0.81 | 3.97 | 507 | 667 |
| | | | | | | | |

^a In CH₂Cl₂. ^b In PrCN. ^c Highest-energy emission peak. ^d Absolute quantum yield. ^e Emission lifetime. ^f Radiative rate constant, $k_r = \Phi/\tau$. ^{*g*} Nonradiative rate constant, $k_{nr} = (1 - \Phi)/\tau$.

an emitting triplet excited state largely centred on the flpy ligand(s) in all cases. Consequently, in the heteroleptic complexes mer/fac-3ab the cyclometalated ppy ligands do not participate in the emission, thus acting as ancillary ligands, because ³LC(ppy) states are expected to lie at higher energies relative to the emitting ³LC(flpy) states. Similar results were found previously for heteroleptic tris-cyclometalated derivatives with thpy and piq ligands.²⁴ The emission spectra of fac-3b and mer/fac-3ab show an additional band at a higher energy (407 nm), with a much lower intensity in comparison with the phosphorescent emission, that can be assigned to residual fluorescence in view of its very short lifetime (<0.2 ns) and the excitation spectra registered at its maximum, which match those corresponding to the phosphorescent emission (Fig. S9, ESI†). We have previously observed residual fluorescence in other Pt(IV) complexes with low-energy ³LC states,²⁴ which implies that the ISC event does not have unit efficiency. Notwithstanding the low intensity of this band together with its extremely short lifetime indicates that Φ_{ISC} is very close to unity (>0.99; see the ESI[†] for more details) and leads to a very efficient population of the triplet manifold. The quantum yields of mer-3ab (0.06) and mer-3b (0.08) are

comparable to those of the previously reported mer- $[Pt(ppy)_2(C' \wedge N')]^+$ complexes $(C' \wedge N' = thpy, piq;$ range 0.02-0.07).²⁴ As expected, the *fac* counterparts are more efficient emitters, with quantum yields of 0.17 (fac-3b) or 0.13 (fac-3ab). For its part, compound 2b shows the highest quantum yield among the complexes studied in this work (0.28). The measured quantum yields can be interpreted by analysing the radiative and nonradiative rate constants (k_r and $k_{\rm nr}$, respectively), which have been calculated assuming that $\Phi_{\rm ISC}$ = 1, since this approximation has only a marginal influence on the final values (see the ESI^{\dagger} for more details). The k_{nr} values are small and generally lower than those found for the previously reported tris-cyclometalated Pt(IV) complexes with ligands of low π - π * transition energies.²⁴ The rigid scaffold of the flpy ligand may contribute to reduce nonradiative processes, as previously observed for Au(III) and Pt(II) complexes with cyclometalated ligands bearing the fluorenyl moiety.^{20,22} In fact, the structure of the emission band shows that the intensity of the 0-0 transition is significantly higher than that of the vibrational peaks, indicating that geometrical distortions in the excited state with respect to the ground state are small.²⁸ In the case of *mer*-3b, k_{nr} is slightly higher compared with the rest of derivatives, but still allows a moderately intense emission, which contrasts with the behaviour of the homoleptic blue emitters mer- $[Pt(C^N)_3]^+$, whose emissions are intense at 77 K but are totally quenched at room temperature because deactivating LMCT states are thermally populated from the emitting state.²³ Reasonably, the possible quenching excited state in mer-3b is not efficiently populated because of the low energy of the ${}^{3}LC(flpy)$ emitting state. In general, $k_{\rm r}$ values are very low, suggesting a very low metal orbital involvement in the excited state. Nevertheless, a small degree of MLCT character must be assumed, because it is crucial to produce efficient phosphorescence in largely ³LC emitters. As

a matter of fact, complex **2b** shows the highest quantum yield of the studied series, mainly because of its significantly higher $k_{\rm r}$, which can be attributed to a higher contribution of metal orbitals to the HOMO as a consequence of its uncharged nature and hence an emitting state with a higher degree of MLCT character. The higher quantum yields of *fac*-**3ab** and *fac*-**3b** compared to the *mer* isomers are also attributable to higher $k_{\rm r}$ values, which indicate that the *fac* geometry leads to a higher metal orbital involvement in the emitting state, as we have noted in a previous study.²⁴ Hence, the observed differences in $\Phi_{\rm P}$ in the present series of complexes are mainly dictated by $k_{\rm r}$, while nonradiative processes are less important.

