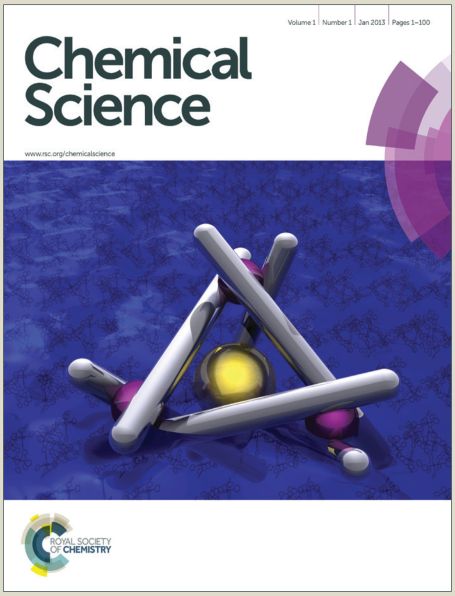
Chemical Science

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemicalscience

Chemical Science RSCPublishing

EDGE ARTICLE

Homoleptic tris-cyclometalated platinum(IV) complexes: a new class of long-lived, highly efficient ^{3}LC emitters†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2013,
Accepted 00th January 2013

DOI: 10.1039/x0xx00000x

www.rsc.org/

Fabio Juliá,[a] Delia Bautista,[b] Jesús M. Fernández-Hernández[a] and Pablo González-Herrero*[a]

The synthesis of meridional and facial isomers of tris-cyclometalated Pt(IV) complexes, $[Pt(C\^{}N)_3]OTf$, where C^N is a *C*-deprotonated 2-phenylpyridine-based ligand or 1-phenylpyrazole, is reported for the first time. The facial isomers exhibit high-energy emissions from essentially ^{3}LC excited states, characterized by lifetimes of hundreds of microseconds and quantum yields up to 0.49 at room temperature in fluid solution, the highest ever found for Pt(IV) complexes. Stern-Volmer studies demonstrate the high sensitivity of the facial isomers toward oxygen and their electrochemical characterization reveals large redox gaps and a strong oxidizing character in the excited state.

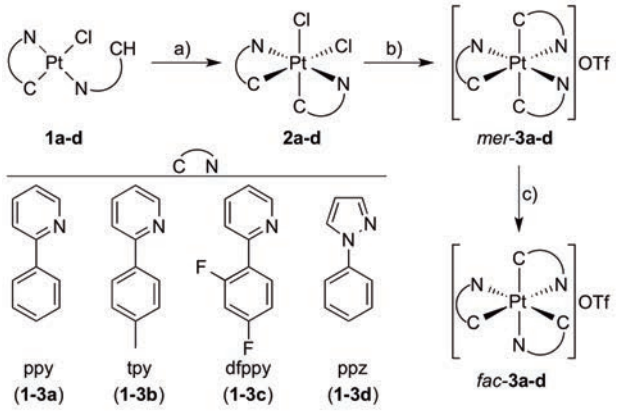
Introduction

Luminescent cyclometalated complexes of transition metals are of extraordinary fundamental and applied interest. The majority of studies in this area have focused on Ir(III) and Pt(II) systems, mainly associated with their suitability as phosphorescent dopants for electroluminescent materials.[1] The strong spin-orbit coupling of these metals and a variable degree of metal orbital involvement in the HOMO facilitate the formation of triplet excited states of mixed ligand-centered (LC or π-π*) and metal-to-ligand charge-transfer (MLCT) character that exhibit high radiative rate constants.[2] Ir(III) complexes with arylpyridines and related ligands are often considered the most efficient and versatile luminophores[1a,1c,3] and indeed the complex *fac*-$[Ir(ppy)_3]$[4] (ppy = 2-phenylpyridine) has become an archetypal organometallic emitter. Particular emphasis has been placed on the development of efficient blue emitters,[5] which has proved to be very difficult because radiationless deactivation pathways become thermally accessible as the energy of the emitting state increases, leading to poor quantum yields at room temperature.[6]

Compounds that exhibit long-lived, triplet excited states are desirable for applications as photoredox catalysts in organic synthesis,[7] luminescent probes for bioimaging,[8] chemosensors,[9] and photosensitizers for singlet-oxygen generation and photodynamic chemotherapy.[8c,10] In this context, considerable efforts have been devoted to extend the lifetimes of ^{3}MLCT states in Ru(II) polypyridyl complexes via equilibration with ^{3}LC states of pendant organic chromophores, which can lead to lifetimes in excess of 150 μs.[10b,11] In recent years, complexes of metal ions that are difficult to oxidize, such as Pd(II)[12] or Au(III),[13] are being increasingly investigated as triplet emitters with long radiative lifetimes. In particular, Che and coworkers have demonstrated the suitability of high-energy, intensely emissive, long-lived ^{3}LC excited states exhibited by cyclometalated Au(III) complexes for photocatalytic C–H bond functionalization, hydrogen production, and energy up-conversion.[14] The discovery of new long-lived and efficient triplet emitters can thus have a substantial impact in the above-mentioned areas of application.