Electrochemistry

The electrochemical properties of tris-cyclometalated compounds 3 were investigated using cyclic voltammetry in MeCN solution. The potentials of the most important redox processes and HOMO/LUMO energy estimations are listed in Table 3, and voltammograms covering the full solvent window (from 2.2 to -2.7 V vs. SCE) are depicted in Fig. 2. The voltammograms of the heteroleptic mer/fac-3ab complexes are very similar to those of the respective homoleptic mer/fac-3b complexes, suggesting that the frontier orbitals are mainly localized on the flpy ligands in all cases, while the participation of the ppy ligands of mer/fac-3ab might be negligible. In contrast, there are significant differences between mer and fac isomers. One (fac isomers) or two (mer isomers) irreversible oxidations are observed within the solvent window. The first oxidation peak in the mer complexes is found at less positive potentials (1.53 and 1.57 V vs. SCE) compared with the fac isomers (1.77 and 1.71 V vs. SCE), which is a common behaviour observed for other tris-cyclometalated Pt(IV) derivatives, 23,24 and implies a higher energy of the HOMO in the mer isomers. As expected, the potentials of the oxidation processes in the present compounds are much lower than those found for *mer/fac*-[Pt(ppy)₃] OTf, because the more extended π -conjugation of the fluorenyl system implies an easier oxidation. Several reduction processes are observed before the solvent discharge limit. The first two

Table 3 Electrochemical data^a and HOMO/LUMO energy estimations^b for complexes 3

| Complex | $E_{\mathrm{pa}}{}^{c}$ | $E_{\rm pc}{}^d$ | $E_{1/2}^{e}$ | $E_{\rm HOMO}$ | $E_{\rm LUMO}$ | $\Delta E_{\text{HOMO-LUMO}}$ |
|---------|-------------------------|------------------|---------------|----------------|----------------|-------------------------------|
| mer-3b | 1.53 | -1.57 | -2.22 | -6.12 | -3.23 | 2.89 |
| mer-3ab | $2.00 \\ 1.57$ | -1.55 | -2.34 | -6.16 | -3.26 | 2.90 |
| fac-3b | $2.02 \\ 1.77$ | -1.73 | -2.23 | -6.28 | -3.13 | 3.15 |
| fac-3ab | 1.71 | -1.87 -1.78 | -2.36 | -6.27 | -3.08 | 3.19 |
| | | -1.90 | | | | |

^{*a*} In V relative to SCE, measured in 0.1 M (Bu_4N)PF₆ anhydrous MeCN solution at 100 mV s⁻¹. ^{*b*} In eV; estimated from the onset values of the oxidation and reduction waves referenced against Fc⁺/Fc (0.40 V *vs.* SCE in MeCN), using a formal potential of 5.1 eV for the Fc⁺/Fc couple in the Fermi scale.^{39 c} Irreversible anodic peak potential. ^{*d*} Irreversible cathodic peak potential. ^{*e*} For the reversible process.





Fig. 3 Orbital energy diagrams from DFT calculations for **2b**, *mer/fac-***3b** and *mer/fac-***3ab**.

Fig. 2 Cyclic voltammograms of compounds 3 in MeCN at 100 mV s⁻¹.

reduction peaks found for the *fac* complexes are irreversible and occur at very close potentials (from -1.73 to -1.90 V vs. SCE); they probably arise from the consecutive reductions of two cyclometalated ligands. The first reduction in the *mer* compounds is also irreversible, but occurs at less negative potentials (-1.57 and -1.55 V vs. SCE) and is not followed by another close-lying peak. At more negative potentials, a reversible or quasi-reversible wave is observed in all cases, probably arising from the reduction and reoxidation of cyclometalated Pt(II) compounds formed in the previous reductions of Pt(IV) species, as proposed in the electrochemical studies of other tris-cyclometalated derivatives.²⁴

DFT and TDDFT calculations

For a better understanding of the excited states of the studied compounds, DFT and TDDFT calculations were carried out for all of them at the B3LYP/(6-31G**+LANL2DZ) level including solvent effects (CH₂Cl₂) at the PCM level. The bond distances and angles around the metal in the optimized ground-state geometries (Table S17; ESI[†]) are in good agreement with the in view of previously expected values reported crystal structures of complexes of the types $[Pt(C^N)_2Cl_2]^{29}$ and mer- $[Pt(C^N)_3]^+$.^{23,24} A diagram representing the energies and composition of the frontier orbitals of the optimized groundstate geometries is depicted in Fig. 3. Detailed compositions and figures showing the topologies of these orbitals are given in the ESI.† In general, the frontier orbitals are mainly composed of π or π^* orbitals of cyclometalated ligands with

some contribution of metal orbitals. It can be observed that, while π^* orbitals of both ppy and flpy lie at similar energies, π orbitals of flpy lie at significantly higher energies relative to those of ppy, which is consistent with the above discussed electrochemical data. As a result, the HOMO is essentially a π (flpy) orbital in all cases, involving very little metal character. Nevertheless, a higher metal orbital contribution to the HOMO can still be discerned for 2b (ca. 2%) with respect to mer/fac-3ab and mer/fac-3ab (ca. 1%), associated with its uncharged nature, which results in higher energy of the occupied d(Pt) orbitals. Consistent with this, the HOMO-3 in 2b involves 12% of metal orbital contribution, while in the cationic compounds the first occupied orbitals with metal contributions higher than 10% are HOMO-9 (mer/fac-3ab) and HOMO-13 (mer/fac-3b). Unoccupied orbitals with significant $d\sigma^{*}(Pt)$ orbital contributions lie at much higher energies in the fac derivatives in comparison with their mer isomers, which indicates that the fac geometry leads to a larger ligandfield splitting. Besides, narrower HOMO-LUMO gaps are found in the mer isomers as a result of a lower LUMO and a higher HOMO, in line with the electrochemical results.

Singlet and triplet excitation energies were calculated at the optimized ground-state geometries by TDDFT in CH_2Cl_2 solution. Listings of selected excitations with their assignments and the estimated percentage of MLCT or LMCT character are given in the ESI.[†] The calculated singlet excitations are in good agreement with the experimental absorption spectra in all cases and confirm that π - π * transitions within the flpy ligand are the main contribution to the lowest-energy band. In

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addition, LLCT transitions also contribute to the absorption profiles of *mer*-**3b** and *mer/fac*-**3ab** as a result of the presence of inequivalent ligands. LMCT contributions are important in the lowest singlet states of *mer*-**3a** and *mer*-**3ab** because of the relatively low energies of unoccupied orbitals with a high $d\sigma^*$ (Pt) character, while they are negligible in the *fac* isomers. The presence of excited states with a significant LMCT character has been noted for other tris-cyclometalated Pt(IV) complexes with a *mer* configuration and proposed to be responsible for the *mer*-to-*fac* photoisomerization.^{23,24}

The TDDFT calculations predict *n* low-lying triplet excitations of the essentially ³LC character (${}^{3}\pi-\pi^{*}$) (Fig. 4), where *n* is the number of cyclometalated ligands, each one confined within a different ligand. In all cases the lowest-energy triplet excitation corresponds to a ³LC(flpy) transition, which has a similar energy in all derivatives (2.47–2.52 eV), in agreement





with the very similar emission energies. ³LC(ppy) excitations in complexes mer/fac-3ab are considerably higher in energy than the ³LC(flpy) ones, in line with the scenario observed in the frontier-orbital analysis. Hence, the ppy ligands are not expected to participate in the emitting state, thus acting as non-chromophoric or ancillary ligands in these complexes. Triplet excitations with a LMCT character higher than 10% are in the range 3.46-3.69 eV for 2b, mer-3b and mer-3ab, while analogous transitions are not found below 4.10 or 4.37 eV for fac-3b or fac-3ab, respectively, as a consequence of the high energy of their $d\sigma^*(Pt)$ orbitals. Nevertheless, the energy difference between the ³LMCT states and the lowest ³LC(flpy) state appears to be too high to efficiently quench the phosphorescence in all cases, allowing moderate emission intensities even in mer-3b, as anticipated in the Photophysical properties section.