Pt(IV) complexes have been mostly investigated for their involvement in oxidative addition/reductive elimination processes relevant to catalysis,[15] and their use as prodrugs in cancer chemotherapy.[16] Of particular interest are photoactivatable Pt(IV) prodrugs, which can be employed in cancer photochemotherapy.[17] However, the emission properties of Pt(IV) complexes have received a very limited attention,[18] which contrasts with the extensive luminescence studies carried out on complexes of other d^6 ions, such as Re(I), Ru(II), Os(II), and Ir(III).[19] Bis-cyclometalated complexes of the type $[Pt(C\^{}N)_2(R)Cl]$ [C^N = ppy, thpy = 2-(2-thienyl)pyridine], obtained from photooxidation of $[Pt(C\^{}N)_2]$ in chlorinated solvents, were the first reported luminescent Pt(IV) complexes;[18a,18b] they emit from metal-perturbed ^{3}LC states with quantum yields in the range 0.05–0.15 and radiative lifetimes up to 270 μs at room temperature. The emitting state in these complexes has very little metal character because of the very low energy of the occupied d orbitals in Pt(IV). Recently, a series of dicationic complexes of the type $[Pt(C\^{}N)_2(N\^{}N)]^{2+}$ (C^N = ppy-based ligand; N^N = aromatic diimine) have been shown to emit from ^{3}LC states with very low quantum yields (0.0005–0.035),[18e] while a number of monocyclometalated Pt(IV) complexes obtained from oxidative addition reactions to Pt(II) compounds have been reported to be non-emissive.[18f,20]

Herein, we report the first series of meridional and facial isomers of homoleptic tris-cyclometalated Pt(IV) complexes, using *C*-deprotonated 2-phenylpyridine (ppy), 2-(*p*-tolyl)pyridine (tpy), 2-(2,4-difluorophenyl)pyridine (dfppy), or 1-phenylpyrazole (ppz) as ligands, and demonstrate highly efficient, long-lived blue emissions from ^{3}LC states in the facial isomers with ppy-based ligands. In addition, their oxidative character in the excited state and high sensitivity toward oxygen quenching are proved.



Scheme 1 Synthetic route to *mer* and *fac* isomers of tris-cyclometalated Pt(IV) complexes. a) $PhICl_2$, CH_2Cl_2; b) 2 AgOTf, excess N^CH, CH_2ClCH_2Cl (90 °C) or 1,2-$C_4H_4Cl_2$ (140 °C); c) hν, MeCN.

Results and discussion

Synthesis

The synthetic route is outlined in Scheme 1. Previous works have shown that Pt(II) complexes of the type [Pt(C^N)(N^CH)Cl] (**1a–d**) are suitable precursors for the preparation of bis-cyclometalated Pt(IV) compounds of the type [Pt(C^N)$_2$Cl$_2$] (**2a–d**) via oxidation with $PhICl_2$.[18e,21] We have achieved the introduction of a third cyclometalating ligand into the coordination sphere of Pt(IV) by reacting complexes **2a–d** with 2.2 equiv of AgOTf and an excess of the corresponding N^CH ligand in 1,2-dichloroethane at 90 °C for 3 d (complexes with non-fluorinated ligands) or 1,2-dichlorobenzene at 140 °C for 4 d (dfppy complex). The abstraction of the two chlorides by the silver ions to form AgCl is necessary for the coordination and subsequent metalation of the N^CH ligand. The fact that the cyclometalation of the fluorinated ligand dfppy required a higher temperature and longer reaction time is possibly associated with the increased difficulty of the C–H activation, because of the lower nucleophilicity of the phenyl ring.[22] This procedure afforded exclusively the meridional isomers *mer*-[Pt(C^N)$_3$]OTf (*mer*-**3a–d**) in 57–91% yields. The facial isomers *fac*-**3a–d** were obtained in 24–43% yields by irradiating diluted solutions of *mer*-**3a–d** in acetonitrile (MeCN) with UV light in a photoreactor. Photoisomerization has been previously reported as an efficient method for the preparation of *fac* isomers of tris-cyclometalated Ir(III) complexes from the corresponding *mer* isomers.[4,23]

Crystal structures

The crystal structures of *mer*-**3b** and *mer*-**3c** have been solved by X-ray diffraction studies[24] (Fig. 1). The Pt–N bond trans to the phenyl group [2.138(2), 2.116(2) Å] is up to 0.1 Å longer than the two Pt–N distances of the mutually trans pyridyls [2.027(2)–2.072(11) Å], because of the stronger trans influence of the phenyl group as compared to the pyridyl. Similarly, the mutually trans Pt–C distances [2.058(11)–2.082(4) Å] are about 0.06–0.08 Å longer than the one trans to a pyridyl group [2.005(2), 2.002(4) Å].