To gain further insight into the nature of the emitting states, we optimized the geometries of the first triplet excited state of the studied complexes. The calculated electronic energies relative to the ground state (adiabatic energy differences) are 2.41 eV (2b; 515 nm) or 2.43 eV (rest of complexes; 510 nm), in good agreement with the experimental emission energies. The spin density isosurfaces of the optimized T₁ states (Fig. 5) correspond to π - π^* excitations primarily localized within an flpy ligand with little metal-orbital participation in all cases, which is in line with the observation of residual fluorescence in the emission spectra. Nonetheless, a simple visual inspection reveals a higher spin density on the metal in the lowest triplet of the neutral complex 2b with respect to the cationic derivatives, which implies a higher metal-orbital participation in the emitting state and a higher MLCT character; analogously, among the studied tris-cyclometalated complexes, a higher spin density on the metal is observed for the lowest triplet of the fac isomers relative to the mer isomers. The calculated natural spin densities on the Pt atom agree with these observations, decreasing in the sequence: **2b** $(0.0116) > fac-3ab (0.0093) \approx fac-3b (0.0092) >$ *mer*-3b (0.0044) \approx *mer*-3ab (0.0043). Thus, they follow the same trend observed experimentally for k_r and can be regarded as a reliable indication of the degree of MLCT admixture in the essentially ³LC emitting states. It is also noteworthy that variations in these small MLCT admixtures have a profound



Fig. 5 Spin density distributions (0.001 e bohr⁻³) for the lowest triplet excited state of the studied compounds.

impact on the emission properties and explain the different emission quantum yields observed for the complexes presented in this work.

Conclusions

A series of luminescent cyclometalated Pt(IV) complexes with the flpy ligand, comprising [Pt(flpy)₂Cl₂], mer/fac- $[Pt(ppy)_2(flpy)]OTf$ and *mer/fac*- $[Pt(flpy)_3]OTf$, have been synthesized and their photophysical properties analysed with the help of DFT and TDDFT calculations. The electrochemical characterization of the tris-cyclometalated derivatives has also been carried out. Notably, complexes fac-[Pt(ppy)2(flpy)]OTf and mer/fac-[Pt(flpy)₃]OTf are the first fac-heteroleptic and mer/ fac-homoleptic tris-cyclometalated Pt(IV) complexes containing a cyclometalated ligand of a relatively low π - π * transition energy. All the studied compounds present strong ¹LC(flpy) absorptions in the near-visible region and display yellow phosphorescence from predominantly ³LC(flpy) states with quantum yields up to 0.28. The case of mer-[Pt(flpy)₃]OTf is especially significant, because it represents the first homoleptic tris-cyclometalated Pt(w) complex with a *mer* configuration that exhibits phosphorescence in fluid solutions at room temperature, which is a consequence of an inefficient population of deactivating LMCT states owing to the low energy of the emitting ³LC(flpy) state. The metal-orbital contribution to the emitting state has been identified as the main factor determining the radiative rates and quantum yields of the studied complexes, while nonradiative deactivation becomes secondary. Hence, the strategy of minimizing nonradiative processes in low-energy Pt(IV) emitters by using a more rigid chromophoric ligand has been successfully applied, providing important insight that may be used for the rational design of new Pt(IV)based emitters.

Experimental section

General considerations and materials

Unless otherwise noted, preparations were carried out under atmospheric conditions. Synthesis grade solvents were obtained from commercial sources. Compounds **2a**,²⁶ flpyH,³⁰ and PhICl₂³¹ were prepared following published procedures. All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 298 K. Chemical shifts are referred to residual signals of non-deuterated solvent. The number of solvation water molecules was calculated from the integral of the ¹H NMR water signal, taking into account the water content of the solvent blank. Elemental analyses were carried out with Carlo Erba 1106 and LECO CHNS-932 microanalyzers. Photoisomerizations were carried out using a UV-Consulting Peschl photoreactor, model UV-RS-1, equipped with a 150 W medium-pressure mercury immersion UV lamp (TQ 150), a quartz cooling jacket, and a 400 mL reaction vessel with a magnetic circulation pump.

Photophysical characterization

UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 750S spectrophotometer. Excitation and emission spectra were recorded on a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450 W xenon lamp, double-grating monochromators, and a TBX-04 photomultiplier. Measurements were carried out in a right angle configuration using 10 mm quartz fluorescence cells for solutions at 298 K or 5 mm quartz NMR tubes for frozen glasses at 77 K. A liquid nitrogen Dewar with quartz windows was employed for low-temperature measurements. Solutions of the samples were degassed by bubbling argon for 30 min; those of mer-3b and mer-3ab were degassed in the dark to prevent partial photoisomerization. Lifetimes were measured using the Fluorolog's FL-1040 phosphorimeter accessory; the estimated uncertainty is ±10% or better. Emission quantum yields were measured using a Hamamatsu C11347 Absolute PL Quantum Yield Spectrometer; the estimated uncertainty is $\pm 5\%$ or better.

Electrochemical characterization

Cyclic voltammograms were registered with a potentiostat/ galvanostat AUTOLAB-100 (Echo-Chemie, Utrecht), employing a three-electrode electrochemical cell equipped with a glassy carbon working electrode (Metrohm, 2 mm diameter), an Ag/ AgCl/3 M KCl electrode reference, and a glassy carbon rod counter electrode. The measurements were carried out at 298 K under an argon atmosphere, using degassed 0.5 mM solutions of the complexes in extra-dry MeCN (Acros Organics) and 0.1 M (Bu₄N)PF₆ as the electrolyte. Prior to each experiment, the working electrode was polished with an alumina slurry (0.05 µm) and rinsed with water and acetone. The electrodes were activated electrochemically in the background solution by means of several voltammetric cycles at 1 V s⁻¹ between -2.7 V and 2.2 V. At the end of each experiment, the reference electrode was checked against the ferrocene/ferricinium redox couple. Potentials are given vs. the standard calomel electrode (SCE).

Synthesis of [Pt(flpy)(flpyH)Cl](1b)

A Carius tube was charged with K₂PtCl₄ (675 mg, 1.62 mmol), flpyH (1.1 g, 4.05 mmol) and a degassed 3:1 mixture of 2-ethoxyethanol/water (30 mL) under a N₂ atmosphere and the mixture was stirred at 80 °C for 2 days. Solvents were removed under reduced pressure, the residue was treated with CH₂Cl₂ (40 mL) and stirred with anhydrous MgSO₄. The suspension was filtered and the filtrate was concentrated to 10 mL. Upon addition of MeOH (100 mL) a yellow solid precipitated, which was collected by filtration, washed with MeOH (10 mL) and vacuum-dried to give **1b**·H₂O. Yield: 555 mg, 44%. ¹H NMR (300.1 MHz, CD₂Cl₂): δ 9.61 (dd with satellites, *J*_{HH} = 5.8, 1.3 Hz, *J*_{HPt} ~39 Hz, 1H), 9.25 (dd with satellites, *J*_{HH} = 5.8, 1.4 Hz, *J*_{HPt} ~43 Hz, 1H), 8.63 (d, *J*_{HH} = 1.2 Hz, 1H), 8.10 (td, *J*_{HH} = 8.0, 1.6 Hz, 1H), 7.84 (m, 2H), 7.74 (m, 1H), 7.64–7.55 (m, 3H), 7.48 (ddd, $J_{\rm HH}$ = 5.9, 1.7, 1.5 Hz, 1H), 7.42–7.21 (m, 8H), 7.06 (ddd, $J_{\rm HH}$ = 5.9, 1.6, 1.4 Hz, 1H), 6.46 (s with satellites, $J_{\rm HPt}$ ~49 Hz, 1H), 1.41 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H), 1.16 (s, 3H). ¹³C{¹H} NMR (75.45 MHz, CD₂Cl₂): δ 162.9 (C), 154.9 (CH), 154.5 (C), 153.1 (C), 151.2 (CH), 148.8 (C), 140.5 (C), 140.2 (C), 139.4 (C), 139.1 (C), 138.7 (CH), 138.3 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 125.5 (CH), 124.1 (CH), 123.0 (CH), 122.1 (CH), 121.6 (CH), 120.6 (CH), 120.0 (CH), 119.5 (CH), 118.4 (CH), 117.8 (CH), 47.2 (C), 46.7 (C), 27.3 (CH₃), 27.1 (CH₃), 26.8 (CH₃), 26.3 (CH₃). Elemental analysis calcd for C₄₀H₃₅ClN₂OPt: C, 60.79; H, 4.46; N, 3.54; found: C, 60.70; H, 4.41; N, 3.59.