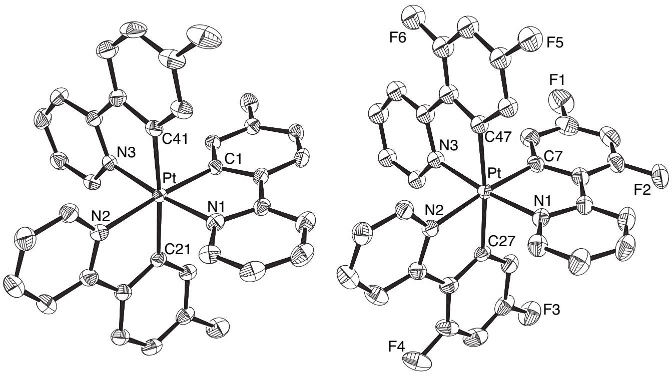


Fig. 1 ORTEP plots (50% probability) of the cation of complexes *mer*-**3b** (left) and *mer*-**3c** (right). H atoms are omitted for clarity.

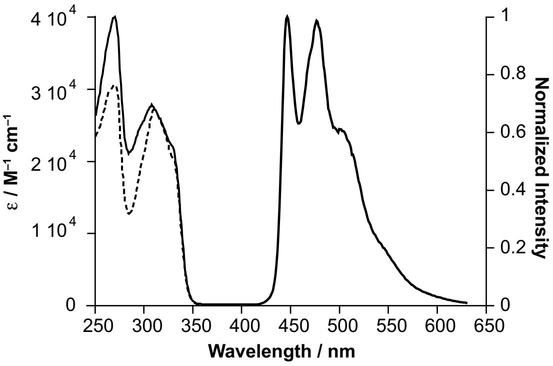


Fig. 2 Excitation and emission spectra (—) and absorption spectrum (---) of *fac*-**3a** in a CH_2Cl_2 solution at 298 K.

Photophysical properties

In CH_2Cl_2 solution, complexes *mer/fac*-**3a–d** display intense absorptions in the range 250–350 nm, which can be ascribed to transitions from π orbitals of the phenyl group to π* orbitals of the pyridyl or pyrazole ring ($^1\pi$-π^*). Consistent with this assignment, the lowest-energy band shifts to higher energies as the phenyl ring in the ppy-based ligands becomes more electron-deficient (**3b** > **3a** > **3c**; see the ESI†). Similar absorptions have been found for previously reported cyclometalated Pt(IV)[18a] and Au(III)[13,25] complexes, for which

^{1}MLCT absorptions are assumed to lie at very high energies and be obscured by ^{1}LC absorptions.[26]

Solutions of *mer*-**3a-d** are only weakly emissive at 298 K in CH_2Cl_2 solution, while they show intense emissions at 77 K in butyronitrile (PrCN) frozen glasses. However, the measured room-temperature emission data for these complexes are not reliable because partial isomerization occurs upon excitation to give the *fac* isomers, which display much stronger emissions (see the ESI† for further details). In view of their intense emissions at low temperature, it is clear that an effective nonradiative deactivation pathway is thermally accessible for the *mer* isomers at higher temperatures, most probably involving the population of a low-lying, dissociative excited state, which would also be responsible for the photoisomerization. Most likely, this state involves electronic transitions from ligand π orbitals to antibonding d orbitals, that is, a ligand-to-metal charge-transfer (LMCT). An analogous contrasting behavior between *mer* and *fac* isomers of tris-cyclometalated Ir(III) complexes has been previously observed.[4]

Table 1 Emission data of *fac*-**3a–d** in CH_2Cl_2 solution at 298 K.

Complex	λ_{em}/nm [a] (τ/μs)[b]	Φ [c]	$k_r \times 10^{-3}$ /s^{-1} [d]	$k_{nr} \times 10^{-3}$ /s^{-1} [e]	CIE *(x,y)*[f]
fac-**3a**	446 (215)	0.49	2.3	2.4	0.18, 0.29
fac-**3b**	454 (248)	0.41	1.7	2.4	0.19, 0.34
fac-**3c**	436 (319)	0.44	1.4	1.8	0.17, 0.23
fac-**3d**	402 (3.44)	0.01	2.9	288	0.20, 0.19

[a] Highest-energy emission peak. [b] Emission lifetime. [c] Absolute quantum yield. [d] Radiative rate constant, $k_r = \Phi/\tau$. [e] Nonradiative rate constant, $k_{nr} = (1 - \Phi)/\tau$. [f] Commission Internationale de l'Eclairage coordinates.

The emission data of *fac*-**3a–d** in CH_2Cl_2 solution at 298 K are given in Table 1. The data in PrCN frozen glasses at 77 K are given in the ESI†. In all cases, the emission spectra are highly structured (Fig. 2) and the highest-energy peak is very close to that of the triplet emission of the corresponding free ligand (Hppy, 430 nm;[27] Htpy, 437 nm;[2b] Hdfppy, 424 nm;[2b] Hppz, 378 nm[28]), resulting in emission colors that range from sky-blue to deep blue. The corresponding excitation spectra closely match the absorption profiles in CH_2Cl_2 solution, which proves that the emissions do not arise from possible impurities. The emission energies in MeCN or dimethyl sulfoxide (DMSO) at 298 K are identical to those in CH_2Cl_2 and the low-temperature emission bands are significantly sharper and only slightly blue-shifted as compared to the room temperature emissions. The lack of solvatochromism and rigidochromism, together with the vibronically structured emissions and long radiative lifetimes, indicate an emitting state of essentially ^{3}LC character. The absence of detectable fluorescence demonstrates a very effective intersystem crossing, which must be attributed to the spin-orbit coupling induced by the metal. ^{3}LC states in metal complexes are capable of producing efficient phosphorescent emission as a result of indirect spin-orbit coupling with higher-lying ^{1}MLCT states,[2a] the effect being stronger when the latter are closer in energy. ^{1}MLCT states are expected to lie at very high energies in cyclometalated Pt(IV) complexes, but very small amounts of MLCT character can have a significant effect in the emitting state,[2b] resulting in higher radiative rates and shorter emission lifetimes than expected for purely organic molecules.

The ppy-based derivatives *fac*-**3a–c** are intensely emissive in deaerated CH_2Cl_2 solutions at room temperature, reaching quantum yields (Φ) up to 0.49, which are the highest ever found for Pt(IV) complexes. In contrast, the ppz derivative *fac*-**3d** is a much weaker emitter (Φ = 0.01) under these conditions. The radiative rate constants (k_r) (Table 1) are two orders of magnitude lower than those found for analogous Ir(III) complexes,[29] which can be attributed to a much lower mixing of MLCT character into the ^{3}LC state. In spite of this, complexes *fac*-**3a–c** exhibit intense emissions thanks to their low nonradiative rate constants (k_{nr}), which are similar to the k_r values and one order of magnitude lower than those observed for Ir(III) analogues. The poor quantum yield of the ppz derivative *fac*-**3d** is clearly attributable to its k_{nr}, which is two orders of magnitude higher relative to the ppy-based complexes. Since this complex is highly emissive at 77 K, it is clear that a nonradiative deactivation pathway becomes accessible at room temperature because the emitting state lies at a very high energy and must be closer to deactivating excited states. Still, the k_{nr} value found for *fac*-**3d** is significantly lower than that of *fac*-[Ir(ppz)$_3$], which is non-emissive in solution at 298 K ($k_{nr} > 10^8$ s^{-1}).[29] Nonradiative deactivation in *fac*-**3a–d** could involve the thermal population of dissociative metal-centered (MC), as in analogous Ir(III) blue emitters,[29] or LMCT states, as observed for cyclometalated Au(III) complexes.[13] MC states are expected to lie at very high energies in Pt(IV) complexes because of the large splitting of the d orbitals, and thus must have a negligible effect in nonradiative deactivation. On the other hand, LMCT states might become accessible given the highly electrophilic character of Pt(IV); we note, however, that these states must lie at higher energies as compared to those of the *mer* isomers, resulting in the high photostability and low nonradiative deactivation observed for the *fac* isomers.

The emissions of *fac*-**3a–d** in the solid state turned out to be very weak. In order to get insight into this behavior, we measured the emission spectra and quantum yields of poly(methyl methacrylate) (PMMA) thin films with variable concentrations of the complexes, as well as neat films, prepared by the spin-coating technique. Figure 3 shows the excitation and emission spectra of *fac*-**3a** at 298 K under an N_2 atmosphere. At concentrations below 25% (wt%), the emissions are identical to those obtained in fluid solutions, while neat films give broad and red-shifted emissions. Excitation spectra are identical to the absorptions in solution and do not change with concentration. Quantum yields undergo a substantial decrease as the concentration increases and are very low for neat films (≤0.03; see the ESI†). This decrease in quantum yields can be attributed to intermolecular quenching via triplet-triplet annihilation,[30] which is enhanced for long-lived excited states. With all probability, the very weak red-shifted emission arises from excimer formation through π-π interactions between the ligands of adjacent cations. Excimer emissions have been observed for previously reported cyclometalated Ir(III) complexes.[31] It is noteworthy that, at 5% concentration, quantum yields are higher than in solution for *fac*-**3b** (0.61), *fac*-**3c** (0.49), and *fac*-**3d** (0.16).

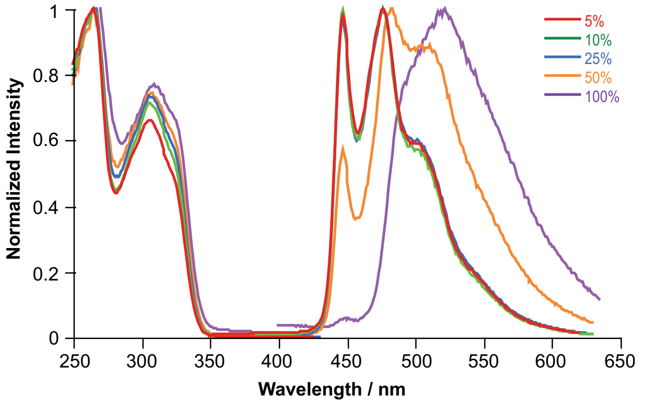


Fig. 3 Excitation and emission spectra of *fac*-**3a** in PMMA thin films at variable concentrations (wt%) and as neat film at 298 K.