Synthesis of [Pt(flpy)₂Cl₂] (2b)

To a solution of **1b** (370 mg, 0.479 mmol) in CH₂Cl₂ (60 mL) was added PhICl₂ (150 mg, 0.545 mmol) and the mixture was stirred at room temperature for 4 h. The resulting suspension was concentrated under reduced pressure (30 mL) and Et₂O (70 mL) was added. The resultant beige precipitate was filtered off, washed with Et_2O (2 × 5 mL) and vacuum-dried to give 2b·0.5CH₂Cl₂. Yield: 375 mg, 97%. ¹H NMR (400.9 MHz, dmso- d_6): δ 9.75 (dd with satellites, J_{HH} = 6.0, 1.0 Hz, J_{HPt} = 28 Hz, 2H), 8.61 (m, 2H), 8.45 (td, J_{HH} = 7.6, 1.4 Hz, 2H), 8.28 (s, 2H), 7.83 (m, 2H), 7.48 (d, $J_{\rm HH}$ = 7.4 Hz, 2H), 7.31-7.20 (m, 6H), 6.24 (s with satellites, J_{HPt} = 34 Hz, 2H), 1.44 (s, 6H), 1.36 (s, 6H). ${}^{13}C{}^{1}H$ NMR (100.9 MHz, dmso- d_6): δ 163.5 (C), 154.2 (C), 150.8 (C), 148.8 (CH), 141.9 (CH), 141.3 (C), 140.5 (C), 139.3 (C), 136.7 (C), 128.5 (CH), 127.2 (CH), 124.6 (CH), 123.0 (CH), 121.7 (CH), 120.8 (CH), 120.2 (CH), 117.4 (CH), 46.2 (C), 26.9 (CH_3) , 26.3 (CH_3) . Elemental analysis calcd for C_{40.5}H₃₃Cl₃N₂Pt: C, 57.28; H, 3.92; N, 3.30; found: C, 57.49; H, 4.02; N, 3.54.

Synthesis of mer-[Pt(C^N)₂(flpy)]OTf

A Carius tube was charged with complex **2a** or **2b** (0.266 mmol), AgOTf (0.585 mmol), flpyH (1.27 mmol) and degassed 1,2-dichloroethane (20 mL) under a N₂ atmosphere, and the mixture was stirred at 90 °C for 2 days. After cooling to room temperature, CH₂Cl₂ (15 mL) was added and the suspension was filtered through Celite. The filtrate was stirred vigorously with Na₂CO₃, filtered and concentrated under reduced pressure (15 mL). Upon addition of Et₂O (60 mL), a solid precipitated, which was filtered off, washed with Et₂O (2 × 5 mL) and vacuum-dried.

mer-3ab. This product was purified by chromatography on silica gel using a CHCl₃/MeOH mixture (9:1) as the eluent. Beige solid. Yield: 57%. ¹H NMR (400.9 MHz, CD₂Cl₂): δ 8.31 (d, J_{HH} = 8.2 Hz, 1H), 8.18–8.01 (m, 7H), 7.94–7.85 (m, 3H), 7.59 (ddd with satellites, J_{HH} = 6.1, 1.4, 0.7 Hz, J_{HPt} = 30 Hz, 1H), 7.45 (d, J_{HH} = 7.5 Hz, 1H), 7.40–7.12 (m, 10H), 7.04 (s with satellites, J_{HPt} = 21 Hz, 1H), 6.49 (dd with satellites, J_{HH} = 7.3, 0.9 Hz, J_{HPt} = 14 Hz, 1H), 6.24 (dd with satellites, J_{HH} = 7.8, 0.8 Hz, J_{HPt} = 30 Hz, 1H), 1.57 (s, 3H), 1.47 (s, 3H). ¹³C{¹H} NMR (75.45 MHz, CD₂Cl₂): δ 167.9 (C), 166.0 (C), 164.4 (C), 161.6 (C), 161.0 (C), 155.0 (C), 152.4 (C), 150.2 (J_{CPt} = 17 Hz, CH), 148.7 (CH), 146.2 (CH), 143.7 (C), 143.1 (C), 142.5 (C), 142.0

(C), 141.9 (CH), 141.5 (CH), 140.7 (CH), 140.2 (C), 138.5 (C), 133.0 (CH), 132.9 ($J_{CPt} = 40$ Hz, CH), 130.6 ($J_{CPt} = 24$ Hz, CH), 128.6 (CH), 127.3 (CH), 127.2 ($J_{CPt} = 30$ Hz, CH), 126.8 (CH), 126.5 (CH), 126.2 ($J_{CPt} = 30$ Hz, CH), 125.8 (CH), 125.4 (CH), 125.1 (CH), 125.0 (CH), 124.8 (CH), 123.1 (CH), 122.3 (CH), 122.2 (CH), 122.0 (CH), 121.3 ($J_{CPt} = 18$ Hz, CH), 120.6 (CH), 47.0 (C), 27.2 (CH₃). Elemental analysis calcd for C₄₃H₃₂F₃N₃O₃PtS: C, 55.96; H, 3.49; N, 4.55; S, 3.47; found: C, 56.00; H, 3.66; N, 4.43; S, 3.65.