Oxygen quenching studies

Owing to their long radiative lifetimes, the emissions of *fac*-**3a-d** in solution are strongly quenched by molecular oxygen, dropping to around 1% in intensity upon exposure to air. Quenching studies were carried out for the most efficient emitters *fac*-**3a-c** by measuring their emission intensity in CH_2Cl_2 solutions saturated with air, O_2, or different Ar/O_2 ratios (see the ESI†). Stern-Volmer constants (K_{SV}) were 350.9 (*fac*-**3a**), 664.5 (*fac*-**3b**) and 239.1 (*fac*-**3c**) atm^{-1}. These values are comparable or higher than those found for representative cyclometalated Ir(III) and Pt(II) complexes (37.5-334.0 atm^{-1})[10a] and demonstrate the high sensitivity of *fac*-**3a-c** to oxygen, which, along with their high quantum yields under an inert atmosphere, makes these complexes suitable for oxygen sensing applications.

Redox properties

The redox properties of complexes *fac*-**3a–d** were investigated using cyclic voltammetry in MeCN solution. The cyclic voltammograms are shown in Fig. 4 and the redox potentials are given in Table 2. Further details and HOMO/LUMO energy estimations are given in the ESI†. All redox processes were irreversible. For the ppy-based complexes, three (*fac*-**3a,b**) or two (*fac*-**3c**) closely lying reduction peaks in the range from –1.60 to –2.09 V vs SCE were observed. The first reduction wave has the same intensity as that of the ferrocene reference, which means that it corresponds to a one-electron process. These peaks shift to more negative potentials in the sequence *fac*-**3c** > *fac*-**3a** > *fac*-**3b**, that is, as the electron-donating character of the ligand increases. This is consistent with a LUMO primarily localized on the heterocyclic portion of the ligand, which is affected by the substituents on the phenyl ring. Accordingly, only for *fac*-**3b** was an oxidation peak observed (2.03 V), which is partially overlapped by the solvent discharge, while for *fac*-**3a** and *fac*-**3c**, oxidation peaks were not observed within the accessible potential range. The trend in the redox potentials within this series of complexes is thus in line with the variations observed in the lowest-energy electronic absorptions (see above).

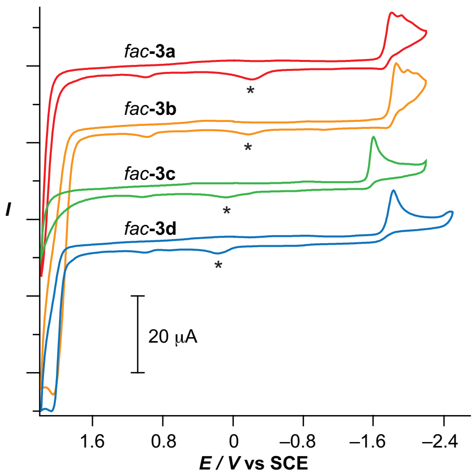


Fig. 4 Cyclic voltammograms of *fac*-**3a-d** in MeCN at 100 mV s^{-1}. The wave marked with an asterisk corresponds to the oxidation a species produced during the irreversible reduction processes (see the ESI†).

The cyclic voltammogram of *fac*-**3d** showed a one-electron reduction peak at –1.82 V; no other reduction processes were detected up to –2.70 V. An oxidation peak was observed at 2.08 V, very close to the solvent discharge limit. Surprisingly, the observed potential for the reduction process is similar to those found for *fac*-**3a,b** and significantly less negative than expected, since pyrazole is a weaker π-acceptor than pyridine and, in fact, ppz complexes of Ir(III) and Pt(II) are always considerably more difficult to reduce than their ppy counterparts.[4,32] One possible explanation is that the LUMO in *fac*-**3d** is no longer localized on the heterocyclic ring, and a metal-centered reduction takes place.

Table 2 Redox potentials of *fac*-**3a–d**.[a]

Complex	E_{pa} [b]	E_{pc} [b]	$E^{(2+/+*)}$ [d]	$E^{(+*/0)}$ [d]
fac-**3a**	–[c]	–1.80 –1.90 –2.01	–	1.00
fac-**3b**	2.03	–1.87 –1.99 –2.11	–0.73	0.89
fac-**3c**	–[c]	–1.60 –1.96	–	1.27
fac-**3d**	2.08	–1.82	–1.07	1.33

[a] All values in V relative to SCE. [b] E_{pa} = anodic peak potentials; E_{pc} = cathodic peak potentials; measured in 0.1 M $(Bu_4N)PF_6$ anhydrous MeCN solution at 100 mV s^{-1}. [c] Oxidation outside solvent window. [d] Estimated excited-state potentials: $E^{(2+/+*)} \approx E_{pa} - E_{0\text{-}0}$; $E^{(+*/0)} \approx E_{pc} + E_{0\text{-}0}$, where $E_{0\text{-}0}$ is the 0–0 emission energy at 77 K in eV.

The excited-state potentials $E^{(+*/0)}$ and $E^{(2+/+*)}$, associated with the half-reactions *fac*-$[Pt(C^\wedge N)_3]^{+}* + e^- \rightarrow$ *fac*-$[Pt(C^\wedge N)_3]$ or *fac*-$[Pt(C^\wedge N)_3]^{2+} + e^- \rightarrow$ *fac*-$[Pt(C^\wedge N)_3]^{+}*$, respectively, were estimated using the energy of the ^{3}LC state and the potentials in the ground state and are given in Table 2. The high $E^{(+*/0)}$ values indicate that the photoexcited species are powerful oxidizing agents and hence *fac*-**3a-d** could, in principle, function as photooxidants in catalytic photoredox reactions via reductive quenching cycles.[7b] For comparison, the corresponding potential of the Au(III) strong photooxidant $[Au(C\text{^}N\text{^}C)L]^+$ (C^N^C = 4-(4-methoxyphenyl)-2,6-di(2-naphthyl)pyridine; L = 1,3-dimethylimidazol-2-ylidene) is 1.18 V vs SCE,[14a] while the commonly employed photoredox catalysts $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$ are weaker photooxidants (0.77 or 0.31 V vs SCE, respectively[7b]). On the other hand, the estimated $E^{(2+/+*)}$ potentials for *fac*-**3c,d** show that the photoexcited species are also moderate reducing agents. The corresponding values for *fac*-**3a,c** are expected to be less negative [$E_{red}^{(2+/+*)} > -0.67$ V vs SCE]. In any case, photoexcited *fac*-**3a-d** could participate in oxidative quenching photocatalytic cycles in the presence of suitable electron acceptors,[7b] generating the species *fac*-$[Pt(C\text{^}N)_3]^{2+}$, which are much stronger oxidants ($E^{2+/+} > 2.0$ V vs SCE) than those formed from $[Ru(bpy)_3]^{2+}$ or $[Ir(ppy)_3]$ (1.29 or 0.77 V vs SCE, respectively[7b]) in such cycles. In addition to their strong photooxidizing character, complexes *fac*-**3a-c** benefit from very long emission lifetimes, which can be an advantage over the widely employed Ru(II) or Ir(III) photocatalysts.

Conclusions

The present work is the first account of the synthesis of *mer* and *fac* isomers of tris-cyclometalated Pt(IV) complexes and their photophysical properties. These complexes show emissions that are blue-shifted and of a higher ^{3}LC character as compared to those of Ir(III) analogues, because of the drastically diminished MLCT contribution to the emitting state. The *fac* isomers exhibit long lifetimes and low radiative rates at room temperature, but they reach the highest quantum yields ever reported for Pt(IV) complexes thanks to relatively ineffective nonradiative deactivation pathways. An examination of their excited-state redox potentials reveals that they may function as potent photooxidants in catalytic cycles that proceed through either reductive or oxidative quenching. In short, the *fac* isomers offer a unique combination of high-energy, long-lived, and highly efficient emission with a strong oxidizing character in the excited state, which makes them very promising as photocatalysts. Investigations into their possible application in different photocatalytic reactions are currently underway in our laboratory.

Acknowledgments

This work was supported by Ministerio de Economía y Competitividad, Spain (project CTQ2011-24016 and FPU grant to F.J.), and Fundación Séneca (project 04539/GERM/06). We are grateful to Prof. José Vicente for continuing support, Prof. Antonio Guirado for providing the potentiostat/galvanostat and Dr. David Curiel for the spin coater.

Notes and references

[a] Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain.

[b] SAI, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain.

†Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data. See DOI: 10.1039/b000000x/

1 (a) M. S. Lowry and S. Bernhard, *Chem. Eur. J.*, 2006, **12**, 7970; (b) M. E. Thompson, P. E. Djurovich, S. Barlow and S. Marder, in *Comprehensive Organometallic Chemistry III*, eds. H. C. Robert and D. M. P. Mingos, Elsevier, Oxford, 2007, pp. 101; (c) Y. You and S. Y. Park, *Dalton Trans.*, 2009, 1267; (d) W.-Y. Wong and C.-L. Ho, *J. Mater. Chem.*, 2009, **19**, 4457; (e) D. A. Vezzu, J. C. Deaton, J. S. Jones, L. Bartolotti, C. F. Harris, A. P. Marchetti, M. Kondakova, R. D. Pike and S. Huo, *Inorg. Chem.*, 2010, **49**, 5107; (f) J. Kalinowski, V. Fattori, M. Cocchi and J. A. G. Williams, *Coord. Chem. Rev.*, 2011, **255**, 2401; (g) R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem. Int. Ed.*, 2012, **51**, 8178.

2 (a) H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, *Coord. Chem. Rev.*, 2011, **255**, 2622; (b) J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 1713.