mer-3b. Pale yellow solid. Yield: 75%. ¹H NMR (300.1 MHz, CD_2Cl_2): δ 8.32 (d, J_{HH} = 8.1 Hz, 1H), 8.28–7.97 (m, 9H), 7.94 (s, 1H), 7.64 (d with satellites, J_{HH} = 6.0 Hz, J_{HPt} = 30 Hz, 1H), 7.50–7.05 (m, 16H), 6.84 (s with satellites, $J_{\rm HPt}$ = 15 Hz, 1H), 6.56 (s with satellites, $J_{\rm HPt}$ = 32 Hz, 1H), 1.66 (s, 3H), 1.60 (s, 3H), 1.57 (s, 6H), 1.48 (s, 6H). ¹³C¹₁H} NMR (75.45 MHz, CD₂Cl₂): δ 168.1 (C), 166.1 (C), 164.7 (C), 161.9 (C), 160.6 (C), 155.1 (C), 155.0 (C), 152.4 (C), 151.2 (C), 150.3 (CH), 148.8 (CH), 146.2 (CH), 144.0 (C), 143.7 (C), 142.5 (C), 141.6 (CH), 141.4 (CH), 140.5 (CH), 138.6 (C), 138.4 (C), 138.2 (C), 137.9 (C), 129.1 (CH), 128.9 (CH), 128.6 (CH), 127.4 (CH), 127.3 (CH), 125.0 (CH), 124.8 (CH), 124.5 (CH), 123.2 (CH), 123.1 (CH), 122.2 (CH), 122.1 (CH), 122.0 (CH), 121.6 (CH), 121.2 (CH), 121.1 (CH), 121.0 (CH), 120.8 (CH), 120.5 (CH), 118.3 (J_{CPt} = 31 Hz, CH), 47.1 (C), 47.1 (C), 47.0 (C), 27.8 (CH₃), 27.3 (CH₃), 27.2 (CH₃), 27.2 (CH₃), 26.9 (CH₃). Elemental analysis calcd for C₆₁H₄₈F₃N₃O₃PtS: C, 63.42; H, 4.19; N, 3.64; S, 2.78; found: C, 63.22; H, 4.29; N, 3.44; S, 2.95.

Synthesis of *fac*-[Pt(C^N)₂(flpy)]OTf

A degassed solution of *mer*-**3ab** or *mer*-**3b** (0.15 mmol) in MeCN (350 mL) was irradiated in a UV photoreactor for 3 h. The solvent was evaporated under reduced pressure and the remaining residue was chromatographed on silica gel using a CHCl₃/MeOH mixture in a 6:1 (*fac*-**3ab**) or 9:1 (*fac*-**3b**) ratio as the eluent.

fac-3ab. White solid. Yield: 24%. ¹H NMR (400.9 MHz, CD₃CN): δ 8.39 (d, J_{HH} = 8.3 Hz, 1H), 8.29 (d, J_{HH} = 8.0 Hz, 2H), 8.15-8.09 (m, 4H), 8.00-7.94 (m, 2H), 7.78 (d with satellites, $J_{\rm HH}$ = 5.1 Hz, $J_{\rm HPt}$ ~9 Hz, 1H), 7.73 (d with satellites, $J_{\rm HH}$ = 5.2 Hz, $J_{\text{HPt}} \sim 9$ Hz, 2H), 7.51 (d, $J_{\text{HH}} = 7.6$ Hz, 1H), 7.39–7.12 (m, 9H), 7.06 (m, 1H), 6.89 (s with satellites, *J*_{HPt} = 47 Hz, 1H), 6.66 (dd with satellites, J_{HH} = 5.5, 0.9 Hz, J_{HPt} = 45 Hz, 1H), 6.64 (dd with satellites, J_{HH} = 5.5, 0.8 Hz, J_{HPt} = 45 Hz, 1H), 1.57 (s, 3H), 1.47 (s, 3H). ${}^{13}C{}^{1}H$ NMR (100.9 MHz, CD₃CN): δ 163.5 (C), 163.4 (C), 163.3 (C), 156.0 (C), 152.9 (C), 148.3 (CH), 148.2 (CH), 144.2 (C), 143.0 (C), 142.8 (C), 142.7 (CH), 142.6 (CH), 141.9 (C), 141.3 (C), 139.0 (C), 133.7 (J_{CPt} = 58 Hz, CH), 133.5 $(J_{CPt} = 58 \text{ Hz}, \text{ CH}), 132.9 (J_{CPt} = 50 \text{ Hz}, \text{ CH}), 129.8 (CH), 128.6$ (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 126.7 (CH), 126.7 (CH), 126.2 (J_{CPt} = 10 Hz, CH), 124.3 (CH), 123.8 (J_{CPt} = 51 Hz, CH), 123.1 (CH), 123.0 (CH), 122.8 (CH), 122.0 (J_{CPt} = 35 Hz, CH), 121.4 (CH), 47.9 (C), 27.6 (CH₃), 27.5 (CH₃). Elemental analysis calcd for C43H32F3N3O3PtS: C, 55.96; H, 3.49; N, 4.55; S, 3.47; found: C, 56.06; H, 3.56; N, 4.78; S, 3.23.