3 X. N. Li, Z. J. Wu, Z. J. Si, H. J. Zhang, L. Zhou and X. J. Liu, *Inorg. Chem.*, 2009, **48**, 7740.

4 A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.

5 (a) S.-C. Lo, C. P. Shipley, R. N. Bera, R. E. Harding, A. R. Cowley, P. L. Burn and I. D. W. Samuel, *Chem. Mater.*, 2006, **18**, 5119; (b) C. H. Yang, S. W. Li, Y. Chi, Y. M. Cheng, Y. S. Yeh, P. T. Chou, G. H. Lee, C. H. Wang and C. F. Shu, *Inorg. Chem.*, 2005, **44**, 7770; (c) C.-H. Yang, Y.-M. Cheng, Y. Chi, C.-J. Hsu, F.-C. Fang, K.-T. Wong, P.-T. Chou, C.-H. Chang, M.-H. Tsai and C.-C. Wu, *Angew. Chem. Int. Ed.*, 2007, **46**, 2418; (d) J. M. Fernández-Hernández, J. I. Beltrán, V. Lemaur, M. D. Gálvez-López, C. H. Chien, F. Polo, E. Orselli, R. Fröhlich, J. Cornil and L. De Cola, *Inorg. Chem.*, 2013, **52**, 1812.

6 (a) C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang and C.-C. Wu, *Angew. Chem. Int. Ed.*, 2008, **47**, 4542; (b) H. Fu, Y.-M. Cheng, P.-T. Chou and Y. Chi, *Mater. Today*, 2011, **14**, 472.

7 (a) L. Shi and W. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687; (b) C. K. Prier, D. A. Rankic and D. W. MacMillan, *Chem. Rev.*, 2013, **113**, 5322.

8 (a) K. K.-W. Lo, A. W.-T. Choi and W. H.-T. Law, *Dalton Trans.*, 2012, **41**, 6021; (b) E. Baggaley, J. A. Weinstein and J. A. G. Williams, *Coord. Chem. Rev.*, 2012, **256**, 1762; (c) A. Ruggi, F. W. B. van Leeuwen and A. H. Velders, *Coord. Chem. Rev.*, 2011, **255**, 2542.

9 (a) B. Higgins, B. A. DeGraff and J. N. Demas, *Inorg. Chem.*, 2005, **44**, 6662; (b) D.-L. Ma, V. P.-Y. Ma, D. S.-H. Chan, K.-H. Leung, H.-Z. He and C.-H. Leung, *Coord. Chem. Rev.*, 2012, **256**, 3087; (c) C. M. Lemon, E. Karnas, M. G. Bawendi and D. G. Nocera, *Inorg. Chem.*, 2013, **52**, 10394.

10 (a) P. I. Djurovich, D. Murphy, M. E. Thompson, B. Hernandez, R. Gao, P. L. Hunt and M. Selke, *Dalton Trans.*, 2007, 3763; (b) R.

Lincoln, L. Kohler, S. M. Monro, H. Yin, M. Stephenson, R. Zong, A. Chouai, C. L. Dorsey, R. Hennigar, R. P. Thummel and S. A. McFarland, *J. Am. Chem. Soc.*, 2013, **135**, 17161.

11 N. D. McClenaghan, Y. Leydet, B. Maubert, M. T. Indelli and S. Campagna, *Coord. Chem. Rev.*, 2005, **249**, 1336.

12 (a) A. Y. Lebedev, M. A. Filatov, A. V. Cheprakov and S. A. Vinogradov, *J. Phys. Chem. A*, 2008, **112**, 7723; (b) P. K. Chow, C. Ma, W.-P. To, G. S. M. Tong, S.-L. Lai, S. C. F. Kui, W.-M. Kwok and C.-M. Che, *Angew. Chem. Int. Ed.*, 2013, **52**, 11775.

13 C. Bronner and O. S. Wenger, *Dalton Trans*, 2011, **40**, 12409.

14 (a) W. P. To, G. S. Tong, W. Lu, C. Ma, J. Liu, A. L. Chow and C. M. Che, *Angew. Chem. Int. Ed.*, 2012, **51**, 2654; (b) W. P. To, K. T. Chan, G. S. Tong, C. Ma, W. M. Kwok, X. Guan, K. H. Low and C. M. Che, *Angew. Chem. Int. Ed.*, 2013, **52**, 6648.

15 (a) C. M. Anderson, R. J. Puddephatt, G. Ferguson and A. J. Lough, *J. Chem. Soc., Chem. Commun.*, 1989, 1297; (b) G. van Koten, J. A. M. van Beek, I. C. M. Wehman-Ooyevaar, F. Muller, C. H. Stam and J. Terheijden, *Organometallics*, 1990, **9**, 903; (c) J. A. M. van Beek, G. van Koten, I. C. M. Wehman-Ooyevaar, W. J. J. Smeets, P. van der Sluis and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1991, 883; (d) C. R. Baar, H. A. Jenkins, J. J. Vittal, G. P. A. Yap and R. J. Puddephatt, *Organometallics*, 1998, **17**, 2805; (e) J. Albert, R. Bosque, M. Crespo, J. Granell, J. Rodríguez and J. Zafrilla, *Organometallics*, 2010, **29**, 4619; (f) M. Crespo, C. M. Anderson, N. Kfoury, M. Font-Bardía and T. Calvet, *Organometallics*, 2012, **31**, 4401; (g) A. Arias, J. Forniés, C. Fortuño, A. Martín, M. Latronico, P. Mastrorilli, S. Todisco and V. Gallo, *Inorg. Chem.*, 2012, **51**, 12682.

16 (a) M. D. Hall, H. R. Mellor, R. Callaghan and T. W. Hambley, *J. Med. Chem.*, 2007, **50**, 3403; (b) E. Wexselblatt and D. Gibson, *J. Inorg. Biochem.*, 2012, **117**, 220; (c) T. C. Johnstone, J. J. Wilson and S. J. Lippard, *Inorg. Chem.*, 2013, **52**, 12234.

17 (a) N. J. Farrer, J. A. Woods, L. Salassa, Y. Zhao, K. S. Robinson, G. Clarkson, F. S. Mackay and P. J. Sadler, *Angew. Chem. Int. Ed.*, 2010, **49**, 8905; (b) J. Pracharova, L. Zerzankova, J. Stepankova, O. Novakova, N. J. Farrer, P. J. Sadler, V. Brabec and J. Kasparkova, *Chem. Res. Toxicol.*, 2012, **25**, 1099; (c) J. S. Butler, J. A. Woods, N. J. Farrer, M. E. Newton and P. J. Sadler, *J. Am. Chem. Soc.*, 2012, **134**, 16508.

18 (a) L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri and V. Balzani, *J. Am. Chem. Soc.*, 1986, **108**, 6084; (b) F. Barigelletti, D. Sandrini, M. Maestri, V. Balzani, A. von Zelewsky, L. Chassot, P. Jolliet and U. Maeder, *Inorg. Chem.*, 1988, **27**, 3644; (c) K. P. Balashev, J. Simon and P. C. Ford, *Inorg. Chem.*, 1991, **30**, 859; (d) H. Kunkely and A. Vogler, *Coord. Chem. Rev.*, 1991, **111**, 15; (e) D. M. Jenkins and S. Bernhard, *Inorg. Chem.*, 2010, **49**, 11297; (f) M. La Deda, A. Crispini, I. Aiello, M. Ghedini, M. Amati, S. Belviso and F. Lelj, *Dalton Trans.*, 2011, **40**, 5259.

19 V. W. Yam and K. M. Wong, *Chem. Commun.*, 2011, **47**, 11579.

20 E. Anger, M. Rudolph, L. Norel, S. Zrig, C. Shen, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous and R. Reau, *Chem. Eur. J.*, 2011, **17**, 14178.

21 J. Mamtora, S. H. Crosby, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2008, **27**, 5559.

22 M. Albrecht, *Chem. Rev.*, 2010, **110**, 576.

23 (a) T. Karatsu, T. Nakamura, S. Yagai, A. Kitamura, K. Yamaguchi, Y. Matsushima, T. Iwata, Y. Hori and T. Hagiwara, *Chem. Lett.*, 2003, **32**, 886; (b) K. Dedeian, J. Shi, N. Shepherd, E. Forsythe and D. C. Morton, *Inorg. Chem.*, 2005, **44**, 4445; (c) A. R. McDonald, M. Lutz, L. S. von Chrzanowski, G. P. M. van Klink, A. L. Spek and G. van Koten, *Inorg. Chem.*, 2008, **47**, 6681; (d) K. Tsuchiya, E. Ito, S. Yagai, A. Kitamura and T. Karatsu, *Eur. J. Inorg. Chem.*, 2009, **2009**, 2104.

24 CCDC953979 and CCDC953980 contain the supplementary crystallographic data for this article.

25 (a) M. A. Ivanov and M. V. Puzyk, *Mol. Spectrosc.*, 2001, **91**, 927; (b) V. K.-M. Au, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *Chem. Eur. J.*, 2011, **17**, 130.

26 M. A. Mansour, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *Inorg. Chem.*, 1998, **37**, 4625.

27 M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet and A. von Zelewsky, *Chem. Phys. Lett.*, 1985, **122**, 375.

28 K. P. Balashev, M. V. Puzyk and E. V. Ivanova, *Russ. J. Gen. Chem.*, 2011, **81**, 1547.

29 T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard and M. E. Thompson, *J. Am. Chem. Soc.*, 2009, **131**, 9813.

30 (a) M. Baldo, C. Adachi and S. Forrest, *Phys. Rev. B*, 2000, **62**, 10967; (b) C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 2000, **77**, 904; (c) C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich and L. De Cola, *Chem. Mater.*, 2012, **24**, 3684.

31 (a) Q. Zhao, L. Li, F. Li, M. Yu, Z. Liu, T. Yi and C. Huang, *Chem. Commun.*, 2008, 685; (b) H. Wu, T. Yang, Q. Zhao, J. Zhou, C. Li and F. Li, *Dalton Trans.*, 2011, **40**, 1969; (c) A. Gutiérrez-Llorente, M. M. Mroz and J. Cabanillas-González, *J. Mater. Chem. C*, 2013, **1**, 3606; (d) S. Jung, Y. Kang, H.-S. Kim, Y.-H. Kim, C.-L. Lee, J.-J. Kim, S.-K. Lee and S.-K. Kwon, *Eur. J. Inorg. Chem.*, 2004, 3415.

32 L. Chassot and A. von Zelewsky, *Inorg. Chem.*, 1987, **26**, 2814.