fac-3b. Beige solid. Yield: 27%. ¹H NMR (400.9 MHz, CD₂Cl₂): δ 8.26 (d, J_{HH} = 8.2 Hz, 3H), 8.08 (td, J_{HH} = 7.8, 0.8 Hz,

3H), 7.95 (s, 3H), 7.71 (d with satellites, $J_{\rm HH}$ = 5.2 Hz, $J_{\rm HPt}$ ~9 Hz, 3H), 7.45 (d, $J_{\rm HH}$ = 7.6 Hz, 3H), 7.35 (td, $J_{\rm HH}$ = 6.5, 0.8 Hz, 3H), 7.27 (d, $J_{\rm HH}$ = 7.2, 1.2 Hz, 3H), 7.17–7.09 (m, 6H), 7.04 (s with satellites, $J_{\rm HPt}$ = 57 Hz, 3H), 1.63 (s, 9H), 1.51 (s, 9H). ¹³C{¹H} MMR (75.45 MHz, CD₂Cl₂): δ 163.0 (C), 154.9 (C), 151.9 (C), 146.7 (CH), 143.7 (C), 141.4 (C), 141.1 (CH), 139.8 (C), 138.2 (C), 128.6 (CH), 127.3 (CH), 125.0 (CH), 123.7 ($J_{\rm CPt}$ = 50 Hz, CH), 123.0 (CH), 121.6 ($J_{\rm CPt}$ = 15 Hz, CH), 120.9 (CH), 120.5 ($J_{\rm CPt}$ = 35 Hz, CH), 47.0 (C), 27.8 (CH₃), 26.9 (CH₃). Elemental analysis calcd for C₆₁H₄₈F₃N₃O₃PtS: C, 63.42; H, 4.19; N, 3.64; S, 2.78.

Computational methods

DFT calculations were carried out with the Gaussian 09 package,³² using the B3LYP hybrid functional,³³ together with the 6-31G**³⁴ basis set for the main-group elements and the LANL2DZ³⁵ basis set and effective core potential for the platinum atom. Geometry optimizations were carried out without symmetry restrictions, using "tight" convergence criteria and "ultrafine" integration grid. Vertical excitation energies were obtained from TDDFT calculations at the ground-state optimized geometries. Triplet-state geometry optimizations were carried out following a two-step strategy.³⁶ Initially, TDDFT optimizations of the two lowest triplets were attempted starting from the ground-state geometry; the resulting lowestenergy geometry was then subjected to spin-unrestricted DFT (UB3LYP) optimizations setting a triplet multiplicity. The solvent effect (CH_2Cl_2) was accounted for in all cases by using the integral equation formalism variant of the polarizable continuum solvation model (IEFPCM).37 All geometry optimizations were followed by vibrational frequency calculations to verify that the obtained structures are minima on the potential energy surface. Natural spin densities were obtained from natural population analyses using the NBO 5.9 program.³⁸

Acknowledgements

This work was supported by Ministerio de Economía y Competitividad, Spain (grant CTQ2015-69568-P), Ministerio de Educación, Cultura y Deporte, Spain (FPU grant to F. J.), Fundación Séneca (grant 19890/GERM/15) and Universidad de Murcia.

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